ORNL/PPA-2013/1

OAK RIDGE NATIONAL LABORATORY

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FOR THE DEPARTMENT OF ENERGY

Laboratory Directed Research and Development Program

FY 2012 Annual Report

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Oak Ridge National Laboratory

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2012 ANNUAL REPORT

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Prepared by
OAK RIDGE NATIONAL LABORATORY
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INTRODUCTION

The Laboratory Directed Research and Development (LDRD) program at Oak Ridge National Laboratory (ORNL) reports its status to the US Department of Energy (DOE) in March of each year. The program operates under the authority of DOE Order 413.2B, "Laboratory Directed Research and Development" (April 19, 2006), which establishes DOE's requirements for the program while providing the Laboratory Director broad flexibility for program implementation. LDRD funds are obtained through a charge to all Laboratory programs.

This report includes summaries of all ORNL LDRD research activities supported during FY 2012. The associated *FY 2012 ORNL LDRD Self-Assessment* (ORNL/PPA-2012/2) provides financial data and an internal evaluation of the program's management process.

ORNL is a DOE multiprogram science, technology, and energy laboratory with distinctive capabilities in materials science and engineering, neutron science and technology, nuclear energy and technology, energy production and end-use technologies, biological and environmental science, and scientific computing. With these capabilities, ORNL conducts basic and applied research and development (R&D) to support DOE's overarching mission to advance the national, economic, and energy security of the United States and promote scientific and technological innovation in support of that mission. As a national resource, the Laboratory also applies its capabilities and skills to specific needs of other federal agencies and customers through the DOE Work for Others (WFO) program. Information about the Laboratory and its programs is available on the Internet at <http:// www.ornl.gov/>.

LDRD is a relatively small but vital DOE program that allows ORNL, as well as other DOE laboratories, to select a limited number of R&D projects for the purpose of

- maintaining the scientific and technical vitality of the Laboratory,
- enhancing the Laboratory's ability to address future DOE missions,
- fostering creativity and stimulating exploration of forefront science and technology,
- serving as a proving ground for new research, and
- supporting high-risk, potentially high-value R&D.

Through LDRD the Laboratory is able to improve its distinctive capabilities and enhance its ability to conduct cutting-edge R&D for its DOE and WFO sponsors.

To meet the LDRD objectives and fulfill the particular needs of the Laboratory, ORNL has established a program with four components: the Director's R&D Fund, the Seed Money Fund, Wigner Fellowship Fund, and Weinberg Fellowship Fund. As outlined in Table 1, these four funds are complementary. The Director's R&D Fund develops new capabilities in support of the Laboratory initiatives, the Seed Money Fund is open to all innovative ideas that have the potential for enhancing the Laboratory's core scientific and technical competencies, and the fellowship funds allow building of staff capability with exceptional new scientists. Provision for multiple routes of access to ORNL LDRD funds maximizes the likelihood that novel ideas with scientific and technological merit will be recognized and supported.

Table 1. ORNL LDRD Program

	Director's R&D Fund	Seed Money Fund	Wigner Fellowship Fund	Weinberg Fellowship Fund
Purpose	Address research priorities of the Laboratory initiatives	Enhance Laboratory's core scientific and technical disciplines	Provide research opportunities for exceptional new scientists in honor of Professor Wigner	Provide research opportunities for exceptional new scientists in honor of ORNL Director Alvin Weinberg
Reviewers	Focus Area Review Committees (FRCs) composed of senior technical managers and subject matter experts	Proposal Review Committee (PRC) composed of scientific and technical staff representing the research divisions assisted by two to three technical reviewers for each proposal	Candidate and full proposal are reviewed by Wigner Fellowship Review Committee (WGRC) composed of ORNL corporate fellows, senior technical manager, and subject matter experts	Candidate and full proposal are reviewed by Weinberg Fellowship Review Committee (WNRC) composed of ORNL corporate fellows, senior technical manager, and subject matter experts
Review process	Preliminary and full proposal review, including a presentation to the FRC, and an annual review of progress	Full proposal review including a presentation to the PRC; review of progress if funding is awarded in two phases	Full proposal review and presentation to the WGRC	Full proposal review and presentation to the WNRC
Review cycle	Annual	Monthly	Once per quarter	Once per quarter
Project budget	Typically ~$750,000	<$190,000	Typically ~$450,000	Typically ~$150,000
Project duration	24–36 months	12–18 months	24 months	24 months
LDRD outlay	~75% of program	~18% of program	~5% of program	~3% of program

Director's R&D Fund

The Director's R&D Fund is the strategic component of the ORNL LDRD program and the key tool for developing and enhancing the core capabilities of the Laboratory. It is organized by initiatives that are aligned with the Laboratory Agenda and solicits proposals that address future DOE and national needs for science and technology.

The success of the initiatives depends to a large extent on the Laboratory's ability to identify and nurture cutting-edge science and technology on which enduring capabilities can be built. These are called focus areas. ORNL uses the resources of the Director's R&D Fund to encourage the research staff to submit ideas aimed at addressing focus-area research goals. Each winter, the Deputy Director for Science and Technology issues a call for proposals. The call emphasizes specific research priorities selected by management as being critical to the success of the following Laboratory initiatives.

- Clean Energy Science and Technology
- Global Security Science and Technology
- Distinctive Scientific Capabilities
- Scientific Discovery and Innovation
- Launch

The focus areas and research priorities within the FY 2012 Director's R&D Fund initiatives are described below.

- *Clean Energy Science and Technology.* The Clean Energy Science and Technology initiative seeks high-quality R&D and revolutionary technologies to advance the generation and use of clean energy. It is subdivided into three focus areas that address critical issues associated with current and next-generation fission reactors, establishing leadership capabilities in fusion research, and promoting research and technology that enables a sustainable transportation infrastructure including electrical energy storage and management. In 2012, $4.40 million of LDRD funds supported 14 projects in this area. FY 2012 LDRD investments were made in projects to accomplish the following.

    - Improve the understanding of nuclear fuel cladding materials behavior to address long-term nuclear waste storage concerns

    - Develop fission and fusion material irradiation testing capabilities in support of DOE Fusion Energy and Nuclear Energy programmatic needs

    - Advance thermonuclear plasma simulation capabilities, plasma source development for fusion material testing applications, and plasma-materials interface science R&D to facilitate development of critical materials for fusion reactors

    - Address critical power grid management issues such as grid disruption, electricity conservation at the utility and consumer level and control of interconnected power systems.

    - Demonstrate the potential for utilizing low-cost lignin sources to develop carbon fiber materials for automotive applications

- *Distinctive Scientific Capabilities.* ORNL maintains core capabilities in the areas of Neutron Science and Technology, Computational Sciences and Engineering, Material Science, and Nuclear Science and Engineering. LDRD investments in this initiative focus on strengthening these capabilities in order to meet current and future national S&T needs. This is our broadest and largest initiative, with four major focus areas intended to: maximize the output and versatility of our unique neutron science facilities; mitigate the technical risks and define the path towards an exascale computing capability; build the tools and expertise that facilitate novel material design and synthesis capabilities that can produce revolutionary materials for energy applications; and extend ORNL's ability to address relevant nuclear science and engineering problems in the areas of isotope production, nuclear fuels, reactor design, and nuclear materials research. In 2012, $9.90 million of LDRD funds supported 40 projects in this initiative. FY2012 LDRD investments were made in projects to accomplish the following.

    - Novel neutron detectors that replace helium-3 with resistive plate detectors with single neutron sensitivity; asynchronous, in situ neutron measurement methods with 10 μs resolution to study microsecond timescale material behaviors; and neutron-based techniques to elucidate the structure and functional characteristics of biomembranes and biomolecular complexes

    - Improved neutron moderator schemes that provide an order-of-magnitude increase in beam brightness and conceptual analyses to upgrade and develop new ORNL neutron facilities to meet national needs

    - Advanced materials for energy applications: progressing the scientific understanding of assembly, properties, and behaviors that facilitates the design and use of revolutionary energy storage materials including, but not limited to, battery polymer membranes, photovoltaic efficiency, anode performance, and electrochemical storage capacity

- o Large-scale, heterogeneous data management, integration, and utilization frameworks to improve knowledge discovery and interpretation of scientific data

- o Translation tools to improve code performance on the diverse range of accessible high performance computing platforms

- o Unique experimental approaches to understand defect transport and damage mechanisms in nuclear materials and coordinated modeling and experimental efforts to investigate nuclear fuel reprocessing cycles

- *Global Security Science and Technology.* Addressing critical national security challenges continues to be one of ORNL's key missions. Investments in this initiative are applied in a focused manner towards problem sets that are best solved using core S&T strengths. Research priorities for this initiative were grouped into three focus areas: (1) cyber protection of energy infrastructure including virtual models of energy systems, protection tools and strategies, and recovery capabilities; (2) innovative forensic science solutions for nonproliferation assurance as well as threat identification including nuclear, biological, and chemical weapons; and (3) development of next-generation technologies for a broad range of homeland security applications including protected wireless communication systems and advanced materials in support of national defense. In 2012, $3.35 million of LDRD funds supported 11 projects in this initiative. FY2012 LDRD investments were made in projects to accomplish the following.

  - o Computational frameworks for identifying and understanding cyber attacks for energy networks with emphasis on multi-scale detection and application capability

  - o New methodologies for integrating and analyzing available data sets for biological threat identification and novel approaches for rapidly and comprehensively compiling identification databases that can be used for biological threat discovery and forensic analysis

  - o Advanced materials in support of defense applications including composite armor and novel membranes for water reclamation systems

- *Scientific Discovery and Innovation.* This initiative aims at producing transformational breakthroughs in fundamental concepts and ORNL signature science areas in support of energy and global security missions. It serves as a proving ground for new R&D concepts with high risk and potentially high value. During the year, the Laboratory invested $6.10 million in 20 LDRD projects. FY 2012 LDRD investments were made in projects to accomplish the following.

  - o R&D in support of biofuel and bioproduct separation and conversion

  - o Decadal scale climate prediction tools and methods, climate-informed resource management and novel carbon capture technologies and concepts

- *Launch.* The Launch initiative pursues potentially disruptive technological solutions to real-world technical problems in areas related to ORNL's mission space. It supports proof-of-principle laboratory demonstration of promising concepts that display high-potential for transformative impact. In 2012, $1.0 million of LDRD funds supported five projects in this initiative.

To select the best and most strategic of the ideas submitted, the Deputy Director establishes committees for each initiative to review the new proposals and associated ongoing projects. The committees are staffed by senior technical managers and subject matter experts, including external members.

Proposals to the Director's R&D Fund undergo two rounds of review. In the first round, the committees evaluate preliminary proposals and select the most promising for development into full proposals. In the second round, the committees review the new proposals and ongoing projects that are requesting second- or third-year funding. After the reviews are completed, the committees provide funding recommendations to the Deputy Director for Science and Technology, who develops an overall funding strategy and presents it for approval to the Leadership Team, ORNL's executive committee headed by the Laboratory Director. All projects selected for funding must also receive concurrence from DOE.

In FY 2012, $32.91 million was allocated to the ORNL LDRD program to support 187 projects, 95 of which were new starts (Table 2). About 80% of the fund's annual allocation is awarded to projects at the beginning of the fiscal year. The remainder is held in reserve primarily to support research projects of new R&D staff members being recruited to address strategic Laboratory needs. The levels of investment in each focus area are summarized in Fig. 1.

Table 2. ORNL LDRD by fund

	Director's R&D Fund	Seed Money Fund	Wigner Fellowship Fund	Weinberg Fellowship Fund
Costs	$24,735,000	$5,539,000	$1,544,684	$898,370
Number of projects	90	79	9	9
Number of new starts	38	53	2	2
Continuing (2nd & 3rd year of funding)	52	26	7	7
Average total project budget (1–3 years)	$619,937	$128,938	$382,566	$159,859
Average project duration	24 months	16 months	24 months	24 months

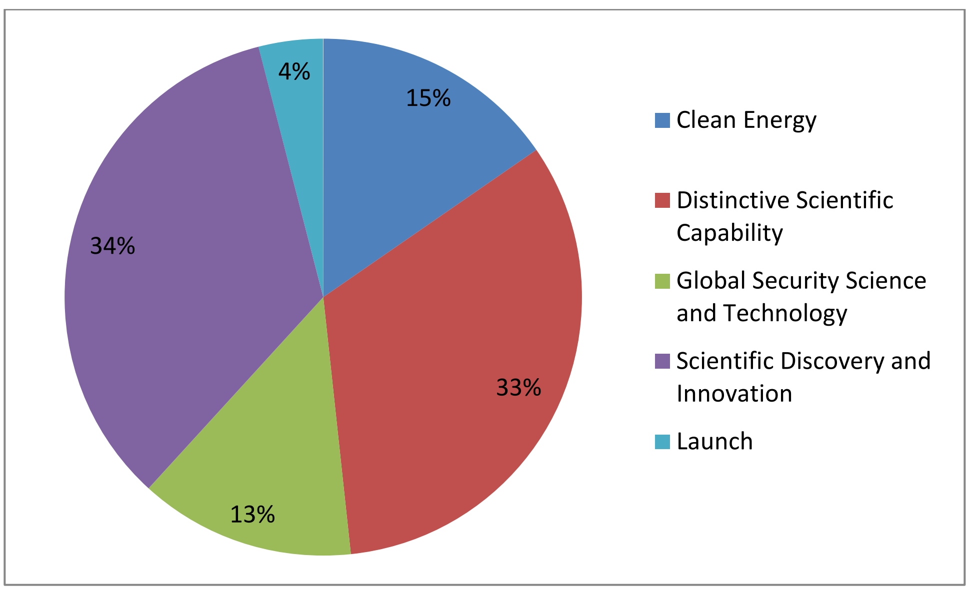

Fig. 1. Level of Director's R&D Fund investment in the Laboratory Focus Areas for FY 2012.

Seed Money Fund

The Seed Money Fund complements the Director's R&D Fund by providing a source of funds for innovative ideas that have the potential of enhancing the Laboratory's core scientific and technical competencies. It also provides a path for funding new approaches that fall within the distinctive capabilities of ORNL but outside the more focused research priorities of the major Laboratory focus areas. Successful Seed Money Fund projects are expected to generate new DOE programmatic or WFO sponsorship at the Laboratory.

Proposals for the Seed Money Fund support are accepted directly from the Laboratory's scientific and technical staff (with management concurrence) at any time of the year. Those requesting more than $30,000 ($190,000 is the maximum) are reviewed by the Proposal Review Committee (PRC), which consists of scientific and technical staff members representing each of the Laboratory's research directorates and a member of the Office of Institutional Planning, who chairs the committee. To assist the committee, each proposal is also peer reviewed by two or three Laboratory staff members selected by the chair. Proposals requesting $30,000 or less are reviewed by the chair normally with the assistance of a technical reviewer. All Seed Money Fund proposals receiving a favorable recommendation are forwarded to the Deputy Director for Science and Technology for approval and require DOE concurrence.

In FY 2012, $5.54 million of the LDRD program was apportioned to the Seed Money Fund to support 79 projects, 53 of which were new starts (Table 2). The distribution of Seed Money Fund support by research division area is shown in Fig. 2.

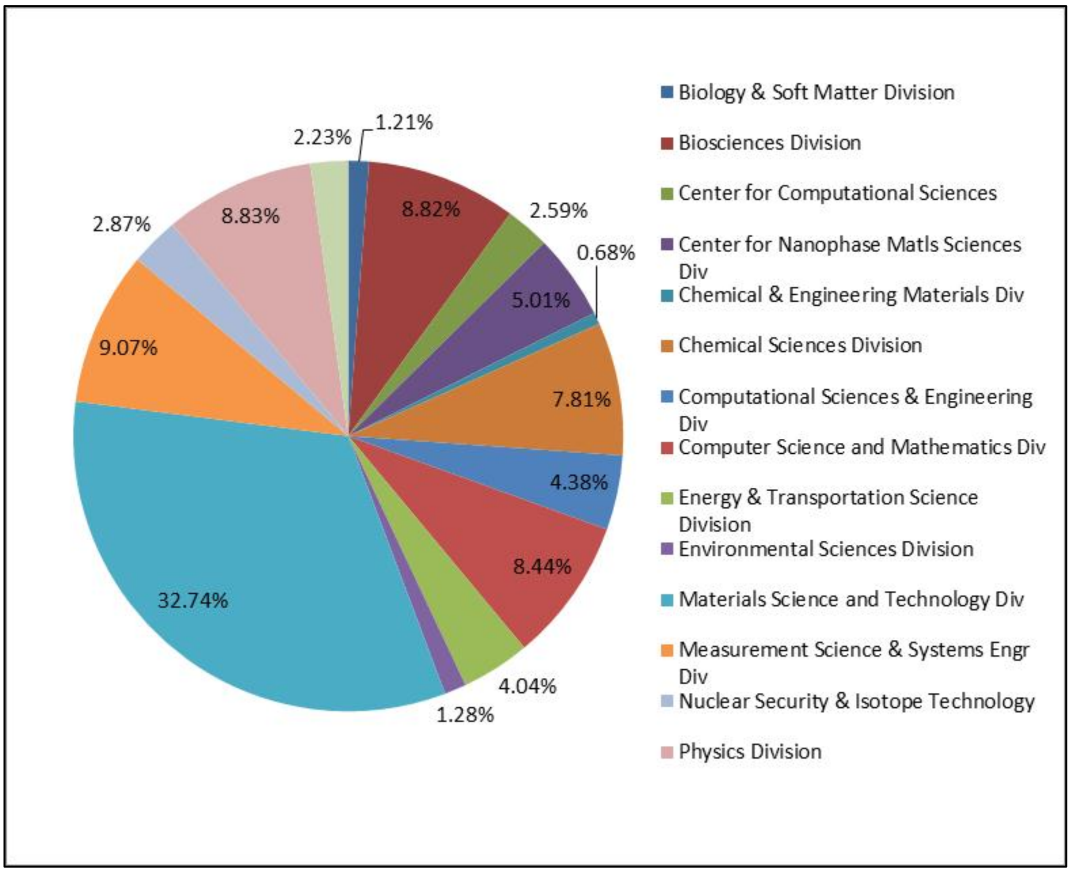

Fig. 2. Distribution of Seed Money Fund by research division for FY 2012.

Fellowship Money Fund

In FY 2012, the awardees of the Laboratory's Alvin M. Weinberg and Wigner Fellowship programs continued to receive funding through the LDRD Program. The fellowship programs were formed to provide research opportunities for exceptional new scientists in honor of Professor Wigner and Dr. Alvin Weinberg (former ORNL director). The appointment of Fellows to ORNL's staff provides an opportunity for outstanding life, physical, computer, computational, social scientists, engineers, and applied scientists to select and pursue research in an area related to national energy problems and interests. Fellows are exceedingly well qualified in their fields of expertise and are no more than 3 years beyond the doctorate. There are no application deadlines for the Fellowship. Each application package, consisting of a fellowship research plan, is considered based on how it meets the criteria for the position. Applications are reviewed by special selection committees once per quarter during the year. The Wigner Fellowship is full-time 2 year appointment, and the Weinberg Fellowship is quarter-time 2 year appointment.

Fellowship proposals are reviewed by Fellowship committees. When candidates apply for a fellowship, they are required to submit their research statement. Once the candidate is selected, a mentor is assigned, who helps him/her prepare the LDRD project proposal that is aligned with the fellow's research statement. Wigner Fellowship proposals are reviewed by the Wigner Review Committee (WGRC), and Weinberg Fellowship proposals are reviewed by Weinberg Review Committee (WNRC). After the reviews are completed, the committees' recommendations are sent to the Deputy Director for Science and Technology for approval. The proposals also go through DOE concurrence.

In FY 2012, $2.44 million of the LDRD program was apportioned to the Fellowship Fund to support 18 projects—9 Weinberg and 9 Wigner Fellowship proposals.

Report Organization

This report, which provides a summary of all projects that were active during FY 2012, is divided into 8 sections: one for each of the Director's R&D Fund initiatives discussed above, the Seed Money Fund, the Wigner Fellowship Fund, and the Weinberg Fellowship Fund. The Seed Money Fund section is further categorized by the research division of the principal investigator. The summaries are arranged by project number, and each summary contains (1) a project description, (2) a discussion of the project's relevance to the mission, and (3) results and accomplishments through the end of FY 2012. Publications resulting from the project are also listed.

SUMMARIES OF PROJECTS SUPPORTED THROUGH THE DIRECTOR'S R&D FUND

CLEAN ENERGY SCIENCE AND TECHNOLOGY

05384

Scalable, Fully Implicit Algorithms for First-Principles Kinetic Simulations at the Ultrascale

L. Chacón, G. Chen, D.C. Barnes

Project Description

This project aims at developing a novel, scalable kinetic algorithmic strategy based on fully implicit nonlinear methods. The approach will be able to exploit ORNL's ultrascale computing capabilities to enable a first-of-a-kind future predictive thermonuclear plasma modeling capability. Plasmas in the regimes of interest for nuclear fusion feature extremely disparate time and length scales. Current first-principles kinetic algorithms are explicit, needing to resolve the fastest time scales and the smallest length scales in the model for numerical stability, and are therefore extremely inefficient. The fully implicit character of our approach will eliminate numerical stability constraints (thus enhancing efficiency possibly by orders of magnitude). Its nonlinear character will deliver enhanced accuracy and nonlinear stability. Our approach will be particle-based and thus naturally suitable for parallel supercomputers. If successful, this research will enable simulations that are presently unattainable with current algorithms even with ultrascale computing and will have direct implications for first-tier DOE projects such as ITER.

Mission Relevance

The project has strong relevance to two DOE missions: energy security and scientific discovery and innovation. Relevance to energy security stems from this project's connection to magnetic fusion energy and the international fusion reactor, ITER (which if successful could help ensure the energy supply of humanity for centuries to come). By enabling a predictive capability, this project may have direct impact on the success of ITER and the US magnetic fusion program and may contribute to ensure a good scientific/technological return on US investment in such an experiment. Relevance to scientific discovery and innovation stems from the strong connection with two offices of the DOE Office of Science: the Office of Fusion Energy Science and the Office of Applied Scientific Computing Research. Success in this project will contribute to the core goals of both offices and will contribute to US scientific prominence in the world.

Results and Accomplishments

Our research in this project to date has confirmed its main premise, namely, that a fully implicit, nonlinear PIC kinetic algorithm is possible, which enables accurate and efficient kinetic simulations. Thus, after more than 20 years of research in implicit PIC methods, we have demonstrated the first fully implicit particle in cell (PIC) algorithm that can take time steps much larger (and mesh resolutions much coarser) than explicit PIC in a stable, accurate manner. We have also made significant progress towards the implementation of our implicit PIC algorithm on graphics processing unit (GPU) architectures, which is of particular relevance to ORNL's future ultrascale computing facilities. There is ample evidence of the tremendous potential for GPU-vs-CPU speedup in explicit PIC simulations. Implicit PIC, however, presents different challenges on a GPU. On the one hand, the most expensive operation in our algorithm is the particle push, which must be performed for all particles once per nonlinear residual evaluation. However, the particle push is a segregated operation in our nonlinear residual computation, which can be independently computed on GPU hardware. This presents a clear, rapid-development path for implicit PIC to effectively exploit upcoming heterogeneous hardware architectures. On the other hand, the optimization of the particle push stage on GPU is complicated by its implicit, adaptive, and charge-conserving nature and has required a tailored implementation. Nvidia Fermi GPU numerical experiments of the particle push stage (including moment accumulation and employing a large implicit time step) demonstrate excellent scalability up to 8000 threads, speedups of up to 300 (in single precision) vs. a 3.3. Intel Xeon™ CPU, and an overall GPU computational efficiency between 20 and 30% of the peak theoretical performance. We have recently extended the approach to use mapped meshes, thus enabling mesh adaptation. We have also succeeded in developing a successful fluid-based preconditioning strategy, which renders the fully implicit kinetic solver optimal. Finally, we have generalized the formulation to the electromagnetic case, while preserving exact charge and energy conservation.

Information Shared

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L. Chacón, G. Chen, D. C. Barnes, “A charge- and energy-conserving implicit, electrostatic particle-in-cell algorithm on mapped computational meshes,” *J. Comput. Phys.*, **233**, 1–9 (2013).

05470

Microelectromechanical Systems–Based Pyroelectric Thermal Energy Scavengers and Coolers

S.R. Hunter, P. Datskos, S. Rajic, Nickolay V. Lavrik

Project Description

The project focuses on developing a new type of high-efficiency, low-grade waste-heat energy converter that can be used to actively cool electronic devices, solar concentrator photovoltaic cells, computers, and larger waste-heat-producing systems while generating electricity that can be used to power monitoring sensor systems or recycled to provide some of the electrical power for these computers and other electrical devices. The project objective is to demonstrate the feasibility of fabricating high-conversion-efficiency microelectromechanical systems–based pyroelectric energy converters that can be fabricated into scalable arrays using well-known microscale fabrication techniques and materials. The specific goals of the project are to demonstrate that overall electrical energy conversion efficiencies in the range of 20–30% and efficiencies up to 80% of the Carnot efficiency limit, and that these efficiencies are achievable with arrays of up to 10^6 converter elements. These energy conversion efficiencies are greater than those previously demonstrated–or proposed–for any other type of waste-heat energy recovery technology. The widespread implementation of this technology will result in large reductions in waste-heat production (and subsequent cooling requirements) and the generation of electrical energy from a wide range of waste heat sources.

Mission Relevance

Energy scavenging and improved systems-level electrical efficiencies are of considerable interest to DOE and other federal agencies such as the Defense Advanced Research Projects Agency (DARPA), as well as industry. During the past year, our project development efforts focused on teaming with industrial partners (L3 and Lockheed Martin) that have already expressed interest in this technology and will help us secure funding from programs at DOE and at DARPA. The ORNL Technology Transfer Office decided to pursue patents with broadly structured patent claims in this technology, and the first patent application was submitted to the United States Patent and Trademark Office during FY 2012.

The DOE Office of Energy Efficiency and Renewable Energy offers frequent DOE laboratory funding opportunities in the Industrial Technologies Program for new energy efficiency approaches, and we plan to pursue funding from these sources. Commercial partners such as L3 (Dallas) that have considerable experience in ferroelectric materials have expressed interest in teaming with ORNL for future projects based on this technology. In addition, several programs at DARPA have energy-scavenging components and, by teaming with defense contractors such as Lockheed Martin, we will pursue these opportunities in FY 2013.

Results and Accomplishments

Our efforts during the prior year focused on the testing, characterizing and optimizing the performance of several thin film and cantilever-based self-resonators and fully integrated pyroelectric capacitive devices. Structures were fabricated with the pyroelectric materials aluminum nitride and P(VDF-TrFE), or silicon dioxide, and incorporated aluminum electrodes, which also acted as one of the bimorph elements. The cantilever structures were fabricated with dimensions from 0.5 to 7 mm in length and 0.5 to 2 mm in width. A vacuum test chamber and data collection system were assembled to temperature cycle the bimorph test cantilever structures and to characterize cantilever thermal heat transfer structures and the pyroelectric and electrical current generating properties of pyroelectric AlN and P(VDF-TrFE) capacitive structures. The chamber was pumped to pressures in the range 20–50 mTorr, which is sufficient to eliminate heat loss by gas conduction and convection in the vacuum chamber. Cantilever structures, along with a heat source and heat sink, were mounted in the vacuum chamber and found to self-oscillate at frequencies from 10 to ~ 50Hz with tip displacements of ~ 10μm when temperature differences of ~ 30^{o}C were applied across the device. The peak temperature change across the cantilever under these conditions was estimated to be ~15K in agreement with the estimated cantilever temperature change based on the modeled cantilever responsivity. This is the first time that self-oscillation has been reported for a heat-driven cantilevered device. Under these conditions, the measured rate of temperature change, dT/dt ~ 300K/sec, is orders of magnitude greater than has been achieved by the pyroelectric converters, and leads to the possibility of much more efficient thermal-to-electrical energy conversion with higher power densities than previously achievable.

Information Shared

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Scott R. Hunter, "Pyroelectric Thermal Heat to Electricity Conversion," invited presentation at The Potential Threat of Future Power and Energy Technology Breakthroughs Workshop, The MITRE Corp., March 27–28, 2012.

Scott R. Hunter and Panos G. Datskos, "MEMS based pyroelectric energy scavenger," DOE Invention disclosure S-115, 324, patent application submitted to the USPTO in November 2011.

Scott R. Hunter, Nickolay V. Lavrik, Thirumalesh Bannuru, Salwa Mostafa, Slo Rajic, and Panos G. Daskos, "Development of MEMS based pyroelectric thermal energy harvesters," presentation and conference proceedings publication at the SPIE Security & Defense Conference 2011, Orlando FL, SPIE Vol. 8035, 80350V-1.

Thirumalesh Bannuru, Slo Rajic, Nickolay Lavrik, Salwa Mostafa, Syed K. Islam, Panos G. Datskos, and Scott R. Hunter, "Pyroelectric MEMS device for thermal energy harvesting in microelectronics and sensor applications," 2011 MRS Spring Meeting, San Francisco.

Salwa Mostafa, Nicolay Lavrik, Thirumalesh Bannuru, Slo Rajic, Syed K. Islam, Panos G. Datskos, and Scott R. Hunter, "A Finite Element Model of Self-Resonating Bimorph Microcantilever for Fast Temperature Cycling In A Pyroelectric Energy Harvester," 2011 MRS Spring Meeting, San Francisco.

05593

Power Flow Control Using Distributed Saturable Reactors

A. Dimitrovski, Y. Liu, B. Ozpineci, M. Pace, J. Gracia, B. McConnell

Project Description

A series-connected reactor can be used to control power flow on a transmission line through a modification of its impedance. Dry-type reactors with constant reactance values (air core) have been used on a few occasions for power flow control. Another type of reactor that uses a saturable ferromagnetic core has been used for fault current limitation in superconductive circuits. This proposal combines these two concepts with new technology in one device that has the potential to revolutionize power systems operation. A saturable core, series reactor with continuous reactance control that uses power electronics to provide and control the bias dc current is proposed. The goal is to create a simpler, more effective, reliable and cheaper power flow control device that will enable power systems, for the first time since their inception a century ago, to operate not just in compliance with the laws of physics but also in a way that is market compatible and friendly, most economical, and most reliable.

Mission Relevance

The control of power flow in interconnected power systems is a major concern for utilities and system operators and has become more urgent with deregulation pushing market transactions. If not controlled, power flows due to these market transactions can lead to a number of issues in system operation. Some of the commonly encountered problems include overloading of lines and transformers; increased system losses; reduction in security margins; contractual violations concerning power import/export; and increased fault current levels beyond equipment ratings.

Thus far, full power flow control has been prohibitively expensive, requiring a large number of complicated and costly devices. Also, the reliability of these complex devices has been in question. Only a partial power flow control is exerted in contemporary power systems with relatively few strategically located controllers. As a result, power systems almost always operate in a suboptimal way in regards to flows, losses, and economic power transport. The cost of such suboptimal operation is significant given the amount of investment in this infrastructure. As an example, this cost is estimated to be around 2 billion dollars per year for the PJM (Pennsylvania, Jersey, Maryland) system only.

The cost of the new controller is estimated to be around two orders of magnitude lower than the current state-of-the-art solutions. Such cost-effectiveness of this new device will allow for system-wide deployment and distributed power flow control on a scale never implemented before. A number of these controllers placed in strategic locations and coordinated by the system operator can eliminate the common transmission system problems listed above and enable, cost-wise, truly optimal power system operation while satisfying technical, security, environmental, and other constraints.

Results and Accomplishments

ORNL's Distributed Energy Communications and Controls (DECC) Laboratory has been used for testing of the 480 V, 150 A prototype of the saturable core reactor. The main setup consists of the prototype itself, a 100 kW load bank, and a 40 V, 600 A, dc power supply. Complete instrumentation and control equipment has been attached to the controller. All the measured and calculated quantities are displayed on a virtual instrumentation interface developed in dSpace® environment. It includes the waveforms of the voltages and currents across all of the ac and dc coils, their harmonic contents, rms values, power consumptions, as well as apparent impedances for each phase of the controller.

The tests performed on the LV prototype, as expected, confirmed the most important characteristic of the power flow controller, its apparent impedance change vs. the bias dc current. The maximum impedance of the LV prototype is 0.18 Ω, which is about 65% of the target impedance. This can be attributed to the much smaller core and gap dimensions required for this unit than what is normally manufactured at the WES' facility. The tolerances of the tools are such that even a small error can result with a significant deviation from the target value. This, however, will not be a problem with the HV prototype or any other production grade unit. What is important is that there is still a very good impedance regulation with the max/min value ratio of around 6. This is in line with the simulation results and proves the feasibility of the approach.

Finally, this device has been deemed capable of controlling not only power flows in steady state conditions but also of dampening slow speed transients like, for example, inter-area oscillations. The measured time constant is around 20 cycles or 1/3 of a second at 60 Hz, well within the range for controlling such oscillations with subcycle periods.

Information Shared

A. Dimitrovski, Magnetic Amplifier for Power Flow Control. Funded proposal #0473-1515, DE-FOA-0000473 (2011).

X. Zhang, K. Lin, K.Tomsovic, A. Dimitrovski, "Optimal Power Flow Control by Use of Magnetic Amplifier," IEEE PES GM 2013.

05659

Real-Time Simulation of Power Grid Disruptions

S. Fernandez, A.D. Dimitrovski, C.S. Groer, Y. Liu, J.J. Nutaro, O.A. Omitaomu, M. Shankar, K.L. Spafford, R. Vatsavai, M.R. Allen, V. Chandola, M. Olama, B. Vacaliuc, D.B. Koch

Project Description

DOE-OE and DOE-SC workshops identified the key power grid problem needing exascale computing is coupling of real-time data streams (1–2 TB per hour) as the streams are ingested to dynamic models. These models would then identify predicted disruptions in time (2–4 seconds) to trigger the smart grid's self-healing functions. We will establish the feasibility, we will define the scientific issues, and we will demonstrate the solutions to important smart grid simulation problems only addressable within an exascale scientific computing application. This objective is accomplished by 1) using the existing frequency recorders on the national grid to establish a representative and scalable real-time data stream; 2) invoking ORNL signature identification algorithms; 3) modeling dynamically a representative region of the Eastern interconnect using an institutional cluster, measuring the scalability and computational benchmarks for a national capability; and 4) constructing a prototype simulation for the system's concept of smart grid deployment. The ORNL enduring capability will 1) establish and demonstrate the ORNL GRIDEYE network as a national resource; 2) develop data processing and simulation metrics to design a national capability justifying exascale applications; and 3) demonstrate running dynamic models to design few-second self-healing is feasible.

Mission Relevance

Key to producing an enduring capability future funding is a center for national grid simulation that will have a variety of DOE-OE missions. Once captured, this center will build on ORNL's long-standing expertise in running large-scale applications for the Department of Energy. The capture of a co-design center for the power grid strategically aligns with ORNL directions for both next-generation computing and innovative analysis for DOE power grid programs. A dedicated institutional cluster runs programs solely for electric grid-related applications which include explicitly parallel planning, real-time dynamics visualization, run-time dynamic control predictions, and impacts analysis. The data for the visualization comes from real-time feeds from the utilities, OASIS web sites, and instrumented sensors that ORNL has deployed in the field.

Results and Accomplishments

The first objective was to develop a database system to receive the data streams from frequency recorders as a simulant for real-time synchro-phasor data. We created a documented data set collected in July 2009. This stream provided a real-time test stream where the data structure, speed, accuracy, latency, and signature potential are tested on simulated live data. We ran simulations of the disruptions within the Eastern Interconnection to obtain frequency signatures for events representing each (n-k) contingency. An integrated prototype was demonstrated using a mix of high-performance computing (HPC) technologies. Real-time event detection was accomplished through the development of the GAEDA (GPU-Accelerated Event Detection Algorithm) software. The signature (scenario library) search was also accelerated using GPUs, attaining a rate of 1.5 million signatures per second per GPU.

These signatures were generated with the THYME simulation package for all (n-1) contingencies in the Eastern interconnect, resulting in a total of 58,789 simulations and approximately 10 million individual signatures. We leveraged Keeneland, the NSF Track2D experimental HPC system. Analysis indicates that 1317/58789 cases (2.24%) exhibit frequency depression exceeding 8 mHz, the sensor's limit of detection. When undetectable events are purged we observe a greater than 40 times faster searching capability. Utilizing compression, total data size is reduced from roughly 8.76PB to 7.01PB, a 20 percent reduction. Fast searching of the library to present potential component losses and future states demonstrated we can search 3 million contingencies within 1000 msec. This places a practical limit of N-10 contingency screens.

Based on the results the prototype database, signature identification modules and dynamic forecasting modules were prototyped. The simulation results from the THYME simulator were interfaced with mobile visualization frameworks (Google Earth platform and Tableau Software). These visualizations displayed the results by representing several parameter values with different visual attributes simultaneously.

A frequency measurement system design provided real-time measurements of frequency transients in an electric power system with a) cyber-security using cryptography, b) a sampling rate of 8000 measurements per second, c) a sensitivity of 25mHz within 80ms, d) a timing system that can accurately time-stamp each measurement, and e) a system cost of less than $1000 per copy.

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Copyrighted Software

UT-Battelle Copyright entitled "GPU Accelerated Event Detection Algorithm" (GAEDA).

Patent Disclosures Filed

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05971

Citizen Engagement for Energy-Efficient Communities (CoNNECT)

O.A. Omitaomu, B.L. Bhaduri, J.B. Kodysh, C. Maness, R. Karthik, A. Myers

Project Description

Energy efficiency and renewable energy are two main strategies presently being promoted for achieving sustainable energy policy. Of these strategies, energy efficiency is relatively easier and cheaper to implement. As a result, there have been some programs that targeted the use of energy efficient technologies and appliances in buildings. However, it is highly unlikely that these programs can scale up to achieve the projected energy savings because they are usually treated as one-time improvements that are not monitored and measured over time. Allowing consumers to easily analyze, share, and benchmark their own energy usage data can lead to an effective and sustainable way to achieve many of the Energy Efficiency and Renewable Energy (EERE) goals. We have developed an integrated multi-partner platform called **C**itizen e**N**gagement for e**N**ergy **E**fficient **C**ommuni**T**ies (CoNNECT) that (i) establishes a community-based network of stakeholders to facilitate consumer engagement for energy efficiency; (ii) provides a prototype internet-based decision support application to better inform and motivate consumers; and (iii) provides data analysis capabilities that will drive the decision support system for comparative visualization and identification of spatial consumption and carbon emission patterns. This platform will strongly position ORNL for future programmatic opportunities in large-scale utility data analytics and EERE programs.

Mission Relevance

The Department of Energy (DOE) Offices of Electricity (OE) and EERE, Solar Program have emphasized the need for residential and commercial customers to curtail their energy consumption since they are responsible for about 40% of the electricity produced in the United States, as well as the need to increase renewable energy integration into electricity generation at the distribution level. Therefore, this project complements DOE missions in the area of energy efficiency and renewable energy integration. The methods, tools, and insights developed in this LDRD project will benefit developing programs within the United States DOE OE, EERE, and Solar Office. The results and capabilities developed during this project are being utilized in the development of proposals to various programs in pursuit of follow-on funding.

Results and Accomplishments

We established an action network that includes utility companies as well as city and county governments for achieving energy efficient communities. We currently have five utility companies, the city of Knoxville, and Knox County as members. The existing partnership has led to the ownership of facility-level data for developing capabilities to achieve energy efficient communities. We also developed a geodatabase that integrates monthly energy consumption data with building characteristics, planimetric, zoning, land use, and topographic data in a novel way that provides new insights about spatial and temporal patterns in energy consumption. This geodatabase is a unique data repository capability at ORNL. We have also developed a framework for engaging citizens for energy efficient and sustainable communities. A feedback technology that implements the framework has also been developed. The technology uses consumer energy usage data to provide mechanisms with which users can monitor and compare behavior to their peers using the age and size of their house as basis for comparison, and allow them to better evaluate their conservation performance over time. Even though the initial proposal is limited to the public, key findings show that the application is of equal value to the utilities. As a result, a modification of the framework has also been developed for a utility version of the feedback technology. The feedback technology has been demonstrated to various utilities including Tennessee Valley Authority and Touchstone Energy Cooperatives and several small businesses. As a result, three companies have either indicated interest or submitted applications to license the technology. The developed technology advanced the state-of-the-art in at least three areas: the leverage of supplementary heterogeneous datasets such as building data to increase customer engagement and energy consumption awareness; the development of a two-sided system (for customers and utilities) with complementary capabilities; and the provision of energy usage history, peer comparisons, and customized suggestions for energy savings.

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Copyrighted Software

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Patent Disclosures Filed

UT-Battelle Invention Disclosure No. 2665 entitled "Citizen Engagement for Energy Efficient Communities."

06085

Experimental Test of an Innovative Intense RF-Plasma Source

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Project Description

The Physics Integration Experiment (PhIX) has been constructed to produce an experimental database for a device comprising the first two building blocks of an innovative rf plasma source. PhIX combines a large cross-section, high-density helicon plasma generator with a magnetic mirror where additional resonant electron heating will increase the energy of the high-density plasma stream. The work will contribute to development of a Plasma Material Test Station (PMTS) that will provide high steady state plasma heat and particle fluxes near a target plate producing plasma conditions similar to those anticipated in the ITER divertor region. Specifically, the database will be used to develop a Prototype High Intensity Source Experiment (PHISX), incorporating supplemental ion heating and a transport section, providing the physics basis to design a PMTS. The PMTS will be used to develop solutions to the challenging problems involved in the development of Plasma Facing Components (PFCs) and materials for the Fusion Nuclear Science Facility (FNSF) and other future fusion devices. The FNSF has been established by the DOE Office of Fusion Energy Sciences as the next-step nuclear and material science and engineering research facility for the ITER era.

Mission Relevance

The PhIX study is directly responsive to the call to "provide critical contributions to resolving the remaining scientific and technical issues associated with materials for fusion reactors… including plasma-material interactions" that is part of the ORNL FY 2011 Scientific Agenda. It involves the combined test of prototypes of fundamental source components of a PMTS. The PMTS will provide data on materials and components needed both for ITER and the design of a Fusion Nuclear Science Facility (FNSF). It includes most of the capabilities called for in a linear test stand as described in the final report of the 2009 OFES Research Needs Workshop. The FNSF, also discussed in the Laboratory Agenda, fits the mission of the "Fusion Energy Contingency" facility identified in the Facilities for the Future of Science report "to complement the research program to be conducted at ITER." It supports the high level goal of the US Fusion Energy Sciences Program to address the R&D needed for "Materials in the Fusion Environment."

Results and Accomplishments

Construction of the PhIX has been completed. The vacuum chamber has been evacuated, and all vacuum leaks have been eliminated. Final connections to magnetic field coils, helicon antenna, and whistler/EBW launchers are being made, and operation will begin in December. The SOLPS5.1(B2.5-Eirene) plasma/neutrals modeling code package has been successfully adapted to PhIX and is being used to explore operating scenarios. It was benchmarked against helicon results with deuterium (D) and showed good agreement between predicted and measured plasma density and temperature profiles for a high density ($n_e = 4 \times 10^{19}$ m^{-3}), high input power (70 kW) case. The GENRAY-C ray-tracing has predicted that a launch location between the two magnets directly downstream of the central chamber will allow full absorption of 18 GHz waves near the resonance zone and close to the center of the plasma. A 100 kW transmitter was brought on line, allowing the helicon device to be operated at the full design power level. Routine production of helium plasmas with 100 kW input power was achieved, with a corresponding power density of ~ 10 MW/m^3, at values of |B| in the helicon antenna region up to the design level of 0.5 T. Plasma densities up to 3×10^{19} m^{-3} were produced at this field, and 6×10^{19} m^{-3} at |B|=0.3 T. Good performance was also achieved with D gas, with densities up to 4×10^{19} m^{-3} achieved at a somewhat lower |B|=0.12 T, with input power = 70 kW.

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06090

Conversion of Lignin Feedstock into an Economic Automotive-Grade Carbon Fiber

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Project Description

Lignin is a valuable co-product from biorefineries that will be available in vast quantities in the near future; therefore, value-added utilization of lignin in applications such as high-value carbon fibers can have a major impact on the economy of biofuels. To date, industrially available lignin has failed to deliver the desired properties of carbonized fiber primarily due to its low molecular weight. All prior work involved melt-processing of lignin and produced brittle and weak as-spun fibers that failed to tolerate any tension during conversion, resulting in porous charred fibers. Thus, one of the specific objectives of the proposed work is to chemically modify commercial lignin to render a carbon precursor fiber that is both strong and extensible with significant intermolecular entanglement. To cost-effectively achieve this goal, the molecular weight of the lignin will be increased through crosslinking and grafting inexpensive linear oligomers such as polyacrylonitrile and polybutadiene. Both solution and melt-processing of these lignin precursors will be investigated. The overarching goal of this project is, therefore, to tune the lignin formulation, associated thermo-chemistry, and fiber formation process so that an economic carbon fiber that meets automotive industry requirements (target tensile strength, 1.72 GPa) can be produced from commercial lignin feedstock. Successful demonstration of the proposed tasks will provide the technical basis for the DOE-EERE Vehicle Technologies Program office to reinvigorate and expand its work on lignin-derived carbon fiber.

Mission Relevance

The US Department of Energy and its Energy Efficiency and Renewable Energy program offices are considering various carbon fiber precursor candidates for use in automotive industries, including polyacrylonitrile-based textiles, polyolefins, and lignin. Among the three candidates, lignin is the only renewable precursor as well as the least expensive ($0.50/lb). Lignin can offer the most environmentally attractive and economically stable carbon fiber, if all the performance criteria are met, as PAN and polyolefins suffer from volatile raw material costs due to fluctuations in the price of crude petroleum. Moreover, added-value uses for lignin will also improve the economics of the processing of biofuels, providing additional motivation to realize a process that will result in lignin-based, automotive-grade carbon fiber that can be commercialized. The limited success in demonstrating feasible routes to adequate-quality carbon fiber from oligomeric lignin feedstock has limited the interest of the DOE program offices in lignin-based carbon fiber. Our fundamentally new technical approach will enable ORNL to demonstrate the production of commercially relevant lignin-based carbon fiber.

Results and Accomplishments

The team has made major breakthroughs on (1) melt-spinning of softwood Kraft-lignin fiber (first report); formulations have 90–99% lignin; (2) stabilization of the fiber tow under favorable condition; (3) flexibility of the fiber as evidenced by the fact that it can be tied to standard carbon fiber tow by a knot. The group has developed lignin characterization protocol and is evaluating interaction parameters with various additives. Size exclusion chromatography (for the determination of lignin molecular weight and molecular weight distribution) and spectroscopic tools such as NMR and FTIR have been successfully used to determine the structure of lignin and lignin macro-initiator for modified precursor development. The FTIR spectra of macoinitiator showed characteristic absorption peaks at 2950 cm^{-1} (aliphatic CH). The 1H NMR spectra of initiator showed several characteristic peaks of methylene and methyl protons at 3.3, 1.6, 1.2, 0.9 ppm, respectively. Currently, the chemistry team is optimizing the reaction conditions for performing acrylonitrile oligomerization. The preliminary neutron reflectivity experiments on the characterization of interactions at lignin-additive interface have been conducted. A part of the team is working on optimization of conversion protocol and managing the export control issues pertaining to this project. At this moment mechanical properties are less than half of the values obtained for other alternative precursors (700 MPa and 50 GPa range). Once we obtain good properties we will demonstrate that this technology is applicable to source-neutral lignin chemistries. Our future work focuses on the improvement in precursor chemistry so that one can get better precursor fiber.

06105

Understanding Used Nuclear Fuel Cladding Performance Characteristics during Very Long-Term Storage

K.T. Clarno, Y. Yan, B. Radhakrishnan, S. Gorti, B. Philip, R. Jubin

Project Description

This project seeks to develop an improved understanding of hydride nucleation in used nuclear fuel (UNF) and the hydride reorientation process and to develop an initial, validated simulation capability. The key deliverables in this project will be a coupled phase-field and crystal-plasticity code to predict the nucleation of several hydride phases in Zircaloy-4 and comparisons with hydride samples for validation. Initial validation will be performed with well-characterized, unirradiated hydrogen-charged zirconium alloys that simulate the mechanical properties of the high-burnup samples under very long-term storage (VLTS) of UNF conditions. Microstructural evolution of the hydrogen-charged sample occurs through the nucleation and growth of hydride precipitates and the coupled evolution of the Zircaloy matrix grains. An experimental facility will be developed to implant hydrogen in clean zirconium and Zircaloy samples, internal pressurization will simulate the drying conditions to initiate the reorientation process, and ring compression tests will measure the strength of the samples that are clean (no hydrogen), naturally hydrided, and radially hydrided. The hydrided samples will also be characterized to visually validate the software.

Mission Relevance

The US Department of Energy's (DOE's) decision to withdraw the license application for the proposed geologic repository at Yucca Mountain has several significant consequences, including (1) the United States no longer has a plan for the disposition of UNF and (2) the US Nuclear Regulatory Commission (NRC) must reevaluate its basis for confidence in the US government's ability to safely store UNF for an indefinite period of time. The former consequence will result in VLTS of UNF and, following VLTS, the transport of UNF; the latter has direct implications for the continued operation of all US nuclear power plants. The relevance of this project is based on developing an improved understanding of hydride nucleation in UNF and the reorientation process and to develop an initial, validated simulation capability that can be used to develop the technical basis for the safe storage and transport of UNF during protracted time periods.

Results and Accomplishments

A literature survey of experimental, modeling, and thermodynamic data was completed to identify the most critical unanswered issues in hydride precipitation and reorientation and existing experimental data that will provide initial validation data for Zircaloy-4. The software has been developed that solves the governing equations using the Fourier Spectral method with the FFTW (Fastest Fourier Transform in the West) library. The time-dependent Ginzburg-Landau and Cahn-Hilliard equations have been independently validated with existing data, and the coupled version has been completed, including the elastic energy terms. The thermodynamic and material data have been collected for various hydride forms in zirconium and Zircaloy-4. This software has contributed to a paper for the 2013 International High-Level Radioactive Waste Management Conference. Related to validation, the zirconium and Zircaloy-4 materials have been acquired, implanted with hydrogen, and characterized using the ring compression test at room temperature. The hydrogen content of the hydrided materials was measured using the Vacuum Hot Extraction Method, and the hydride morphology was examined by metallography and scanning electron microscopy. The ring compression tests have lead to another paper for the 2013 International High-Level Radioactive Waste Management Conference. The design of the hydride reorientation system has been completed, the parts have been acquired, and the preliminary safety review has been completed.

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06129

A Hydraulically Isolated Fuels and Materials Irradiation Capability for HFIR

J.L. McDuffee, J.J. Carbajo, D.K. Felde, L.J. Ott, K.R. Robb

Project Description

Currently the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) requires most materials and all fuel experiments to be placed in an external containment to ensure that internal contaminants such as fission products cannot be released into the primary coolant. It also requires that all experiments can withstand various accident conditions (e.g., loss of coolant) without generating vapor bubbles on the surface of the experiment in the primary coolant. The effect of these requirements is to artificially increase experiment temperatures by introducing a barrier between the experimental materials and the HFIR coolant and to reduce experiment heat loads to ensure no boiling can occur. A proposed materials irradiation design would remove these limitations by providing the required primary containment with a separate internal cooling flow. Experiments can then be irradiated without as much concern for coolant contamination (e.g., from cladding failure from advanced fuel pins) or for specimen heat load. This proposal is to design and test a new materials irradiation experiment design that uses a heat pipe cooling system to allow experimental materials direct access to a liquid coolant and that also increases the range of conditions that can be tested in HFIR. Once developed and tested, this design will provide a unique capability to validate the performance of current and advanced fuels and materials.

Mission Relevance

The U.S. Department of Energy (DOE) through the Basic Energy Sciences, Fusion Energy, and Nuclear Energy programs has been the primary long-term driver behind the recent growth in the demand for irradiation experiments. In particular, the Fusion Energy program has supported a wide variety of irradiation experiments over many decades, and the Light Water Reactor Sustainability Program and the Fuel Cycle Research and Development Program have each recently invested in new or ongoing irradiation projects at HFIR. In addition to these long-term sponsors, a significant portion of the current workload is from Work-For-Others contracts with private entities. A heat-pipe-cooled irradiation platform represents a strategic opportunity to augment and continue to grow ORNL's neutron irradiation capability through enhanced experiment flexibility.

Results and Accomplishments

A detailed analysis of the operating characteristics of the available HFIR irradiation locations was conducted and summarized into a technical report. The large vertical experimental facilities (VXF) location, which has the largest available volume of any irradiation site in HFIR, was selected as the baseline irradiation location for a thermosyphon experiment. The available thermal neutron flux is more than ample to simulate the conditions in a light water reactor.

A working computational model for an irradiation experiment cooled with a thermosyphon was developed. The research team has taken a multi-pronged approach by using two methods simultaneously. The first method focuses on previously developed empirical correlations for the heat transfer coefficients in the evaporator and condenser sections. The flow is approximated using the homogenous equilibrium model. The second approach is to use the RELAP5-3D code, a commonly used two-phase thermal-hydraulic simulator. The team rejected the standard RELAP5 code due to its inability to converge to a solution in a standard test case. The advantage of using the RELAP5-3D code is that the research team can benefit from established coding and model validation.

Significant progress was made to establish a working design that meets the design requirements. The research team has developed a working model in the Pro-E design software. All of the basic parts, assemblies, and some preliminary sketches are complete. The secondary cooling system has been designed, fabricated, and delivered. Final design details for the thermosyphon are near completion, and fabrication will begin soon.

Information Shared

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06146

Science of the Plasma-Materials Interface at Extreme Conditions

F.W. Meyer, H.M. Meyer III, H. Hijzai, J. Dadras

Project Description

We propose a new coordinated theoretical and experimental approach to study plasma-material interactions under the extreme conditions of high-radiation damage and high temperature. Such extreme material conditions are projected for next-generation fusion reactors, whose plasma-facing walls will be exposed to >MW/m^2 neutron and plasma-particle loading and will therefore operate at high temperatures. We will characterize the effects of displacement damage (vacancies, interstitials, bubbles, voids, etc.) and helium (He)-ash accumulation on surface morphology and on fundamental low-energy plasma-material interface (PMI) processes, such as sputtering, hydrogen (H) retention, reflection, sticking, implantation, trapping/detrapping, and diffusion, in high-damage-level reactor materials at reactor-relevant temperatures. Using the unique capabilities of the Multicharged Ion Research Facility (MIRF), we will produce neutron-like damage by exposure of the material to high-energy self-ions of appropriate energy, followed by intense He^+ and H^+ low-energy beam exposure to simulate the He ash and cold fusion edge plasma. Using ORNL leadership computer facilities, we will employ various atomistic and continuum dynamics approaches to simulate high-energy damage production and low-energy PMI processes. This proposal is an innovative first step towards development of a fundamental reactor-relevant PMI science to position ORNL for a leadership role in this important new area of fusion research.

Mission Relevance

The first wall of magnetic fusion reactors must sustain large (~10 MW/m^2) heat and particle (neutron, ions) fluxes. The resulting material damage and high operating temperatures will significantly affect plasma wall interactions. A recent report to the Fusion Energy Sciences Advisory Committee found that four of the top five critical knowledge gaps for fusion involve the plasma-materials interface. More recently, the understanding of materials in extreme fusion reactor environments was identified as one of the two high-level goals in fusion research in the coming decade. It is recognized that the present national (OFES) investment towards reaching this high-level goal is only a small fraction of what is needed; this inadequate funding level will require development of a new fusion materials science program to define and construct the Fusion Nuclear Science Facility (FNSF).

Results and Accomplishments

In Year I of this LDRD project, we have accomplished the following tasks.

1) We have developed intense W beams for use in creating W targets damaged to >100 dpa levels by irradiation with self-ions.

2) In the course of the beam development we have made a number of electron cyclotron resonance (ECR) source changes that significantly increased source output.

3) We have used the W self-ions to expose W targets to damage doses in excess of 100 dpa, both at room temperature and at ~1200 K; the resulting damage was characterized using focused ion beam scanning electron microscopy (FIB/SEM) and focused ion beam transmission electron microscopy (FIB/TEM).

4) Using an intense He ion beam decelerated to energies in the range 50–200 eV, we have irradiated W targets heated to ~1200K to fluences in excess of 10^{20} cm^{-2} to study the early phases of W nanopfuzz formation. Using ex situ SEM and FIB/SEM, we were able to identify changes in surface morphology and nanostructures, such as surface rippling, bubble formation, and near-surface recrystallization, occurring below the physical sputtering threshold.

5) In order to increase available He ion beam intensity, a new beamline deceleration module was designed and fabricated, by which an order-of-magnitude increase in fluence was obtained.

6) We explored the effect on low-energy He ion-induced W surface morphology changes of prior damage of the W target, by exposure first to a high damage dose of W self-ions.

7) In parallel with the experimental work, modeling efforts were pursued to simulate the W self-ion damage cascade using LAMMPS on Jaguar and Kraken.

06160

Integrated Computational Modeling and Innovative Processing to Eliminate Rare Earths from Wrought Magnesium Alloys

B. Radhakrishnan, Z. Feng, R. Dehoff, S. Gorti, R. Patton, W. Peter, A. Shyam, S. Simunovic

Project Description

The project seeks to integrate micromechanical material models, process models, and experimental data through a multi-objective optimization tool to design a microstructure that optimizes two conflicting material properties. The integrated approach addresses a critical need in the microstructural design of structural materials for vehicle applications where conflicting properties have to be optimized, and provides the necessary framework to enable innovation in processing and the exploration of new micro-mechanical concepts. The integrated approach will be used to develop a rare earth–free wrought magnesium alloy that meets or exceeds the current specifications in rare earth–containing alloys for strength and ductility. The approach will target three innovative processes – friction stir extrusion, ultrasonic roll bonding, and additive roll bonding to introduce mechanical alloying of magnesium with titanium to provide additional twin and slip systems in the alloy in the ultra-fine grain size range. Mechanical alloying will offer the potential to utilize nanotwins as structural barriers to dislocation flow as well as to allow glide of dislocations at the twin-matrix interface – a novel concept that has demonstrated simultaneous increase in strength and ductility in ultrafine-grained copper.

Mission Relevance

The proposed research focuses on the development of an integrated computational modeling and experimental effort that exploits the state-of-the-art high-performance computing capabilities and the unique processing capabilities of the laboratory to design the next-generation wrought magnesium alloys with exceptional strength and ductility for automotive and other lightweight applications. The proposed integrated approach is generic, and it is very valuable for the rapid development of the next-generation alloys and processes for structural materials used in critical technology mission areas of DOE including Vehicle Technology and Industrial Technology programs. The outcome of the project is also significant to the DARPA program because it will result in ultra-lightweight armor applications, highly mobile military tactical vehicles, and other critical lightweight applications in military technologies. Reduction of structural weight is critical in space applications and therefore is very relevant to the mission of NASA, especially for outer space explorations.

Results and Accomplishments

An initial benchmark problem was defined that relates material microstructure and two different attributes of the microstructure, grain orientation and grain misorientation distribution, and couples with a genetic algorithm to optimize the two attributes. The problem was successfully solved. The problem was then extended to a coupling between a material micro-mechanics code that defines two material properties, strength and ductility as a function of the above microstructural attributes with a genetic algorithm. The two codes were run in parallel and an optimization of the strength and ductility was demonstrated. The optimization approach is being extended to other optimization methods that exist in the computational tool kit DAKOTA. Methods have also been developed to represent the input texture for optimization studies using orientation distribution functions that describe strong basal texture and weak basal texture in magnesium alloys. The crystal plasticity code used for the property computations has been extended to AZ31 alloy incorporating additional twin and slip systems as demonstrated in previous mechanical alloying studies of titanium with magnesium. An additional glide system along the twin-matrix interface has also been introduced in order to study the influence of slip along the twin-matrix interface on the strength and ductility of AZ31. On the experimental side, a number of severe deformation processing experiments were attempted in order to demonstrate mechanical alloying of titanium with Mg/AZ31 alloy. The friction stir processing (FSP) approach showed a clear demonstration of titanium solubility in AZ31 and has been selected as the process of choice moving forward.

Information Shared

Two presentations (1 oral and 1 poster) at the MRS Symposium, Boston, MA, November 25–30, 2012.

06237
An Approach for Linking Glass Composition and Structure to Long-Term Performance

E.M. Pierce

Research Plan

Solid-solution interfacial reactions play a critical role in the evolution of geologic systems (e.g., weathering of primary minerals and CO_2 drawdown). In addition to geologic systems, solid-water interactions are also important for a range of areas with energy and industrial applications (e.g., natural gas recovery, battery research, and numerous industrial chemical separation processes that utilize heterogeneous catalytic reactions). Furthermore, the need to accurately forecast estimates of radionuclide release from corroding nuclear waste glass has also resulted in a significant focus on ascertaining an improved understanding of the interfacial mechanisms and rates that control glass-water interactions.

The objective of the research outlined in this LDRD proposal is to develop a mechanistic understanding of the processes that control the long-term corrosion of nuclear waste glass, specifically alumino-borosilicate glass. The specific aim is to improve our understanding of the processes that control the formation and conversion of an amorphous hydrated surface layer (e.g., gel layer) to a structurally ordered crypto-crystalline or crystalline alteration product during the glass-water reaction. The gel layer (e.g., three-dimensional hydrated surface layer) forms when network bonds in the glass are hydrolyzed by water and relatively insoluble elements contained in the glass (e.g., Al, Fe, Si) condense at the glass-water interface. Upon completion of this project, the technical approach, tools developed, and knowledge gained will provide some of the critical insights needed to link macroscopic reaction kinetics to nanometer-scale interfacial processes. This insight will enable multiple continua models to adequately and accurately describe the microscopic processes (e.g., growth and dissolution) that represent two of the underlying phenomena controlling radionuclide release from corroding nuclear waste glass. The technical challenge of improving the scientific basis for the disposal of nuclear waste glass represents one key aspect that must be addressed to enable a sustainable nuclear fuel cycle.

Mission Relevance

A major objective for the Department of Energy (DOE) Office of Nuclear Energy (NE) is the development of sustainable nuclear fuel cycles with the goal of developing a suite of options that will enable future decision makers to make informed choices about how to best manage the used fuel from reactors (NE 2010). Each of the existing fuel cycle options—once-through, modified open cycle, and full recycling—being considered as part of this effort presents unique scientific challenges as it relates to the disposal of nuclear waste. Two of the three fuel cycle options—modified open and full recycling—contain a reprocessing scheme that is expected to produce borosilicate glass as a candidate waste forms.

Results and Accomplishments

In the second year (FY 2012) of this LDRD, the major achievements included (1) fabrication of a new in situ small-angle x-ray scattering reactor that allows for characterization of glass surfaces during corrosion, (2) a publication of new perspective on interfacial reaction mechanisms occurring at the glass-water interface and control surface layer development, and (3) a modeling publication that highlights the origin and dynamics of silica being incorporated into the hydrated surface layer during the glass-water reaction. Based on these activities, next year's work will focus on obtaining in situ measurements of surface layer formation and improvements in the cell design to allow for measurements at temperatures less than 100°C.

06244
Demonstration of Electric Vehicle Dynamic On-Road Wireless Power Charging

J.M. Miller, O.C. Onar, P. Ning, C.P. White, L. Seiber, C. Coomer, S. Campbell

Project Description

The aim of this project is to demonstrate in-motion charging of an electric vehicle (EV) from the roadway. To implement this, coupling coils were mounted into floor pads used previously for an in-motion weighting program at the National Transportation Research Center (NTRC). An existing high-power inverter was used to energize a pair of floor-mounted coils, and a mating coil was mounted beneath the demonstration vehicle chassis with integrated rectifier and filter before connection to the vehicle battery pack. In June 2012 the first successful demonstration of in-motion wireless charging of an EV took place in the laboratory of the NTRC.

This project is focused on the development and refinement of key functional elements of wireless power transfer (WPT) for in-motion applications that now limit its introduction and commercialization. These include grid-side power conversion and regulation, coil-to-coil transfer efficiency, and bidirectional communication between the vehicle and the grid. At the end of FY 2011 the program identified the three most pressing challenges to be addressed as (1) coupling coil efficiency greater than 97%, (2) grid side regulation of power flow control, (3) control strategy that optimizes power coupling and method to sequentially energize roadway coils, and (4) implementation of carbon-carbon ultracapacitor module in active parallel combination with the GEM vehicle battery to smooth its charging current.

During execution of this project, the coupling coils were validated to have 97.3% efficiency at high power and regulation was performed on the grid-side power inverter. Control strategy is still under way, especially the means to selectively energize coupling coils passing beneath the vehicle being charging and controlling the power flow in the process. During FY 2013 the team will make contact with semiconductor researchers for development and availability of an ac switch (semiconductor) that would greatly facilitate coil sequencing. For demonstration work, and given the unavailability of such an ac switch, the team will use alternative technical solutions to sequence the primary coils.

Another goal of this project is to promote the adoption of international standards governing wireless power charging. ORNL is a member of the Society of Automotive Engineers (SAE) wireless charging task force SAE J2954 and is proactive in advocating the allocation of frequency spectrum in the 10 kHz to 100 kHz space for WPT. To this end, the team is developing stationary WPT charging at 25 kHz and in-motion wireless charging at 48 kHz. To facilitate this, the team has obtained sample quantities of high-speed insulated gate bipolar transistors (IGBT) from a leading semiconductor manufacturer for this project.

This project will include demonstration of short range radio communications in the context of vehicle to infrastructure (V2I) that will also facilitate WPT standard adoption. The team will procure B&B ZP24D-250RM-SR radios that operate in the 2.4 GHz range for communication of vehicle battery status and charging parameters to the base WPT unit.

Mission Relevance

Wireless charging is now seen by DOE and many in the automotive field as the enabling technology if widespread implementation of electric vehicles is to occur. The ease of use is seen as the technology advance that will make battery or plug-in vehicles accepted by the average household. However, the game-changing potential for WPT can only be realized if in-motion technology is widely accepted. Pioneering work on high-efficiency and high-power coupling coil designs now under way in this LDRD project will facilitate faster progress on DOE Vehicle Technology Program–funded wireless power stationary charging. ORNL has successfully advanced coupling coil designs for high efficiency and promoted the adoption of a single center frequency for international standards on wireless charging. During FY 2012 numerous demonstrations of the in-motion wireless charging technology were done, including showcasing the ORNL design to visiting DOE Vehicle Technologies program executives, members of the USCAR consortium, and U.S. Department of Transportation (DOT) research and innovative technology administration (RITA) executive.

When developed, this system will benefit not only DOE interests but DOT interest for roadway electrification and addressing public–private interests in the use of electricity for transportation.

Results and Accomplishments

During FY 2012 the in-motion wireless power transfer (WPT) charging project built on the design work done in late FY 2011 using pull-ahead funding. The project at that time was focused on use of a thre-wheel all electric vehicle, a BugE obtained from Elite Power Solutions of Phoenix, AZ, and used by students at the University of Tennessee in Knoxville. In-motion charging coils were designed by the project engineers specifically to fit that vehicle. The vehicle was obtained on loan to ORNL from UTK and was found to have been completed stripped of battery pack (36 V lithium-ion) and electric traction drive system (inverter, controller and motor). It was then returned to UTK and noted to be not useable by the ORNL team. In its place a GEM electric, low-speed, neighborhood electric vehicle (NEV) was obtained on loan for 1 year from the ORNL main campus.

The in-motion demonstrator vehicle contains a 72 V lead-acid battery pack and 60 V traction motor with power electronic controller. Because of the expense in purpose designed WPT coupling coils, the coil sets fabricated for the initially proposed BugE vehicle were used on the GEM. During FY 2012 these coils were characterized and tested up to 3 kW power transfer using an available high-frequency power inverter operating at approximately 25 kHz. Because the GEM EV demonstrator has a standard 1.7 kW on-board-charger (OBC), the WPT power level was reduced to 2.2 kW maximum. During demonstrations the GEM vehicle was outfitted with a light pole that served as a visual indicator of charging power. During FY 2012 the team had not yet incorporated the radio into the power flow control as the available unit requires installation of a gateway for battery data input and conversion to RS232. The base radio has provision to output transmitted messages back to RS232 and thence as input to the Digital Signal Processor (DSP) controller used in WPT power regulation. The DSP controller used in our WPT work has a clock speed of 150 MHz, a serial interface speed of over 9 Mbit/s, and word length of 32 bits.

During FY13 the GEM vehicle will continue being used, and it will be equipped with the above mentioned radio. The floor-embedded coils will be expanded from the present two to a full complement of six. The high-frequency power inverter designed around warp IGBT's operating at 48 kHz will be tested and further demonstration performed using this inverter. Also planned for FY 2013 will be the inclusion of carbon-carbon ultracapacitor module in the GEM vehicle battery compartment in active combination with the lead-acid battery pack to smoothen the charging power to the battery that has pulsing character now as the vehicle passes over floor coils.

This report covers FY 2012 pull-ahead funding of LDRD#6244 (formerly #6021), "Demonstration of Electric Vehicle Dynamic On-Road Wireless Power Charging," for the reporting months of October – September 2012. Wireless power transfer, wireless power charging, and inductive power transfer (IPT) have been used synonymously for magnetic resonance coupling in the open literature.

Information Shared

Invited Presentations

Invited to SAE World Congress 2012 to lead a "Chat with the Experts" session on Wireless Charging of EV and PHEV batteries, at the 2012 SAE World Congress in Detroit, 24–26April 2012.

Invited presentation to IEEE International Electric Vehicle Conference, IEVC2012, panel on New Trends in EV Development, chaired by Dr. Zoran Filipi, CU Conference Center, Greenville, SC, 6 March 2012.

John M. Miller, "Wireless PEV Charging," Electrical & Electronics Technical Team, USCAR Office, Southfield, MI, 26 April 2012.

Invited by Clemson University-International Center for Automotive Research to the 2012 IEEE International Electric Vehicle Conference, to speak on Wireless Power Charging, Greenville, SC, 4–8 March 2012.

Invited presentation, "Wireless Power Charging Fundamentals and Challenges," SAE 2012 Electric Vehicle Technology Symposium, San Diego, CA, 21–22 February 2012.

Invited presentation, "Wireless Power Charging Fundamentals and Challenges," SAE 2012 Electric Vehicle Technology Symposium, San Diego, CA, 21–22 February 2012.

Invited panelist on 4th Workshop on EV's: Transportation and Electricity Convergence, Houston, TX, 2–3 November 2011.

John M. Miller, "National Laboratory Perspective on PEV's," Electric Vehicles, Transportation and Electricity Convergence, EV-TEC2011, Houston Medical Center, 2 Nov. 2011.

John M. Miller, "Wireless Power Transfer Fundamentals and Challenges," Electric Vehicle Wireless Power Transfer, EVWPT2011 and IECON Industry Forum, Crown Metropol, Melbourne, Australia, 7–10 November 2011.

John M. Miller, ORNL's Wireless Power Transfer technology and laboratory demonstration to Ms. Patricia Hoffman, Assistant Secretary, U.S. DOE, 11 Oct. 2011.

Conference/Journal Papers

John M. Miller, Cliff P. White, Omer C. Onar, Phil M. Ryan, "Grid Side Regulation of Wireless Power Charging of Plug-in Electric Vehicles," IEEE 4th Energy Conversion Congress & Exposition ECCE2012, Raleigh, NC, 15–20 September 2012.

John M. Miller, Omer Onar, "ORNL's In-motion WPT System," Conference on Electric Roads and Vehicles, CERV2012, Newpark Resort and Hotel, Park City, UT, 16–17 February 2012.

Michael Pickelsimer, Leon Tolbert, Burak Ozpineci, John M. Miller, "Simulation of an Electric Vehicle Class Wireless Power Transfer System as Viewed from the Power Grid," IEEE International Electric Vehicle Conference, IEVC2012, CU-ICAR, Greenville, SC, 4–8 March 2012.

Invention Disclosures/Patents

PCT/US12/43095 filed on Wireless Power Transfer Electric Vehicle Supply Equipment Installation and Validation Tool

PCT/US12/45904 filed on Vehicle to Wireless Power Transfer Coupling Coil Alignment Sensor

PCT/US12/40086 filed on Regulation Control and Energy Management Strategy for Wireless Power Transfer

Non-Provisional #13/447,447 filed on Above Resonance Operation of Wireless Power Transfer Vehicle Charging

PCT/US12/ in draft stage December 2012 on Stationary and Dynamic Wireless Power Charging using Point of Load Controlled High Frequency Power Converters

PCT/US11/47830 filed on Above Resonance Frequency Operation for Wireless Power Transfer

Regular Patent Docket number 201202956 on Buffering Energy Storage Systems for Reduced Grid and Vehicle Battery Stress for Wireless in-motion Wireless Power Transfer
Election decision pending on Coupling Coefficient Wireless Power Transfer Coil Set
PCT/US12/43088 filed on Graphene-Coated Coupling Coil for AC Resistance Reduction

06477

Model-Inspired Science Priorities for Evaluating Tropical Ecosystem Response to Climate Change

F.M. Hoffman, L. Gu, R.J. Norby, X. Yang, D. Weston, J. Kumar

Project Description

Carbon cycling in tropical forests and the feedbacks from tropical ecosystems to the climate system are critical uncertainties in current Earth System Models (ESMs) that must be resolved to more reliably project global responses to climate change. The objectives of this project are to provide model improvements and initial model experiments and analyses that define the critical science objectives for a future Next-Generation Ecosystem Experiment (NGEE) project focused on tropical ecosystems and to provide guidance for an intensive campaign of structured observations and manipulative experiments. Improvements in how ESMs represent photosynthesis and phosphorus limitations to carbon cycling will be implemented and evaluated. Model experiments using CLM4 will define the relative sensitivity of tropical forests to elevated CO_2, climate warming, and drought. Cluster analysis that combines current-generation models with climate and geophysical data will provide quantitative delineation of tropical regions that are most important for intensive observations and modeling. Together, these model products will guide the development of an experimental framework, define critical field experiments, and initiate the iterative process of model-experiment interaction.

Mission Relevance

A long-term goal of the DOE Office of Biological and Environmental Research (BER) is to determine the effects of multi-nutrient limitation on the responses of tropical forest ecosystems to climate change. DOE intends to meet this objective through a new multi-Laboratory NGEE Tropics project contained in budget plans for FY 2013. At a science scoping workshop hosted by DOE on June 4–6, BER defined a prospected NGEE Tropics project that will "be a model informed field study that results in iterative refinement of high resolution predictive models and be based on field studies in the most climate sensitive tropical geographies that provides a high scientific return on investment." This project provides model improvements and initial model experiments and analyses that define the critical science objectives for a new NGEE Tropics project.

Results and Accomplishments

While initially planned for a 1 year duration beginning in October 2012, this project was started in August 2012, primarily so that an intensive field campaign at the Smithsonian Tropical Research Institute (STRI) in Panama could be performed prior to the wet season. The resulting leaf gas exchange measurements and laboratory analyses on various tropical plant species will drive model improvements in how ESMs represent photosynthesis and phosphorus limitation. With assistance from Dr. Klaus Winter, senior staff scientist at STRI, the first field measurements were conducted at the Parque Natural Metropolitano and Gamboa in September 2012. Initial results for a limited number of tropical species indicate (1) no discernible control of leaf nitrogen on photosynthetic parameters, (2) the current parameterization of stomatal conductance in the Community Land Model (CLM4) may not be well suited for tropical species, and (3) mesophyll conductance significantly limits photosynthesis in tropical species. Additional measurements are needed to determine the consistency of these results across tropical species and establish new model parameterizations. Leaf gas exchange measurements will be collected at three sites—Parque Natural San Lorenzo, Gamboa, and Parque Natural Metropolitano—during a second field campaign, planned for early 2013. Cranes will be used to access tree canopies at two sites to obtain leaf gas exchange measurements in closed tree canopies to complement ground-based measurements. In addition, initial work to implement a phosphorus limitation mechanism and to configure a version of CLM4 for global simulations with mesophyll conductance was performed during the initial 2 months of the project.

Information Shared

F.M. Hoffman, L. Gu, R. J. Norby, X. Yang, D. Weston, and J. Kumar, “Model-Inspired Science Priorities for Evaluating Tropical Ecosystem Response to Climate Change,” abstract for BER poster session (October 24, 2012), Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

F.M. Hoffman, L. Gu, R. J. Norby, X. Yang, D. Weston, and J. Kumar, “Model-Inspired Science Priorities for Evaluating Tropical Ecosystem Response to Climate Change,” poster presented at BER poster session (October 24, 2012), Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA.

06654

Advancing Lignin-based Carbon Fibers from Lab Scale into the Commercial Market

T. Rogers and A. Naskar

Project Description

Lignin-based carbon fibers are of great interest to industry both in the United States and across the globe. Lignin is an abundant, renewable raw material and is the only known potential carbon fiber material which is not petroleum based. Lignin also offers the potential to significantly reduce the cost of producing carbon fiber, which could lead to the development of many new market applications. One of the barriers to the development of these fibers has been the lack of market pull from industry. While lignin is abundant and inexpensive in its raw form, it will require some investment to process these materials before they can be converted into carbon fiber, and without a market for those fibers, there has been no incentive for potential lignin suppliers to make those investments.

This project specifically addresses the resolution of key technical barriers to commercialization of lignin-based carbon fibers that are not being addressed in currently funded work. This work addresses key barriers that must be resolved to achieve successful commercialization of functional carbon fibers for thermal insulation. These key barriers are (i) qualification of multiple lignin sources and (ii) development of a rapid stabilization process.

Mission Relevance

This project is highly relevant to DOE's energy resources mission and the biomass program specifically. Lignin is an abundant and renewable raw material and is currently a by-product of both bio-refineries and pulp and paper manufacturers. If lignin can be converted into carbon fiber, a high-value product, it would significantly enhance the economics of producing biofuels.

Results and Accomplishments

This work aimed to fill strategic gaps in the path to commercialize carbon fiber. We have identified potential sources of lignin that can be obtained in large quantities from partners and that can be spun and converted to CF at reasonable costs.

Eight different industrial lignin samples were analyzed using a common screening protocol to determine each lignin’s suitability as a carbon fiber precursor. The screening protocol includes (i) thermal analysis, (ii) compositional analysis, (iii) fiber spinning trials, (iv) molecular weight analysis, (v) oxidation/stabilization trials, and (vi) carbonization trials. The results from this analysis will be used to determine the top three lignin sources to use in scaling trials at the Carbon Fiber Technology Facility in 2013. Among the eight samples analyzed were hardwood and softwood lignins that came from bio-refineries and pulp mills. The sample pool also included an annual grass lignin from a bio-refinery. Four of the eight samples that were analyzed had very promising results. We will continue to receive and analyze lignin samples in 2013 from companies that have the motivation and ability to supply lignin at the commercial scale.

Significant progress was also made toward developing a rapid stabilization process. A small reactor (400 g capacity, bench scale) was designed to demonstrate that devolatilization can be used to improve stabilization kinetics without loss of fiber spinnability. Spun fibers demonstrated less than 10 hours of stabilization time compared to its control, which exceeded 100 hours. This technique will be further investigated in 2013 in an effort to develop a commercially viable stabilization process. Stabilization time will likely need to be further reduced by another order of magnitude.

DISTINCTIVE SCIENTIFIC CAPABILITIES

05388
Multiphase Self-Organized Interfaces for Polymer Photovoltaic Technologies

S.M. Kilbey II, B.G. Sumpter, D.L. Pickel, W.T. Heller, J.F. Ankner, R. Shaw, J. Chen, M. Ramanathan, J.A. Calderon, M.D. Dadmun

Project Description

Through a joint experimental and theoretical/computational effort, we have investigated the underlying science needed to develop nanoparticle-polymer photovoltaic (PV) devices having tailored heterojunction interfaces comprising self-organized blends of semiconducting conjugated polymers and semiconductor quantum dots (SQDs) as well as conjugated polymer/fullerene composites. Understanding how to manipulate the donor/acceptor morphology and tailor heterojunction interfaces in bulk heterojunction thin films is crucial for optimizing photocurrent generation and creating low-cost, efficient polymer-based PV cells. Research activities aimed at understanding the nanoscale structure and properties of polymer-nanoparticle interfaces will yield fundamental knowledge of the links between electronic and morphological states of the systems, ultimately enabling the ability to tailor blends comprising semiconducting quantum dots or fullerenes (acceptors) and semiconducting polymers (donors) that make up the photoactive layer of a PV cell. This project addresses major needs in the fundamental design of photoactive layers and integrates expertise in computation, scattering, spectroscopy, and polymer science and physics to address challenging problems in soft and hybrid materials for energy conversion technologies.

Mission Relevance

Driven by the need for energy security and reinforced by the need for a cleaner environment, technologies that harness renewable energy sources are receiving increased interest. In this regard, the development and deployment of large-area, low-cost, and efficient PV systems is of considerable importance and wholly consistent with Laboratory and DOE Office of Science missions. Through this research program, barrier issues in polymer-based PV systems are being addressed, existing capabilities across the Laboratory in computational, neutron, and soft matter sciences are being integrated, and new capabilities in these areas are also being developed. The interdisciplinary research team developed here is well positioned to respond to future, anticipated calls in the area of materials for energy conversion technologies (solar, battery, etc.), and aspects of the work continue with the sponsorship of the Center for Nanophase Materials Sciences.

Results and Accomplishments

A variety of accomplishments related to understanding morphology development and excitonic processes and improving charge transport in PV systems based on conjugated polymers and nanoparticles, including both SQDs and fullerene-based derivatives, have been attained during this research program. New capabilities in the synthesis of well-defined conjugated polymers with appropriate chain-end functionality have been developed, which has enabled studies of block copolymer-based compatibilizers to optimize the nanoscale morphology of donor-acceptor blends. Insight into the thermodynamic origin of the ability of the block copolymer compatibilizer to tune morphology has been gained using computational methods. The photophysics of oligomeric paraphenylenes (OPPs) was investigated using large-scale quantum density functional calculations, and results from computation were compared to measured optical absorbances of OPPs in thin film form and end-tethered poly(para-phenylenes) used to compatibilize electrode-like surfaces. Particularly impressive changes in performance, ostensibly related to surface dipoles that enhance charge extraction, have been revealed in bulk heterojunction blends containing conjugated polymer-modified electrodes. New capabilities in spectroscopic imaging of donor-acceptor blends, light- and thermal-aging studies of PV blends, and sample environments for carrying out neutron scattering studies have been developed and used to examine the nanoscale morphology of organic PV systems. These results as well as the underlying new capabilities, for example, electrical current atomic force microscopy, developed through this research program are being used to advance the understanding of the intimate links between assembly, structure, and optoelectronic properties.

Information Shared

W. M. Kochemba et al. "In-Situ Formation of Pyridyl-Functionalized Poly(3-hexylthiophene)s via Quenching of the Grignard Metathesis Polymerization: Toward Ligands for Semiconductor Quantum Dots," *Chemistry of Materials* (published on-line October 2012: dx.doi.org/10.1021/cm302915h)

J. Chen et al. , "Ternary Behavior and Systematic Nanoscale Manipulation of Domain Structures in P3HT/PCBM/P3HT-b-PEO Films," *Journal of Materials Chemistry*, **22**(26), 13013–13022 (2012); featured on inside front cover.

W. M. Kochemba et al., "End-group Composition of Poly(3-hexylthiphene)s Prepared by In Situ Quenching of the GRIM Polymerization: Influence of Additives and Reaction Conditions," *Journal of Polymer Science: Part A. Polymer Chemistry*, **50**(14), 2762–2769 (2012).

J. Alonzo et al., "Assembly and Characterization of Well Defined High Molecular Weight Poly(p-phenylene) Polymer Brushes," *Chemistry of Materials*, **23**(19), 4367–4374 (2011).

Z. He et al., "Enhanced Performance Consistency in Nanoparticle/TIPS Pentacene-Based Organic Thin Film Transistors," *Advanced Functional Materials*, **21**(19), 3617–3623 (2011).

Z. Sun et al., "P3HT-b-PS Copolymers as P3HT/PCBM Interfacial Compatibilizers for High Efficiency Photovoltaics," *Advanced Materials*, **23**(4), 5529–5535 (2011).

Other information shared: nine invited presentations, ten contributed presentations and six conference proceedings.

05404

Asynchronous In Situ Neutron Scattering Measurement of <10-μs Transient Phenomena at Spallation Neutron Source

K. An, R.A. Riedel, S.D. Miller, J.A. Kohl, H. Choo, J. Jones

Project Description

The advent of extremely high neutron flux, unique time event data acquisition, and novel instrumentation at the Spallation Neutron Source (SNS) opens up new possibilities, especially for in situ dynamic and kinetic studies. Unlike conventional histogram data at other time-of-flight neutron sources, the time event data acquisition scheme at SNS records neutrons with an intrinsic timing resolution of 100 ns. The objective of this project is to develop a transformational asynchronous in situ neutron measurement method that enables unprecedented <10-μs time resolution. A new technique will be developed making use of both neutron scattering and pump parameters in time event data acquisition mode, as well as real-time data analysis and visualization algorithms. A demonstration study will examine dynamic ferroelectric domain reorientation behavior in piezoelectric ceramics, which occurs at timescales from 1 to ~100 μs during application of electrical fields. The proposed asynchronous approach will increase timing resolution on the SNS instrument suite by three orders of magnitude from 10 ms to 10 μs; fundamentally change the way to measure time-dependent materials behavior using neutrons; and allow study of transient phenomena otherwise not possible. These advanced capabilities will open new scientific and program-development opportunities in broad areas of dynamic mechanical behavior, in structural materials, and phase transformation and energy-conversion processes in functional materials.

Mission Relevance

DOE has new research areas in the Office of Science Financial Assistance Funding Opportunity Announcement (DE-PS02-09ER09-01): In Basic Energy Sciences, Part (a) Materials Sciences and Engineering, "Major research areas include fundamental dynamics in complex materials, correlated electron systems, nanostructures, and the characterization of novel systems." Part (b) Chemical Sciences, Geosciences, and Biosciences seeks "New experimental techniques are developed to investigate chemical processes and energy transfer over a wide range of spatial and temporal scales: from atomic to kilometer spatial scales and from femtosecond to millennia time scales." Both parts can leverage the pump-probe technique, providing novel approaches to experimentation. The new and unique capabilities developed from this project will strongly position DOE-funded SNS to pursue scientific problems that cannot be handled at other neutron scattering facilities. It will strengthen the in-house scientific capability and also attract high-quality collaborative research projects. It will benefit scientific programs related to "real-time, in situ, time-dependent materials phenomena studies" from the DOE Office of Basic Energy Sciences and the DOE Office of Energy Efficiency and Renewable Energy, the Department of Defense (DoD), Army, Navy, Air Force, and industry.

Results and Accomplishments

High temporal resolution (HTR) sample environment data acquisition (SE-DAQ) technique and a new "meta event" data structure, which consists of high temporal resolution for the SE-DAQ, have been developed. This new technique allows 100 ns HTR for SE-DAQ. New asynchronous data reduction codes have been developed to post-synchronize both the meta and neutron event data. With those newly developed capabilities, time-resolved asynchronous neutron diffraction measurements of scientific phenomena were performed with different time resolution from minutes to microseconds. More SNS users benefit from this unique capability to capture fast transient phenomena under mechanical loading, electrical field, at elevated temperatures, etc.

HTR SE-DAQ is required for intrapulse synchronization of fast transient phenomena. The proposed intrapulse synchronization is the main development effort of this year including 1-MHz HTR DAQ for sample environments by utilizing the neutron event DAQ with 100-ns time resolution, which will satisfy the proposed <10-μs temporal resolution requirement. To implement the meta event DAQ for multiple analog signals of generic sample environments, a new 16-bit analog-to-digital (ADC) conversion system was developed to record fast meta events. This innovative design integrates seamlessly the detector and SE-HTR DAQ with same time resolution as well as similar data structure, which allows robust data reduction and post-synchronization by implementing the new data reduction code to the existing VDRIVE program.

A new in situ high-voltage AC field sample environment was built for studying ferroelectric materials. The structural change of $BaTiO_3$ under different AC frequency was explored with the new capability. Time-dependent μ-second temporal-scale transient phenomena were observed. Using the technique of asynchronous data collection, we measured the structural changes in a 111-oriented domain-engineered $BaTiO_3$ single crystal during the application of square-wave ac electric fields at two different frequencies, 120.1 Hz and 480.1 Hz, on VULCAN. The phase variation of 0.1 Hz allows the neutrons to probe continuously and reversibly in pulses with a maximum time resolution close to an instrument bin width until statistically significant data are collected. This reduces the effort of synchronized experimental control with complex sample environments, as in the conventional pump probe approach. Meta and neutron event data are reduced to 10 segments in one waveform cycle with 800 µs and 200 µs temporal resolution for 120.1Hz and 480.1 Hz, respectively.

The new developed technique is introduced to SNS users. Time-resolved experiments at VULCAN have benefited from this novel technique, including studies of in situ deformation of lightweight materials under loading, phase transformation during heating, lithium intercalation of batteries during charge, etc. More user projects benefit from the unique capability to perform time-resolved study on a wide range of scientific topics. Other LDRD projects benefit from the novel development of this project: "Can Neutrons Do It: Probing Performance of Li-Ion Batteries In Situ" and "Material Degradation Phenomena and Mitigation for Nuclear Reactor Life Extension."

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Seven invited talks

05424

Revolutionary Radiation Transport for Next-Generation Predictive Multi-Physics Modeling and Simulation

J.C. Wagner, T.M. Evans, S.W. Mosher, D.E. Peplow, J.A. Turner

Project Description

Nuclear power is a viable and proven technology for carbon-free production of electricity. For some time, efforts have been under way to develop advanced nuclear energy systems that offer significant improvements with respect to cost, safety, and sustainability. However, the pace at which these new technologies can be developed and deployed into viable options and our ability to advance the state of the art for such systems are limited by inherent approximations in our aging computational tools and approaches. There is a definite need for, and programmatic opportunities associated with, drastic, not incremental, improvements in our modeling and simulation (M&S) capabilities. Responding to this need, this project proposes to leverage our recently developed and unique hybrid (deterministic/Monte Carlo) radiation transport methods, codes, capabilities, and associated experience to establish a revolutionary change in radiation transport M&S and to ensure that ORNL remains at the forefront of this transition. We will develop a parallel, hybrid radiation transport M&S package that will be operable within a multi-physics framework and provide a distinguishing anchor for pursuing programmatic funding for further capability development. The work will emphasize fission reactor analysis, though it will provide an enabling, predictive M&S capability that could substantially advance the state of the art in many areas and support a leadership role in computational modeling for nuclear energy and national security applications.

Mission Relevance

The work is focused on developing an enabling, "game changing" radiation transport capability that will have direct applicability and benefits to addressing the nation's nuclear technology challenges, including (1) design of new nuclear power systems and support of safe, economical, and extended operation of existing fission-based reactors; (2) full-scale fuel cycle facility analyses for safety and safeguards; (3) national security applications; and (4) evaluation of risks associated with geologic disposal of defense and commercial nuclear waste. The proposed capability will have direct relevance to the following organizations: DOE Office of Nuclear Energy, related to large-scale reactors, fuels, waste disposal, shielding, and safeguards M&S; DOE Office of Science, Fusion Energy Science Program, related to M&S for ITER, the proposed Fusion Nuclear Science Facility, and hybrid fusion–fission concepts; Department of Homeland Security and Defense Threat Reduction Agency, related to M&S for applications such as detection of nuclear material and radiation dose from an improvised nuclear device in an urban environment; and the National Nuclear Security Administration (NNSA), related to M&S to support nuclear nonproliferation and safeguards. This LDRD was successful in securing follow-on funding to continue development of the capability under the sponsorship of the Consortium for Advanced Simulation of Light Water Reactors (CASL). CASL is a DOE Energy Innovation Hub for M&S of nuclear reactors.

Results and Accomplishments

During the first year, the team developed ideas and methods for overcoming the two foremost technical challenges to enabling high-fidelity Monte Carlo-based radiation transport for reactor core simulations on high-performance computers (HPC). A new hybrid deterministic/Monte Carlo k-eigenvalue transport method (extension of FW-CADIS method) was developed that overcomes the major limitation of conventional Monte Carlo by distributing computational effort, and hence statistical precision, uniformly across the region of interest. Additionally, a novel multi-set overlapping domain (MSOD) domain-decomposition algorithm was developed to exploit the computational power that HPC platforms (like Jaguar) provide. During the second year, the team focused on implementing and testing the new ideas and methods. A new multi-decomposition parallel, combinatorial geometry Monte Carlo transport code named Shift was developed and underwent initial verification, validation, and parallel performance testing. The Shift hybrid transport code was developed within the Denovo transport toolkit to take full advantage of Denovo's existing massively parallel deterministic radiation transport capabilities. We have demonstrated the effectiveness of the FW-CADIS method for improving both source and flux convergence efficiency. We have developed and implemented a new, novel technique for estimating mesh tally variances in domain-decomposed problems. Additionally, we have conducted additional testing and evaluation of our hybrid and domain-decomposition approaches using challenging benchmark problems found in the literature. During the third and final year the team focused on continued implementation and testing of the new methods. Two major activities included integrating the hybrid methods and implementing continuous-energy physics into the Shift code. As of the writing of this report, funding has been secured and development is continuing on the Shift code under the sponsorship of CASL. The initial developmental funding provided under this LDRD was required to enable development of this game-changing radiation transport capability from theory to practice in a short time.

Information Shared

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05432

The Search for Common Themes in Unconventional Superconductivity: Spin Excitations in Organic Superconductors

A.D. Christianson, G. Ehlers, M.D. Lumsden, T.A. Maier, D. Mandrus, S.E. Nagler, C. Wang

Project Description

Organic metals, molecular magnets, and superconductors have attracted considerable attention due to the possibility of designing materials for specific applications with the vast array of organic complexes available through modern synthetic techniques. Despite this, very little is known about the pairing mechanism or the magnetic interactions found in organic superconductors and related molecular magnets. Here we propose to remedy this through inelastic neutron scattering studies of the excitations in organic superconductors and closely related materials with particular emphasis on the evolution of the spin excitations from the antiferromagnetic to the superconducting side of the phase diagram. The project consists of three components: (1) sample synthesis and characterization, (2) theory and simulation, and (3) experimental inelastic neutron scattering studies. The combination of these components will lead to an unprecedented understanding of the excitations in organic superconductors and may yield common themes for the investigation of unconventional superconductivity.

Mission Relevance

The project will provide key additional knowledge of the physical behavior of organic superconductors and related molecular magnets and will contribute to the broader understanding of unconventional superconductivity and magnetism and consequently has the potential to contribute to a materials-based solution to the energy crisis. As such this project has direct relevance to the mission of the Division of Materials Sciences and Engineering in the DOE Office of Basic Energy Sciences.

Results and Accomplishments

We have made steps towards optimizing the synthesis of deuterated organic superconductors and organic charge coordination polymers; for example, a jumbo-sized growth cell was developed. Sizeable crystals of $[Cu(pyz)_2(HF_2)]X$ ($X = ClO_4$, BF_4, PF_6, SbF_6) have also been synthesized. We have performed comprehensive neutron scattering measurements employing several instruments at the Spallation Neutron Source and the High Flux Isotope Reactor of the magnetic coordination polymer $CuF_2(D_2O)_2$-(pyz), and the resulting data has been analyzed and published in *Physical Review B.* Initial neutron scattering experiments have also been performed on an additional magnetic coordination polymer. The theoretical modeling component of this project has made substantial headway on the simulation of the magnetic properties of the organic superconductors and has calculated the expected response for inelastic neutron scatting based upon a model with d-wave pairing.

Information Shared

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05445

In Situ Neutron Scattering Studies of Fuel Cell Materials

A. Huq

Project Description

The goal of this project is to study a variety of solid oxide fuel cell (SOFC) materials using a combination of materials synthesis, electrochemical characterization, in situ powder neutron diffraction, and inelastic scattering. The driving goal is to develop comprehensive structure-function relationships that describe the oxygen ion/proton conducting and electrocatalytic properties of materials being developed as electrolyte and electrode materials for high-temperature electrochemical devices, including fuel cells and electrochemical reactors. Historically, neutron diffraction has played a crucial role in the study of metal oxides (e.g., high technetium superconductors) due to its high sensitivity towards oxygen in the presence of heavier elements; however, neutron scattering has not been widely applied to SOFC materials. In situ neutron scattering studies under conditions that simulate the dynamic fuel cell operating environment can provide unique information that cannot be obtained by any other means such as structure; defect location, concentration, and ordering; phase transitions as a function of chemical composition, temperature, and oxygen partial pressure; phase separation and decomposition; phase behavior in in situ dynamic ion-conducting environments; and vibration and diffusion properties of mobile species. These parameters directly determine the cell performance and must be understood in order to move towards intelligent materials design.

Mission Relevance

The goal of this LDRD project is to provide a multi-technique platform for in situ characterization of new materials for SOFC electrodes and electrolytes to understand their operating mechanism under realistic temperature, partial pressure of O_2 (pO2), doping concentration, etc. Neutron diffraction has already been proven to be an important tool for characterization of SOFC fuel cell materials; however, to our knowledge the combination of thermo-gravimetric measurements with a controlled gas environment in a furnace is not available at most neutron facilities (the authors are aware of only two similar devices at ISIS and HMI primarily developed for gas absorption studies), and a successful implementation of such a system will provide unique opportunities for the study of fuel cell materials along with other areas of research at SNS. This work fits well within the mission of DOE BES.

Results and Accomplishments

This was the final year of the project, which resulted in several publications and more have been submitted.

Project I: Calcium-doped $La_{1-x}Ca_xNbO_{4-d}$ (x = 0–0.025 in steps of 0.005) has been structurally characterized using room temperature X-ray powder diffraction. The results suggested that with increasing amounts of calcium substitution upto 2.0%, a pure monoclinic phase is obtained at room temperature. However, the scanning electron microscopy/enery dispersive spectrometry (SEM/EDS) and impedance results as a function of doping level and temperature suggest that the solubility of CaO in $LaNbO_4$ may be limited to between x = 0.005 to x = 0.01. For the x = 0.025 samples, small amounts of $Ca_2Nb_2O_7$ impurities were observed by x-ray diffraction (XRD). The conductivity increased dramatically from 2.22×10^{-5} S cm^{-1} for x = 0 to 3.89×10^{-4}S cm^{-1} for x = 0.005 at 850°C in humidified air; then it decreased slightly to 2.25×10^{-5} S cm^{-1} for x = 0.02 due to the segregation of the impurities at grain boundaries. It was also determined that the activation energy for the total conductivity shows the lowest value at x = 0.005 for monoclinic and x = 0.01 for tetragonal $La_{1-x}Ca_xNbO_{4-d}$ phase. Increasing the sintering temperature did not change the bulk resistance, whereas it is beneficial for reducing the grain boundary resistance that becomes prominent at low temperatures.

Project II: The phase decomposition of the $RBaCo_2O_{5+\delta}$ (R = Y and Ho) layered perovskite at 800^{o}C was observed, which will restrict their applications as cathodes in SOFC. However, appropriate amount of strontium substitution (≥ 60 % for R = Y and ≥ 70 % for R = Ho) for barium stabilized the $R(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ phase at high temperatures. In addition, the chemical stability of the $Y(Ba_{1-x}Sr_x)Co_2O_{5+\delta}$ against the GDC electrolyte was improved significantly by the strontium substitution for barium. Among the various compositions investigated, $Y(Ba_{0.3}Sr_{0.7})Co_2O_{5+\delta}$ + GDC composite cathode delivered the optimum electrochemical properties with stable phase, demonstrating the potential as a cathode in SOFC.

Additional Benefits**:** The sample environment that was developed as a result of this LDRD continues to be a unique setup to probe structural properties of materials related to electrochemistry (lithium ion battery and SOFC) and catalysis. In cycle 2011-A, two successful neutron experiments showcasing the capability of the system were performed. One of these was carried out on $NdBaCo_2O_{5+\delta}$ layered perovskite, which has attracted great interest due to its good mixed oxide–ion and electronic conducting (MIEC) properties as well as fast surface oxygen exchange property. Phase pure $NdBaCo_2O_{5+\delta}$ (NBCO) was characterized using neutron powder diffraction under in situ conditions: 573–852°C and 10^{-1}–10^{-4} atm oxygen. The tetragonal (*P4/mmm*) space group provided the best fit for the data, which did not exhibit vacancy ordering. Total oxygen stoichiometry values ranged from 5.51–5.11. The lattice parameters for both tetragonal models were identical to within three decimal places and showed anisotropic crystal expansion with temperature. However, the crystal contracted in the *c*-direction with decreasing pO_2 at a given temperature due to all sites shifting toward the increasingly vacant $Nd\text{-}O_3$ layer. Analysis of atomic displacement parameters indicated that oxygen anion transport occurs through the vacancy-rich $Nd\text{-}O_3$ layer. Other collaborations resulted in several publications describing the structure function relationship of electrode materials for Solid Oxide Fuel Cell.

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05484

Novel Nanostructured Photovoltaic Solar Cells

J. Xu, C.E. Duty, H.N. Lee, B. Smith, X. Zhang

Project Description

Aiming to increase photovoltaic (PV) efficiency, we proposed to create a nanocone-based three-dimensional (3D) heterojunction for solar PV conversion and to obtain fundamental understanding of the key phenomena necessary for its function. The 3D heterojunction will be a matrix structure formed by cone-shaped n-type ZnO nanorods that are surrounded by p-type semiconductor. The merit of our design is that it enhances charge-transport efficiency within the nanostructure and tunes bandgap energies of the heterojunction semiconductors to match the solar light spectrum. ORNL's advanced capabilities in (1) synthesis of cone-shaped nanorods, (2) II-VI pulsed laser deposition (PLD), (3) nanostructure modeling, and (4) pulsed thermal processing (PTP) will enable us to produce a prototype PV device using our novel concepts. Our deliverables are (1) demonstration of 5% ~10% PV efficiency and (2) key insights into the functionality of nanostructure-based PV devices. Upon completion of the project, we will be able to provide a benchmark for the efficiency of a nano-architecture PV cell (none exists at present), and we will possess the basic knowledge of how to push PV efficiency beyond the Shockley-Queisser limit (~31%).

Mission Relevance

The current DOE roadmap in developing more efficient PV solar cells is generally focused on the following generations of PV technologies. Generation I is silicon-based PV, which is quite mature. Gen II is thin film II-VI and chalcopyrite PVs, which currently is increasing its market share and best efficiencies. Gen II (tandem III-V) makes the most efficient cells but at a considerable cost; these are marketed mostly to NASA and concentrator applications. Gen III (Advanced concepts) PV is not commercial but holds some possibility for a significant technology breakthrough. To contribute to this roadmap, this work is to develop a novel PV device that combines n-ZnO/p-ZnCdTe with nanostructures. This approach holds promise for increasing photoelectrical conversion efficiency and lowing cost of fabrication.

Results and Accomplishments

The challenge in achieving high PV efficiency at low cost is to tolerate defects in the PV material. Efficiency in a thin film, planar PV is limited by two conflicting requirements. If the film is too thin, then the light cannot be completely absorbed, but if the film is too thick, then the photogenerated charges are increasingly trapped at defects in the thick film. A nanojunction PV is a promising approach to circumvent this problem because the minority carriers only need to travel a short lateral distance while the matrix is thick enough to absorb most of the light. With these constraints in mind, we developed nanocone-based tip-film semiconductor PV cells [1–3]. These new solar cells consist of n-type ZnO nanocones surrounded by a p-type polycrystalline (PX) CdTe. The ZnO nanocones serve as the junction framework and the electron conductor. The p-type CdTe serves as the primary photon absorber medium and hole conductor. With this device, we were able to obtain a photoelectric conversion efficiency of 3.2%. This efficiency is 80% greater than that of a planar structure of the same materials. Although this preliminary efficiency is moderate compared to market PVs, to the best of our knowledge, this efficiency is among the highest for nanostructured PV cells. The key factor underlying this achievement is more efficient charge transport in the nanostructured PV cell.

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05547
A Transformational, High-Energy Density Secondary Aluminum Ion Battery

G.M. Brown, S. Dai, N.J. Dudney, H. Liu, T.J. McIntyre, M.P. Paranthaman, X.-G. Sun

Project Description

The objective of this project was to develop an aluminum ion battery that has the voltage and capacity to can make a transformational change in energy storage. Aluminum has attractive properties as an anode for a secondary storage battery, with a theoretical voltage comparable to lithium. Aluminum also has a distinct advantage in energy density (8140 Whr/kg vs 1462 Whr/kg for lithium) due to its trivalency. Previous attempts to utilize aluminum anodes in batteries were plagued by high corrosion rates, parasitic hydrogen evolution, and sluggish response due to the formation of an oxide layer on the aluminum electrode surface. To overcome these deficiencies, we have taken advantage of new developments in electrolytes, and we utilized an advanced electrolyte/electrode composition employing room-temperature ionic liquids, resulting in significant improvements in anodic efficiency and therefore battery performance. In this ionic liquid medium, the $AlCl_4^-$ ion will be the predominant anion as well as the chemical form of Al(III) in solution. The initial plan was to choose a cathode electrode material such that the mobile $AlCl_4^-$ species would be directly intercalated or intercalated as an Al(III) ion into the cathode material. Thus far we have been unable to experimentally realize this goal, but we have developed a rechargeable Al-MnO_2 battery, consisting of reversible aluminum dissolution–deposition at anode (Al) and lithium insertion-extraction at cathode (λ–MnO_2) in a room temperature ionic liquid electrolyte (lithium chloroaluminate in 1-ethyl-3-methyl imidazolium chloroaluminate). We have characterized the fundamental cell performance (voltage) and optimized electrolyte composition, anode composition, and cell kinetics. A prototype battery in a coin cell format was constructed, and this novel battery architecture shows an average discharge voltage of 2.0V, rechargeable capacity with tens of cycles, and good stability without self-discharge.

Mission Relevance

There is great interest and motivation for the United States to make a transition from fossil energy–based electricity to the generation from renewable sources such as solar or wind. These sources offer enormous potential for meeting future energy demands. However, the use of electricity generated from these intermittent sources requires efficient electrical energy storage. For large-scale solar- or wind-based electrical generation to be practical, the development of new electrical energy storage systems will be critical to meeting continuous energy demands and effectively leveling the cyclic nature of these energy sources. Among the most critical needs for this nation's secure energy future are transformational developments in electrical energy storage for use in vehicles to include batteries made from novel materials that would increase the level of energy storage per unit volume and mass. In this project we have carried out research aimed at the development of a battery based on an aluminum anode that has the potential to have sufficient specific energy to be transformational. Aluminum is a very attractive electrode material for batteries, due to its advantages in abundance, cost, and theoretical energy density. As a battery anode, aluminum features a trivalent electrochemical redox reaction, with a theoretical specific capacity of 2980 mAh/g and volumetric capacity of 8040 mAh/cm^3, values which are close to and four times those of lithium, respectively. The results obtained in this program were of relevance to ORNL's bid for leadership in the electrical energy storage hub. The results obtained in this program will be of assistance in getting funding from other sources.

Results and Accomplishments

Good progress was made in prior years toward the development of a high-specific-energy density, rechargeable battery with an aluminum anode, a MnO_2 cathode, and a room-temperature ionic liquid ethylmethylimidazolium chloride-aluminum trichloride ($EMImCl\text{-}AlCl_3$) as the electrolyte. We were successful in demonstrating a novel concept of a hybrid aluminum anode–lithium ion battery, a concept that allowed us to demonstrate the feasibility of a rechargeable Al-MnO_2 battery system. The operation principle of this new battery is aluminum metal as the anode, λ–MnO_2 (spinel structure) as the cathode, and lithium chloroaluminate dissolved in 1-ethyl-3-methyl imidazolium chloroaluminate as the electrolyte. During charge-discharge cycle, the electrochemical redox reactions are reversible as aluminum dissolution-deposition, which occurs at the anode, and lithium insertion-extraction, occurring at the cathode. The cathode reaction is a typical intercalation process that is well established to occur in lithium ion batteries. The electrolyte works as a reservoir to provide and store lithium cations and chloroaluminate anions. The imidazolium cations in the electrolyte serve as charge carriers to neutralize the charge balance. The reactions are described as follows.

Anode: $Al + 7AlCl_4^- \leftrightarrow 4Al_2Cl_7^- + 3e^-$
Cathode: $2MnO_2 + Li^+ + e^- \leftrightarrow LiMn_2O_4$
Overall: $Al + 7AlCl_4^- + 6MnO_2 + 3Li^+ \leftrightarrow 4Al_2Cl_7^- + 3LiMn_2O_4$

CR2032 coin cells were used as prototypes to evaluate the performances of Al/MnO_2 batteries in ionic liquid electrolytes. The charge and discharge curves appear as a two-stage process, which corresponds to the dual-peak redox behavior typical of lithium-ion battery cathodes. The first discharge plateau is around 2.15 V, and the second around 1.95 V. The specific charge and discharge capacity are 65 mAh/g and 74 mAh/g based on MnO_2 weight. The cell is charged to 2.4 V by a current of 15 mA/g and kept at 2.4 V until the current was less than 1.5 mA/g. The discharge capacity is 94 mAh/g at the first cycle, and it decreased to 54 mAh/g after 50 cycles. The capacity decreases in the first 10 cycles, and then remained relatively stable after 20 cycles. The open circuit voltage (OCV) of the battery is 2.12 V, and the value is quite stable in an observation at open circuit condition for up to 24 hours. This is the first demonstration of a rechargeable Al-MnO_2 battery in ionic liquid-based electrolyte. This potentially valuable intellectual property has been protected with a patent application.

In the course of conducting this research it has become apparent that the chloroaluminate anion of the ionic liquid electrolyte is extremely corrosive, particularly to the metal oxides and related materials that have been used as lithium ion battery cathode materials. A series of experiments were conducted in which a lithium ion–conducting membrane was used in an attempt to isolate the chloroaluminate-containing electrolyte in the anode compartment from more traditional lithium ion battery electrolytes in the cathode compartment. These experiments were unsuccessful because the chloroaluminate anion reacted with the lithium ion–conducting membrane.

ORNL has received several serious expressions of interest from companies regarding the intellectual property we have developed. In June, 2012 we had extensive discussions with David Eaglesham, CEO of Pellion Technologies, a start-up company in the Boston area developing batteries. In June, 2012 we also had discussions with John Fallavollita, founder and CTO of Z13 Technologies Inc. Fallavollita is founder and former CEO of IOSIL Energy Corporation. In June 2011 we had discussions with Christian Fau of the Automobile Technology Research Division of Honda R&D Americas, Inc.

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05551

Neutron Imaging of Fluids within Plant-Soil-Groundwater Systems

H. Bilheux, E. Perfect, M. Kang, C.-L. Cheng, J. Warren, J. Horita, S. Voisin

Project Description

This project develops a collaborative science program to investigate and model the phase structure and flow dynamics of fluids (water, brines, air, CO_2) within plants, soils, and rocks using noninvasive, nondestructive neutron imaging techniques. The theoretical treatment of fluids in porous media has improved substantially over the last several decades; however, model validation using time-resolved (seconds to minutes), high-resolution (10's of μm) measurements of fluid distributions in heterogeneous natural systems has been a major obstacle. Neutron imaging provides high sensitivity to light elements in fluids (e.g., hydrogen) and deep penetration into plants and earth materials. Utilizing the HFIR R&D CG-1 imaging beamline, we have developed in situ measurement to investigate soil-plant-atmosphere water exchange dynamics, water retention, unsaturated flow and solute transport in the vadose zone, and multi-phase flow and transport in groundwater systems. The scientific objectives of this proposal are to (1) develop quantitative imaging techniques to accurately measure 3D phase structures and 2D fluid flow in porous media, (2) test and refine imaging/modeling capabilities using homogenous model systems, and (3) apply imaging/modeling capabilities to identify fluid pathways, rates of flow, and interactions between porous media, fluids, and plants under dynamic and complex environmental drivers.

Mission Relevance

The transport and interactions of water, CO_2, and other fluids within rocks, soils, and plants play an important role in controlling and determining (a) fluxes of water and CO_2 between the atmosphere and biosphere, (b) fate of subsurface nutrients and contaminants, and (c) transport of energy-rich geologic fluids (geothermal fluids, oils, and gases). While various direct and indirect techniques have been used to investigate fluid flow dynamics within rock-soil-plant systems, suitable real-time measurement capacity is still not well developed. Advanced numerical modeling of multi-phase fluid flow also requires experimental data to validate predictions in extremely heterogeneous porous media at micro- to meso-scopic scales. This LDRD project combines expertise in root-, soil-, and rock-fluid interactions with the expanding capabilities in neutron imaging facilities, and will likely position ORNL at the forefront of neutron imaging applications to environmental and subsurface sciences, and open up new funding and cooperative opportunities beyond the DOE arena. This proposal will increase and diversify the user community within neutron sciences.

Results and Accomplishments

The theoretical treatment of multiphase fluids in heterogeneous earth materials has improved substantially over the past several decades. However, model validation using time-resolved (seconds to minutes), high-resolution (10's of microns) nondestructive measurements of fluid distributions in natural porous media remains a major obstacle, particularly in the presence of plant roots. Neutron imaging provides deep penetration into variably saturated rocks and soils, coupled with high sensitivity to light elements (e.g., hydrogen) in pore fluids and root cells. Supported by LDRD (ORNL, LOIS ID: 5551) and JDRD (UTK) funding, our group has been using the CG-1D neutron imaging beamline at the ORNL High Flux Isotope Reactor since fall 2010 to quantify the distributions of air and water in partially saturated porous media subjected to controlled initial and boundary conditions. Some preliminary experiments were also conducted at the NIST BT-2 beamline. Multiple 2D (radiography) and 3D (tomography) data sets have been acquired and are currently being analyzed for model validation purposes. This research will form the basis of Misun Kang's doctoral dissertation. We have five manuscripts published or submitted to peer-reviewed journals based on this work, with four more in preparation. We presented four conference papers in 2012. In spring 2012 Dr. Perfect developed and taught a graduate seminar course at UTK based on this research. We are actively seeking external support to continue and extend this research into areas such as geologic carbon sequestration and geothermal energy. We submitted two proposals for external funding in 2011.

Information Shared

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05604

Novel Resistive Plate Avalanche Chamber for Neutron Detection

Y. Diawara, L. Crow, J. Hayward, V. Sedov, M. Kocsis, X. Zhang

Project Description

A novel neutron detection technology employing solid materials as a neutron converter is proposed here. It retains the desirable performance characteristics of gaseous detectors (direct conversion) and scintillators (no parallax) while offering high-count-rate capability. Gaseous and scintillator-based detectors are the most widely used for neutron detection technologies. He-3 gaseous detectors have a number of very attractive features for neutron scattering including large active area, direct conversion process, high dynamic range, and low gamma sensitivity. However, the spatial resolution and the parallax errors of these neutron detectors are fundamentally limited, respectively, by the particle (protons and tritons) range and the conversion volume design; moreover, the He-3 shortage will limit its future use in neutron detection. The scintillators, when coupled to photomultiplier tubes (PMTs), achieve large active area, single-neutron sensitivity and no parallax broadening. Unfortunately their dynamic range and their detective quantum efficiency are limited. The low rate capability of these detectors limit their applications in high flux experiments such as in small-angle neutron scattering (SANS) and reflectometry. The proposed neutron converter, integrated in a resistive parallel plate avalanche chamber, will offer some unmatched characteristics, including high counting rates, better position resolution than present gas detectors, and the possibility of matching the shape of detectors to specific applications.

Mission Relevance

The proposed project addresses the issue of the He-3 replacement by a solid converter, a growing need for neutron scattering facilities worldwide. Its application could also be expanded beyond neutron scattering to many other fields (homeland security, medical, etc.). Therefore, the proposed detector design is deemed to be of primary importance to neutron science. It is a versatile detector that will meet the counting rate requirements of present neutron scattering instruments. Its relevance to ORNL includes a design tailored to the needs set by the experiments on high-intensity neutron beams provided by the Spallation Neutron Source (SNS) and the High Flux Isotope Reactor (HFIR). In addition, applications where the combined features of space resolution and throughput rate capabilities will play a fundamental role are protein crystallography small-angle scattering and time-resolved observations of kinetic processes. Finally, the development of this detector technology will reinforce recognition of ORNL as a leader in neutron detection among the community of users of neutron source facilities.

Results and Accomplishments

Significant technical and scientific accomplishments have been achieved on the second prototype of the He-based gaseous detector. The two detectors have been tested, and their high-rate capability (1million counts per second) has been demonstrated. The position resolution was measured using a 2 mm mask, and background level below 0.1 counts per second was achieved. In addition, the second prototype uses a solid nanostructure (aerogel) layer as a neutron converter. The nanostructure converter has been prepared and used in the detector. It detects neutrons with a low efficiency. It has been tested in as a converter in a beam monitor, and future steps are focused on increasing the efficiency to above 50%.

Information Shared

A patent application based on this technology and entitled "A porous material neutron detector" has been awarded (US patent 8,153,988).

A paper entitled "A High Count Rate Neutron Beam Monitor for Neutron Scattering Facilities" has been accepted for publication by the IEEE Transactions on Nuclear Science.

Because of the high-rate capabilities, the resistive plate can be used as a beam monitor since all present monitors saturate at high rate. An invention disclosure based on this application and entitled "High Rate Neutron Beam Monitor" has been submitted to ORNL ID number 201002497.

05608

Fundamentals of Ionic Conductivity in Polymeric Materials for Energy Storage Applications: How to Decouple Ionic Motions from Segmental Dynamics

A. Sokolov, Y. Wang, A. Agapov, F. Fan, A. Kisliuk, T. Zawodzinski, C.-N. Sun, K. Hong, X. Yu, J. Yang, J. Mays, T. Saito, R. Kumar

Project Description

Polymer membranes have attracted much attention during the past several decades because they provide elegant solutions to many difficulties in battery technology. However, the relatively low ionic conductivity in polymer membranes has become the bottleneck for developing batteries with higher power density, shorter charging time, and better operations at low temperatures. Despite numerous studies in the past, a clear understanding of the ion transport mechanism in polymer electrolytes is still missing. In this project, we demonstrated that contrary to the widespread belief that segmental motion controls ionic conductivity, the ion motion can actually decouple from the structural relaxation of the polymer matrix. Moreover, our study revealed the connection between the chemical structure of polymers and the degree of decoupling. We showed that the decoupling phenomenon could be utilized to design polymer membranes with extremely high ionic conductivity. The principles demonstrated in this research will provide a "game-changing" approach to the development of solid polymer electrolyte batteries for energy storage applications.

Mission Relevance

Development of efficient electrical energy storage systems has been identified as a critical task for addressing national energy needs in the United States. This project is aiming to obtain a clear understanding of the fundamental principles governing ionic conductivity in polymeric materials for energy storage applications. The results of this project will serve as guidelines for the design of next-generation batteries and fuel cells with dramatically improved performance. Our ongoing research is therefore highly relevant to the DOE mission and will put ORNL at the forefront of the polymer electrolyte field. In addition, we expect that the developed knowledge and new concepts will be helpful in addressing the problem of CO_2 capture, and thus help ORNL to secure funding for CO_2 sequestration from DOE and industry.

Results and Accomplishments

One of the focuses of our study is the relationship between ionic conductivity and segmental relaxation in polymer electrolytes. Our analysis shows that the ionic conductivity can be decoupled from segmental dynamics and the strength of decoupling correlates with fragility but not with glass transition temperature. This correlation is consistent with the recent theoretical ideas that chains with rigid backbones have significant frustration in packing. This is also supported by our simulations of flexible and rigid polymers. As a result, ions may utilize the loosely packed structure of fragile (rigid) polymers and diffuse through the polymer matrix even when segmental dynamics is slow or frozen. These results call for a revision of the current theoretical picture of ionic transport in polymer electrolytes. We have also developed a method to separately determine free ion mobility and number density from the dielectric spectra of polymer electrolytes. This progress gives us a solid foundation for studying polymer electrolytes as well as other ionic conductors and makes it possible to quantitatively analyze the influence of material structure on the ion diffusion and solvation. In the search of polymer electrolytes with high conductivity, we have synthesized a number of polymers with pedant polar groups to increase the static permittivity. One of these polymers has a permittivity that is significantly higher than most of the conventional polymers. We have further demonstrated that the ionic dissociation energy decreases with an increase in polymer permittivity. This result will help to guide the synthesis of highly conductive polymers. In summary, two main design principles have been obtained from our 2-year research: (1) polymers with frustrated packing should be used to decouple ionic conductivity from segmental relaxation; (2) polymers with high dielectric permittivity should be used to achieve high free-ion concentration. We were able to achieve conductivity in one of the polymer electrolyte close to 10^{-4} S/cm at room temperature (not yet published).

Information Shared

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05630
Scalable and Efficient Infrastructure for Exascale Analysis and Visualization

J. Meredith, S. Ahern, D. Pugmire

Project Description

Analysis and visualization of the data generated by scientific simulation codes is a key step in enabling science from computation. However, a number of challenges lie along the current hardware and software paths to exascale scientific discovery. First, only advanced parallelism techniques can take full advantage of the unprecedented scale of the coming machines. In addition, as computational improvements outpace those of I/O, more data will be discarded and I/O-heavy analysis will suffer. Furthermore, the limited memory environment, particularly in the context of in situ analysis which can sidestep some I/O limitations, will require efficiency of both algorithms and infrastructure. Finally, advanced simulation codes with complex data models require commensurate data models in analysis tools. However, the de facto standard Visualization Toolkit (VTK), supporting open source scientific tools such as VisIt and ParaView, has simplistic parallelism, a demonstrated lack of efficiency, and a data model incapable of supporting paradigms used in many simulations. We propose research and development towards a new library, with infrastructure and key algorithms to support advanced parallelism and efficiency, as well as a robust data model and native in situ support needed by the coming generation of exascale hardware and software.

Mission Relevance

This project is relevant to the US Department of Energy (DOE) and other agencies on several levels. First, the path to scientific discovery via exascale supercomputing is fraught with obstacles in terms of massive parallelism, unique hardware environments, and heavy I/O burdens. As visualization and analysis are key to extracting scientific results from simulation, our proposal will investigate solutions to these obstacles in this context. Furthermore, the models and capabilities of DOE simulation codes are surpassing those of current visualization libraries, and we propose an initial investigation into the support infrastructure to address these needs. Other DOE funding calls and workshop reports highlight the importance of increased funding for analysis and visualization systems capable of exploiting the potential of simulations at the extreme scale, and this goal aligns directly with those of our proposal.

Results and Accomplishments

In year 2, we extended the data model in our Extreme-scale Analysis and Visualization Library (EAVL) to incorporate more features that are important for exascale computing but remain poorly supported in existing analysis libraries, such as face and edge data, high-order fields, and arbitrary refinement grids. We also created a full data-parallel application programming interfact (API) and runtime necessary for algorithm developers to productively support the high core counts and fine-grained parallelism coming in future architectures. This API takes the form of a flexible functor/iterator approach, where developers combine sequences of data model-aware parallel execution patterns in a manner agnostic to target architecture. This single-source algorithm is then executed by our runtime with fine-grained parallelism on multi-core CPUs or many-core devices including GPUs and the Intel Xeon Phi (MIC).

We published and presented two peer-reviewed papers on EAVL this year at international conferences: GPGPU5 in London and EGPGV in Cagliari, Italy. We also gave an invited presentation on EAVL at the DOE Computer Graphics Forum in Albuquerque, and our panel proposal was accepted for SuperComputing 2012 in Salt Lake City. Thanks to our exploratory work, ORNL is now receiving funds to improve EAVL's support for Scientific Discovery through Advanced Computing (SciDAC) applications and in situ analysis techniques through the Scalable Data Management, Analysis and Visualization SciDAC (SDAV) Institute. We recently gave an in-depth tutorial on EAVL (several hours of instruction, plus hands-on time) in Albany, NY, for SDAV project members at other institutions. Finally, EAVL is now hosted publicly for open collaboration; see http://ft.ornl.gov/eavl and https://github.com/jsmeredith/eavl/wiki for documentation, source code, and examples.

Information Shared

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05653

Ultrascale Algorithms for Verifying Security Properties of Compiled Software

S.J. Prowell, M. Pleszkoch, K. Sayre, J. Horey, R. Linger

Project Description

We propose to develop a system, deployed on high-performance hardware, to automate the extraction of a catalog of a computer program's behavior. This machine-readable catalog can be manipulated to determine program characteristics or verify behavioral constraints. The ability to rapidly analyze unknown programs to verify security constraints is a fundamental and significant contribution to national security. Only through direct analysis of the compiled program can precise and provable security claims be established. Our fundamental research hypothesis is that it is possible to automatically determine certain binary program characteristics in order to verify that important security constraints are not violated, and that this analysis can be done sufficiently rapidly to enable its use on dynamic or downloaded content.

This project takes advantage of Oak Ridge National Laboratory's (ORNL) leadership capabilities in computational science and will create a unique capability for rapid analysis of software. This capability has wide applicability, including vulnerability discovery for embedded systems (e.g., smart meters), rapid and automated reverse engineering of unknown programs (e.g., PC or HPC binaries), and verification of software for critical infrastructure (e.g., energy grid control software).

Mission Relevance

This effort directly addresses the DOE mission for energy security—specifically it addresses milestone two of the DOE Roadmap to Achieve Energy Delivery Systems Cybersecurity, which calls for "tools for real-time security state monitoring and risk assessment of all energy delivery system architecture levels and across cyber-physical domains commercially available." The effort also directly addresses ORNL's missions in national security and high-performance computing by advancing computational cyber security methods, enabling the rapid assessment of the security properties of software that is an irremovable–and often outsourced–part of our national critical infrastructure.

Results and Accomplishments

A system for rapid, robust detection of "no-op sleds" used to execute malicious payloads in dynamic content has been developed. The system uses a novel algorithm in combination with the function extraction system to determine whether a sequence of bytes contains a probable no-op sled. This system can be deployed to serve as a semantic firewall for web traffic.

The HPC port of the function extraction system developed for this effort was selected by the US Department of Homeland Security as one of eight projects, nationwide, for its "transition to practice" program.

Information Shared

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05665

Distributed Computational Framework for Massive Heterogeneous Data Fusion

J. Horey

Project Description

We proposed to build a distributed computational framework to fuse large-scale, heterogeneous, streaming data sources. Such a framework is needed because current state-of-the-art tools, such as geographic information systems, do not operate in a parallel manner and do not scale to large datasets. Applications that integrate large volumes of streaming geospatial sensor data, such as Intelligent Transportation Systems from the US Department of Transportation's IntelliDrive^{SM} initiative,* would clearly benefit from such a framework. Our framework, *SenseReduce*, employs a functional paradigm that integrates streaming sensor data and geospatial datasets to enable developers to write parallel applications with minimal effort. In addition, our system will be the first distributed knowledge discovery framework that enables data fusion algorithms to operate over a variety of geospatial data types and computational substrates.

We will produce an implementation of our framework targeting distributed environments, thus enabling researchers to explore and analyze streaming geospatial datasets at unprecedented scale. We will also validate the efficacy and scalability of our framework by developing a distributed traffic simulation coupled with novel ITS algorithms.

Mission Relevance

The proliferation of sensing technologies and the increased volume of geospatial data provides unique knowledge discovery opportunities. Potential applications range from scientific (studying climate change), to industrial (discovering regional power grid trends), and urban safety. For example, the DOT Intelligent Transportation Systems program envisions applications integrating real-time data from sensors

* The IntelliDrive^{SM} Logo is a service mark of the US Department of Transportation.

to improve the safety, mobility, and efficiency of highway transportation. In addition, the DOE Smart Grid initiatives envision sensors and actuators embedded within the electric grid. For both sets of applications, sensor data must be fused rapidly with geospatial data (e.g., roads, line topologies, etc.) to make some set of computational decisions (e.g., change traffic light patterns, reroute power, etc.). Key enabling technologies needed by both sets of applications include a distributed computational framework to fuse streaming data sources.

Results and Accomplishments

SenseReduce is comprised of a set of Java modules. The major modules include the following.

- The base computation classes where user-defined computation is specified
- Datastructures: vector features and raster data
- Schedulers: responsible for tasking computation to the available hardware
- Data stores: responsible for storing and accessing the spatiotemporal data
- Compute nodes: responsible for executing the computation

The primary method by which users interact with SenseReduce is via Java application programming interface.

The SenseReduce architecture is defined and includes interfaces between major modules. The core datastructures are usable and can actively manipulate real-world spatiotemporal data. Versions of the scheduler, data storage, and compute nodes exist that can execute user-defined jobs locally. In addition, a preliminary implementation for distributed execution has been tested on a local virtual machine to evaluate the effect of varying the number of CPUs.

We also began development of a distributed traffic simulator. These models have been implemented in Matlab. To handle unreliable sensor measurements, we have developed a systems-level model of the underlying sensor systems. We have three separate modules implemented in Matlab that identify possible faults and estimate the probability of faulty sensor readings. In conjunction with sensor data fusion, we have developed algorithms to predict and control vehicles and infrastructure with the goal of reducing traffic congestion and vehicle fuel. These algorithms analyze the speed of lead vehicles and account for elevation changes along the travel route. We developed a method to efficiently calculate a speed profile for each vehicle, and implemented the method in Matlab.

Information Shared

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05714

Advanced Alloy Development for the Next-Generation Liquid-Fluoride-Salt-Cooled Nuclear Reactors

G. Muralidharan, S. Dai, D.E. Holcomb, W. Ren, M.L. Santella, R.R. Unocic, D.F. Wilson

Project Description

Development of a structural alloy tailored to the high-temperature creep strength and liquid salt corrosion resistance needs of Fluoride-Salt-Cooled High-Temperature Reactors (FHRs), a reactor class being investigated by the DOE-NE Advanced Reactor Concepts program for production of electricity and high-temperature process heat, is necessary to increase FHR efficiency and component lifetime. The primary objective of the proposed project was to develop and demonstrate an effective computation-based design methodology for the development of alloys that combine good high-temperature creep strength with high-temperature liquid salt compatibility. Work was performed to understand the relationships between alloy compositions, microstructures, and the two critical material properties of interest over nontraditional compositional ranges. Based upon the developed relationships, computational thermodynamic models were used to identify new candidate alloy compositions. An initial set of candidate alloys were identified and were experimentally assessed for their resistance to liquid-fluoride-salt attack, and creep resistance in inert atmosphere. Measurements of their high-temperature creep behavior in liquid fluoride salt and their ease of fabrication were also planned. Experimental results will allow refinement of the predictive capability of the developed methodology, thus enabling future rapid, cost-effective alloy development at ORNL.

Mission Relevance

The FY 2012 DOE-NE advanced reactor concepts program plan identifies FHRs as one of its two primary supported advanced reactor concepts (the other being sodium-cooled reactor). Thus the next few years appear especially opportune to encourage programmatic growth. This project was aimed at initiating a larger DOE-NE sponsored program on developing and fully qualifying an FHR tailored alloy (likely a $50M+ 10 year program). One of the major deterrents to DOE investment is the conventional wisdom that alloy development is an extremely protracted and a prohibitively expensive process. Successful development of an accelerated methodology to alloy development will increase DOE-NE's support of a much-needed alloy development program for this class of reactors. Also, increasing the efficiency of solar thermal power systems is critically dependent on increasing the temperature of the heat transport technology, and hence the knowledge developed in this project is readily applicable to the DOE-EERE solar thermal program.

Results and Accomplishments

The computational thermodynamic modeling tool, JMatPro, was used to calculate the equilibrium microstructure of alloys with particular reference to types and amounts of strengthening phases present in the alloys as a function of temperature and composition space (consisting of several alloying element additions and with minimum acceptable chromium levels). Based on this modeling, a series of model alloys with desirable microstructural strengthening characteristics (solid solution strengthening combined with carbide or gamma' strengthening) were defined, successfully cast, and fabricated into small plates. High-temperature testing of the alloys showed that these alloys possessed 10 to 200 times improved creep rupture life at 850°C at 12 Ksi stress in an inert environment when compared to Alloy N. Isothermal exposure of selected alloys to FLiNaK at 850°C in sealed capsules demonstrated that these alloys also had excellent corrosion resistance. A system for evaluating the creep performance of alloys in the presence of molten fluoride salt was designed and constructed. In this approach, the liquid fluoride salt is contained within a hollow cylindrical specimen with the specimen acting as its own environmental chamber, thus simplifying salt containment, monitoring of specimen deformation, and specimen failure detection. The successful identification of several new alloys with improved properties within the 2 years of this project demonstrates the effectiveness of the computation-based methodology developed in this work. Results from this project have already resulted in the submission of five invention disclosures (three of them on new alloys) with one additional invention disclosure on new alloys in preparation.

Information Shared

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05716

Why Coatings Work: Nanoscale View of High-Voltage Cathode Surfaces

G.M. Veith, L. Baggetto, M. Chi, A. Payzant, J. Browning, M.K. Miller, N.J. Dudney

Project Description

The goal of this LDRD project is to demonstrate the ability to determine the structure and conductivity paths through the polyhetero protective coatings on high-voltage cathode materials and predict ways to improve coatings. Accomplishing this goal requires utilization of advanced techniques to deconstruct the structure and composition of the complex multiphase protective coating. Therefore, we will integrate the subnanometer spatial and chemical resolution of the Local Electrode Atom Probe (LEAP) and aberration-corrected Scanning Transmission Electron Microscopy (STEM) to determine the mosaic of phases that comprise the surface of the high-voltage $LiCo_{0.33}Ni_{0.33}Mn_{0.33}O_2$ cathode material with and without protective Al_2O_3 or $AlPO_4$ coatings. Critically for follow-on opportunities and novelty, other national laboratories (ANL, LBL, BNL, SRNL) do not have LEAP or the sample synthesis expertise needed to execute the proposed line of research. Most importantly, this LDRD project lays the foundation for a more comprehensive program focused on developing both an understanding and predictive ability to design and fabricate the protective coatings essential to lithium-ion batteries for maximum rate, capacity lifetime, safety, and other technologies such as photovoltaics and catalysis.

Mission Relevance

The proposed project directly addresses DOE and the nation's needs to identify new mechanisms to increase energy utilization and storage. The ability to design protective coatings will be of direct interest to EERE, which is seeking new ways of protecting electrode surfaces and improving the cyclability of battery materials. Furthermore the corrosion issues we are investigating are fundamental problems in a number of energy storage and utilization technologies including nuclear reactors and photocatalysts, which are areas of fundamental research supported by the Office of Science.

Results and Accomplishments

We have developed the methodology to prepare atomically smooth battery cathodes, with the same electrochemical performance as bulk cathode powders, which can be cycled and characterized in situ using neutron reflectometry. Electrodes of $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) were cycled in standard battery electrolytes versus Pt, $Li_4Ti_5O_{12}$ (LTO), and lithium anodes. Data collected on the LMNO electrodes revealed the formation of a thin condensed lithium-rich layer at the surface of the electrode at open circuit voltage (OCV). This layer evolves upon cycling to form a dense fluorine-rich layer from the reaction of $LiPF_6$ salts with the LMNO at 4.75 V. Similar studies on LTO anodes reveal a similar condensed layer on the OCV and lithiated sample. These layers make up the very earliest steps of the solid electrolyte interphase (SEI) layer that forms on electrodes. Experiments performed washing the electrodes reveal significant changes in the SEI layer compared to the in situ SEI layer, indicating that by washing the electrode significant portions of the SEI are removed. This material is essential to understanding the chemistry of the SEI. These thin-film electrodes were also fabricated into needle-like specimens for atom-probe tomography. Evaporation of these electrode materials is not trivial, resulting in inhomogenous data collection. Studies were performed to optimize the material evaporation. Preliminary analysis indicates preferential segregation of metal ions, which may impact SEI formation.

Information Shared

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05740

Material Degradation Phenomena and Mitigation for Nuclear Energy Systems

Z. Feng, Z. Yu, K. An, X.-L. Wang, W. Zhang, R.E. Stoller

Project Description

This LDRD project aims at advancing our knowledge of the fundamentals of defect transport and damage mechanisms under the extreme temperature, stress, and radiation conditions relevant to current and future generation nuclear energy systems. We propose to develop and demonstrate a unique neutron experiment approach – the coupled simultaneous small-angle neutron scattering (SANS) and wide-angle neutron diffraction (WAND) – for in situ and time-resolved interrogation of the nano-scale and the macroscopic material damage phenomena, and most intriguingly, the dynamic interactions between the two length scales under combined high-temperature, stress, and radiation conditions. A multi-scale modeling framework will also be developed to collaborate with the SANS/WAND experiment results to connect the nano-scale damage process with the macroscopic material deformation and failure behavior under the extreme environment.

Mission Relevance

This LDRD project aims at advancing our knowledge of the fundamentals of defect transport and damage mechanisms under the extreme temperature, stress, and radiation conditions relevant to current and future generation nuclear energy systems. It supports the missions of the DOE Offices of Fusion Energy Sciences and Nuclear Energy, the Nuclear Regulatory Commission, and the commercial nuclear power industry. Specifically, the results have attracted the interests of the DOE/NE LWR Sustainability Program (LWRSP) and EPRI's Long-Term Operation Program in weld repair of irradiated materials. Results of stress effects on helium bubble evolution are also likely to stimulate interest from DOE/OFES. The unique WANS/SNAS in situ experimental approach can also be extended to research other structural and functional materials beyond the nuclear energy systems, to investigate different damage and failure mechanisms, microstructural evolution under far-from-equilibrium conditions, which is a very broad and fruitful R&D field in materials science.

Results and Accomplishments

On in situ WAND, we have successfully determined the phase transformation kinetics in an advanced high-strength steel (AHSS) under far-from-equilibrium conditions. The dependency of phase transformation kinetics on the heating rates has been quantified. A unique lattice spacing change of face-centered cubic (FCC) crystalline structure was observed, suggesting a direct quantitative measure of the diffusional processes that affect the non-equilibrium phase transformation processes. The feasibility of SANS was demonstrated through studying the strain-induced nano-precipitates dissolution phenomenon in aluminum alloys, and the SANS results were corroborated by high-resolution TEM. An integrated multi-scale modeling framework has been developed to handle the effects of combined stress and temperature on the kinetics of nano-cavity growth and its influence on the material damage behavior. The integrated model, for the first time, has the essential feature to predict the damage and failure at the continuum level with nano-scale helium bubble kinetics. The newly developed in situ WANS and SANS capability has generated considerable interests from DOE program offices and from nuclear, automotive, and primary metal industry sectors. In part due to the success of this LDRD, over $2.1M research funding has been received from DOE/NE, DOE/EERE, EPRI, and NRC.

Information Shared

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05749

Hercules: A User Guided Translation Tool to Facilitate Application Porting to New Peta/Exascale Architectures

O. Hernandez, C. Kartsaklis, W. Joubert, C.-H. Hsu

Project Description

The goal of this project is to help scientists improve the performance of applications on new platforms by building a translation tool to help identify new sources of parallelism, rearrange data layouts, and control the compilation process. The tool, code named HERCULES, will have a user interface to display static analysis results such as inter-procedural dependencies and parallel dataflow information, with a transformation menu to perform parallel loop optimizations, memory layout rearrangements, and inter-procedural optimizations. It will operate on multiple levels of compiler intermediate representations that translate C/C++/Fortran, Message Passing Interface (MPI), Unified Parallel C, Co-Array Fortran, OpenMP, and Compute Unified Device Architecture (CUDA) programs to object code. In addition, HERCULES will provide reconfigurable cost models to allow the user to guide the optimization process and better quantify the effectiveness of transformations for the target system. We will investigate how to define a scripting language to specify code structures (patterns) and user-directed transformations to apply to the code. This information will be stored in a program repository and may be queried or reused within a single application or across applications. We envision HERCULES working with several production open-source compilers, the primary focus being the Open64 compiler.

Mission Relevance

Leadership-class computers at Department of Energy (DOE) laboratories deploy hundreds of thousands of compute cores with complex hardware to solve mission-critical science problems. Multiple programming models will likely be needed to exploit the power of such systems, making them complex to program. Currently, few code transformation tools exist to help the programmer navigate this complex environment and help the user manage the complexity of adapting their codes to new platforms minimizing laborious code changes. The HERCULES system automates this process by allowing the programmer to specify code transformation patterns that can be applied repeatedly across large code bases, such as parallelization transformations or data structure changes. The system automates the process of applying transformations by using compiler technology to control the translation process of the codes. It also provides a separation of concerns between the science application and the platform-specific performance optimizations, by abstracting transformations and simplifying the code maintenance workflow.

Results and Accomplishments

We completed the following work during the year of the project: (1) We revised and created a robust code transformation system, based on the first-year work and initial implementation, that enables a complete workflow of the tool from pattern matching application code, to querying of program analysis and applying source-to-source transformations and/or produce optimized object code. (2) We improved the pattern matching engine and a parser capable of detecting source code patterns using an underlying PROLOG technology that can match code on Department of Energy (DOE) by testing it on sources from applications (Denovo/3d Sweep, Community Atmosphere Model/Spectral Element (CAM/SE)), and High Performance Linpack (HPL) benchmark. These patterns, transformations, and application facts are stored in a persistent database that can be queried offline (post-translation) or online (during compilation process). (3) We improved and simplified the pattern-matching language that can be incrementally applied to existing applications written in C/C++/Fortran/OpenMP/MPI. The language is based on user-level directives with built-in functions and primitives to facilitate pattern creation. In addition, we implemented a new functionality where the user can define the pattern and transformations directly on the application source code, instead of saving them into a pattern-matching/transformation scripts. This benefits users who are only interested in applying a transformation on a specific code region using the HERCULES system. (4) In addition, we implemented additional patterns and transformations that impact Oak Ridge Leadership Class Facility (OLCF) applications, including pattern matching and detection of arrays-of-structures and structures-of-arrays, transformations for heterogeneous platforms including GPU round-robin distribution, loop collapsing, inter loop nest fusion and support for OpenMP parallelization with automatic data scoping. (5) We installed and developed a programming environment for the HERCULES system to make it available to OLCF systems.

Information Shared

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05767

Study of Gas-Phase Separations for Closed and Modified Open Used Nuclear Fuel Reprocessing

J. Johnson, B. Spencer, C. Rawn, B. Del Cul, E. Collins, R. Hunt, R. Jubin

Project Description

The objective of the proposed work was to establish ORNL as a leader in the investigation of high-temperature reactions of used nuclear fuel with gaseous species. The topic is relevant to science-based development of dry processes for future nuclear fuel cycles and for safe storage of used fuel. Voloxidation is a dry process in which used nuclear fuel is oxidized to release volatile and semi-volatile components. While experimental studies have been performed to demonstrate the process, there are currently significant gaps in the understanding of the process fundamentals and little predictive capability. The knowledge gap is greater for related technologies under consideration, such as halide volatility or dry nitration processes. Experimental studies and model development are needed to (1) close the knowledge gaps and (2) establish the predictive capability that meets the DOE Office of Nuclear Energy's near-term goal to define and analyze fuel cycle technology options that increase the sustainability of nuclear energy. This work closes the gaps by developing phenomenological models of gas-solid thermal processing of used fuel and establishing a unique experimental capability for data collection and model validation. Creating this capability to increase the comprehensive understanding of new and original gas-phase separations processes through coupled theory and experimentation, this project appropriately positions ORNL as an innovator of methods for head-end processing of used fuel for reprocessing or preconditioning fuel for storage. It also provides a vital research capability for examining factors related to safe storage of used nuclear fuel, which has gained increasing attention in light of the Blue Ribbon Commission's activities and the recent Fukushima disaster.

Mission Relevance

The capability to perform coupled experimentation and model development aligns with the Office of Nuclear Energy's goal for science-based research and development to define and analyze fuel cycle technologies for developing options that increase the sustainability and availability of nuclear energy. With increased interest in voloxidation methods for fuel conditioning and head-end processing, further development of our understanding of such processes is necessary. The Separations and Waste Forms Technical Area of the Nuclear Energy Fuel Cycle Technologies Program has identified gas treatment separations as key processes for which better understanding and modeling is greatly needed. This work has helped to close these gaps in knowledge.

Results and Accomplishments

Efforts through FY 2012 were focused on three main objectives: (1) use capabilities developed in FY 2011 for phenomena isolation studies to better understand the reaction mechanisms, (2) explore the UO_3 phase formed from NO_2 oxidation in the proposed advanced voloxidation schemes, and (3) finalize the model developed in FY 2011 and gather data from the oxidation of real clad used fuel pieces for comparison. These objectives were met by the following accomplishments. (1) Clad surrogate pellets were reacted in macro thermogravimetric analysis (TGA) systems under controlled conditions including vibration and oxygen partial pressures. (2) The oxidation reaction interface was characterized using neutron diffraction mapping to determine the phases present and the definition of the interface. (3) Phenomena models were further developed, and the reaction mechanisms were deduced from the models and acquired data. (4) Ex situ x-ray diffraction (XRD) and neutron diffraction measurements at the Spallation Neutron Source (SNS) were employed to resolve the structure of ε-UO_3. (5) A system for in situ XRD analysis of the reaction kinetics of U_3O_8 to UO_3 was developed and used to measure the kinetics of reaction. (6) A TGA unit for hot cell use was designed, fabricated, and installed to collect oxidation rate data for actual used nuclear fuel samples for comparison with surrogate data and the developed models.

Experiments preformed provided significant insight into a variety of aspects of oxidation of used fuel under assorted conditions. The results closed significant gaps in our understanding of rate-controlling phenomena in voloxidation processes, resolved never before developed structures for ε-UO_3, and developed a method to measure kinetics of uranium oxide oxidation with NO_2 by in situ XRD. A number of publications are currently being prepared as a result of this work and follow-on funding was awarded.

05768

A Predictive Analysis Toolbox for Ultrascale Data Exploration

C.T. Symons, S.R. Sukumar, B.H. Park, M. Shankar, R.R. Vatsavai, R.K. Archibald, A.R. Ganguly, S.J. Prowell

Project Description

The ability to produce ultrascale data far surpasses any current ability to understand it. There is no standard set of techniques or libraries that enables a domain scientist to effectively take advantage of the computational power necessary to analyze data at such scales. This project is relying on a novel, coordinated-learning framework that is specifically designed to take advantage of the availability of incredibly large amounts of data concerning a system under study. The approach is based on state-of-the-art machine learning techniques, and it allows incorporation of domain knowledge in a very simple and effective way, while not presuming the presence of any such knowledge. The core algorithms and application programming interfaces (APIs) of the toolbox are being developed in conjunction with two diverse domain experts in an attempt to provide an accessible library that can serve a wide variety of potential users. The end result will be an ORNL-brand, ultrascale-data-analysis toolbox that enables a variety of scientists who are currently stymied by the scale of their data to effectively leverage the power of ultrascale computing platforms for knowledge discovery via predictive analysis.

Mission Relevance

The DOE Office of Science has initiatives for ultrascale computing and scientific discovery that require high performance computing. Because large-scale simulation-based approaches have demonstrated the value of high-performance computing to science, there has been less attention paid to the relative lack of extreme-scale analytical routines that are not based on simulation. Such approaches are necessary to support many forms of scientific discovery that are important to DOE and the nation in general. This toolbox helps address that important gap by supporting discovery of important interactions through an integrated analysis of systems data in the form of extreme-scale, highly interdependent observation data. Since the project is developing new scientific exploratory capabilities for ultrascale datasets, it is directly aligned with some of DOE's core missions. Furthermore, the type of exploratory analysis for complex data supported by the project could provide substantial value to Department of Defense and other agencies that are overwhelmed with complex, interrelated data.

Results and Accomplishments

The main algorithmic core of the approach underlying the toolbox has demonstrated nearly linear scalability on multi-core platforms, and successful examples of information discovery have been demonstrated as well. The project incorporates a large set of learning algorithms that can be wrapped within the overall framework, depending on the characteristics of the data. For example, internal learners can be modified to accommodate data that is sequential (e.g., temporal), partially labeled, etc. Although the parallel nature of the framework itself is the critical aspect in terms of scalability, many of these core learners have been parallelized to enhance scalability even further. Existing open-source libraries were leveraged in the development process, as appropriate.

Several domain experts were consulted in order to formulate significant unsolved analysis problems to which the approach is applicable. Data from several domains was utilized through the course of the project, including climate, cyber security, text analysis, and manufacturing. Analysis has demonstrated applicability to multiple problem spaces that deal with large, complexly interacting systems. The project also developed a new method for visualization of complex nonlinear relationships indicated as being significant in the analysis. Application of approaches developed through this work to the intrusion detection domain have demonstrated state-of-the-art results, including an ability to detect almost all previously unseen attacks with trivial false positive rates on both a cyber test range and on operational data.

The work performed on this project resulted in the following two invention disclosures: Invention Disclosure Number 201202902, authored by Christopher T. Symons, Justin M. Beaver, Rob Gillen, and Thomas E. Potok; and Invention Disclosure Number 201102611, authored by Christopher T. Symons, Sreenivas R. Sukumar, and Mallikarjun Shankar.

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05777

Enhanced Directionally Selective Moderator for SNS

E.B. Iverson, and F.X. Gallmeier

Project Description

The Directed Moderator combines moderating material and single-crystal layers to enhance the brightness of neutron beams emitted in selected directions, chosen to align with the beamlines served by that moderator. This enhancement may result in increased beam brightness by a factor five over all wavelengths greater than 1 Angstrom, and additional gains (for as much as a factor ten overall) between 1 and 4 Angstroms and at very long wavelengths. These gains result from neutron refraction, reflection, and Bragg scattering within the crystalline material in such a way as to dramatically increase the likelihood that any given scattering event results in a neutron emitted in a useful direction. The physics associated with these gains is not present in currently available general-purpose neutron transport codes. If successful, we will provide a moderator concept that enhances the beam brightness at the Spallation Neutron Source (SNS) by an order of magnitude.

Mission Relevance

This research is directly aligned with ORNL's intent to "design, construct, and operate neutron sciences facilities of the highest efficiency and effectiveness… (and) further the state of the art of neutron … source technology to enable leading-edge research." Order-of-magnitude increases in source performance can open fundamentally new avenues of research, and dramatically improve the throughput of studies currently under way.

Results and Accomplishments

We implemented and tested refraction and reflection in a standard neutron transport code system (MCNPX). We tested previously available crystallographic capabilities in the same code and found them to be adequate for powder materials but not for oriented materials; we implemented crystallographic scattering from oriented materials. We designed and tested the Laminated Stack Moderator, composed of alternating layers of moderating material and multi-layer crystalline vanes. The Laminated Stack Moderator confirmed the gains coming from Bragg scattering within the Convoluted Moderator's crystalline vanes and from geometric effects, and further provides ample quantitative results suitable for validating simulation methods.

05839

Motional Changes in Biomolecular Complexation

J.C. Smith

Project Description

The research is directed at understanding the dynamical changes on complexation in biological systems by combining computer simulation with experiments on the next-generation Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. Inelastic scattering experiments on ligand binding will be interpreted using analytical modeling and normal mode analysis, together with calculations on methyl group dynamical perturbations. Spin-echo spectroscopic experiments will be performed on ligand-perturbed slow domain motions and corresponding software developed to interpret the experiments with molecular dynamics.

Mission Relevance

Recent DOE press releases, reports, R&D, and budget priorities indicate that this proposal is well aligned with DOE's research focus for the next 5 years. The present proposal will begin to address the roadblocks to improving our understanding of the use of computer simulation in the analysis neutron scattering with computer simulation. The groundwork covered in the project will place ORNL in an advantageous position to support programs in DOE, Office of Science (BER, BES, ASCR).

Results and Accomplishments

Protein function often requires large-scale domain motion. An exciting new development in the experimental characterization of domain motions in proteins is the application of neutron spin-echo spectroscopy (NSE). NSE directly probes coherent (i.e., pair correlated) scattering on the ~1–100 ns timescale. We performed an all-atom molecular dynamics (MD) simulation of a protein, phosphoglycerate kinase, from which we calculated small-angle neutron scattering (SANS) and NSE scattering properties. The simulation derived and experimental solution SANS are in excellent agreement. The contributions of translational and rotational whole-molecule diffusion to the simulation-derived NSE and potential problems in their estimation were examined. Principal component analysis identified types of domain motion dominating the internal motion contribution to the NSE signal, the largest being classic hinge bending. The associated free-energy profiles are quasiharmonic and the frictional properties correspond to highly overdamped motion. The amplitudes of the motions derived by MD are smaller than those derived from the experimental analysis, and possible reasons for this difference were examined. In further work we established an interpretation of neutron spin-echo in terms of De Gennes narrowing, which may well be found to have some considerable generality. This work is presently being written up for publication.

A solid basis has now been established for the interpretation of spin-echo spectroscopy from globular proteins. This should provide the basis for future successful research proposals, some of which have already been submitted. Neutron spin-echo will be incorporated into the arsenal of neutron techniques available to structural biologists.

Information Shared

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05842

Highly Polar Oxides for Photovoltaics beyond p-n Junctions

H.M. Christen, G.E. Jellison, Jr., H.-S. Kim, D.J. Singh

Project Description

The goal of this proposal is to show that highly polar oxide materials can yield efficient photovoltaics (PVs) without the need for p-n junctions. This is motivated by the realization that cost-competitive, high-efficiency PVs will only be realized if a radically new and scalable approach is found to go beyond converting all absorbed photons to electrons of identical energy. Recent reports of PV effects in ferroelectrics and our development of highly polar oxides by pulsed-laser deposition motivate an approach that is fundamentally different from current PV methods: separating the electron-hole pairs by the permanent polarization of highly polar oxides. With this proposal we seek to (1) understand the fundamental mechanism of the PV effect in polar materials; (2) determine the stability of the polarization of ferroelectrics and pyroelectrics under illumination; (3) find pyroelectric materials with a large polarization and an appropriate absorption spectrum; and (4) enhance their electronic mobility by tuning the dielectric permittivity.

Mission Relevance

The work seeks to find completely new approaches to solar PV energy conversion by introducing polar oxides as a cost-effective alternative to existing PV device structures. It thus directly supports the mission of DOE to explore new pathways of providing affordable, renewable energy to the nation.

Results and Accomplishments

A clear and definite a link between dielectric constant and electronic mobility in complex-oxide materials was observed, using the test system of doped (conducting) ferroelectic crystals. In addition, a substrate heater designed for growth at higher temperatures than achievable in conventional pulsed-laser deposition systems was implemented. In the synthesis of nickel-doped lead zirconate-titanate films to reduce band gap in this perovskite material, a complex, undesired phase separation mechanism was observed, making it impossible to verify theoretical predictions of bandgap lowering. However, the results led to a better understanding of phase stability and epitaxial control of such materials.

Information Shared

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05843

Theoretical Studies of Decoupling Phenomena in Dynamics of Soft Materials

A. Sokolov and V. Novikov

Project Description

Understanding the dynamics of soft materials is the key to understanding and controlling their unique properties. However, current knowledge of the dynamics of these materials is very limited and many phenomena are not yet understood even on a qualitative level. Among them is a decoupling of various processes from a structural relaxation. It includes (i) decoupling of chain relaxation from segmental relaxation in polymers; (ii) decoupling of ionic conductivity from the structural relaxation; (iii) decoupling of protein's biochemical activity from the solvent's viscosity; etc. The major goal of the proposed research is to develop a solid theoretical foundation that can address and explain these decoupling phenomena. The work will be done mostly on an analytical level using theoretical models of polymer dynamics and the concept of dynamic heterogeneity in disordered materials. It will help in guiding the experiments and in explaining results accumulated using various techniques, including neutron scattering studies performed at the Spallation Neutron Source (SNS). This fundamental understanding is crucial for the development of new materials for energy applications (such as batteries, fuel cell, organic photovoltaic cells, carbon capture), for bio-related technologies (enzymatic activity, bio-inspired catalysis), and processing of lightweight materials (polymers).

Mission Relevance

Soft materials (polymers, colloids, biomaterials, etc.) attract significant attention of researchers due to their potential application in many fields, from energy and lightweight materials, to bio-technologies and bio-medical applications. Molecular motions play the key role in most of the unique properties of soft materials.

However, understanding and controlling the microscopic mechanisms of molecular motions still remain a great challenge. The project is focused on development of fundamental understanding of decoupling phenomena in the dynamics of soft materials. It has direct connections to DOE missions because it addresses problems important to electrical energy storage (batteries), carbon capture, fuel cells. Also, an explanation of the decoupling of segmental and chain relaxations in polymers and its dependence on polymer structure is necessary for a broad variety of applications, from polymer processing to biotechnologies.

Results and Accomplishments

Current use of neutron scattering spectroscopy for soft materials focuses mostly on analysis of incoherent scattering, that is, individual atomic motions. In general, significantly more can be learned from the analysis of collective dynamics, that is, from analysis of coherent neutron scattering. In particular, collective dynamics might provide additional microscopic information on dynamic heterogeneity, cooperativity and decoupling effects not accessible through the incoherent scattering. While there are a few studies that employ coherent scattering from soft matter, the major obstacle is the absence of a theory of coherent scattering for the dynamics at the mesoscopic scale, especially when motion is relatively slow, such as in supercooled liquids and proteins. There are reasonable approximations at the atomic level and at the continuum level. However, there is no theory that bridges these two limits, although the important dynamic events leading to decoupling often occur at this mesoscale. During this period we developed a theory of the coherent quasielastic neutron scattering in glass-forming systems that can describe the scattering in the mesoscale region of wave-vectors q. The theory predicts the decoupling effects for the collective relaxation time at mesoscopic and microscopic scales, connects it to the decoupling between viscosity and diffusion in glass-formers, and explains its unusual q- dependence found earlier by the coherent neutron scattering in Ca-K-NO_3 supercooled liquid.

Another interesting problem we worked on in the current year is the possible role of quantum effects on the decoupling in low-temperature glass-forming liquids. The quantum effects we considered are zero-point vibrations and quantum tunneling. As a first step in solving this problem we investigated how quantum effects may change the glass transition temperature, the temperature dependence of viscosity or structural relaxation time, and respectively, fragility of supercooled liquids. We suggested a theoretical model that predicts importance of the quantum effects at the glass transition temperature if it is less than about 0.5 of the Debye temperature. We have shown that quantum effects may lead to a significant decrease of the glass transition temperature Tg with respect to the melting temperature Tm, so that in materials where Tg is near or below ~ 60 K, the ratio Tg/Tm can be much smaller than the typical classical value of 2/3. Furthermore, it is demonstrated that the viscosity or structural relaxation time in such low-temperature glass-formers should exhibit highly unusual temperature dependence, namely, a decrease of the apparent activation energy upon approaching Tg (instead of usual increase).

06026

Optimization of ORNL Neutron Sources to meet National Mission Needs

P.D. Ferguson, K.W. Herwig, F.X. Gallmeier, J.K. Zhao, W.B. Bailey, B. Riemer, W. Lu, I. Remec, J.M. Risner

Project Description

The ultimate goal of this project is to determine a strategy for neutron source development and upgrades that will position ORNL to meet national mission needs through the mid-21st century. Objectives to be studied during the project include (a) expanding Spallation Neutron Source (SNS) mission space to include non-scattering missions, (b) upgrading HFIR's multi-mission capabilities to ensure it remains the touchstone for research reactor performance well into the 21st century, and (c) improving the R&D and functional integration of the two facilities to deliver additional value stemming from their colocation on the ORNL site.

Mission Relevance

ORNL is home to the two most intense neutron sources of their type in the world, the most powerful research reactor, the High Flux Isotope Reactor, and the most intense pulsed-spallation neutron source, the Spallation Neutron Source. These facilities have critical roles in providing access to neutron scattering facilities to researchers both domestically and internationally. HFIR also provides critical infrastructure for isotope production and materials irradiation. This LDRD project will develop a white paper detailing options and recommending a strategy for enhancing both of these facilities specifically in analysis of the options for a second SNS target station and a second cold source at HFIR.

Results and Accomplishments

We have explored options for a second SNS target station with an emphasis on providing neutron beams tailored to smaller samples, faster kinetics, and larger length scales. This has led us to focus on a concept of 10 Hz, pulse-stealing mode operation at between 300 and 500 kW of average beam power, and a target/moderator system that provides the brightest source of neutrons. These considerations have led us to optimize on smaller moderators whose volumes are in close proximity to a high-performance, solid, rotating target. We have considered four instrument categories: small angle and spin-echo, multi-chopper inelastic spectrometers, high-resolution neutron powder diffractometers, and extremely small sample instruments. We have performed initial Monte Carlo simulations of some of these instruments and will complete our analysis in the coming year.

A second cold source at HFIR will take advantage of the large diameter and high brightness of the HB-2 beam port to develop the world's most intense steady-state cold neutron facility. The HB-2 cold source brightness has been estimated previously, but a detailed study has not been completed. Currently, detailed Monte Carlo calculations are being completed to place an upper limit on the source brightness. An iteration with engineering will determine if a heat shield is required to prevent vaporization of the hydrogen. Detailed calculation of the flux on sample, including guide calculations for both the existing cold source and the proposed HB-2 cold source, will be completed in the second year of the LDRD.

06073

Lignin-Based High-Performance Lithium-Ion Anode Materials Synthesized from Low-Cost Renewable Resources

O. Rios, W. Tenhaeff, A. Johs

Project Description

This study combines unique ORNL capabilities and expertise to develop a transformational anode material with tunable electrochemical performance suitable for various funding initiatives. Not only will this new material enable a complete redesign of the anode by acting as current collector and lithium insertion material, eliminating the extra mass and expense of inactive materials in conventional designs, but the material will be made from low-cost, renewable sources with an approach that leverages advanced carbon fiber technologies at ORNL while developing strategic intellectual property (IP) and demonstrating exceptional capabilities. Lignin-based carbon fibers (LCFs) exhibit controllable turbostratic disorder, which distinguishes them from typical carbon fibers and conventional anode material. Additionally, via the synergistic application of technologies unique to ORNL in advanced processing, lignin precursor chemistry and characterization, we will control the stabilization and carbonization of lignin to tailor the electrochemical performance of the anode material. Various aspect ratio fibers will be synthesized conventionally and under high magnetic fields to manage the surface to bulk ratios and mechanical strength along with interfacial and transport properties through structural control. A prototypical LCF battery will be produced, while the strong neutron scattering contrast between lithium and carbon will facilitate in situ fundamental investigations of the insertion mechanisms to maximize performance.

Mission Relevance

Combining multidisciplinary expertise and unique ORNL technologies in battery materials and electrolytes, low-cost carbon materials, oxidation and graphitization under high magnetic fields, and world-class neutron scattering tools will allow our team to more effectively address ongoing economic issues associated with energy storage. These materials can be readily integrated with other efforts, such as the design of structural batteries and flexible metal current collector-free carbon fiber–based batteries, initiating a new low-cost approach. Additionally, the highly tunable electrochemical performance associated with controllable surface-to-volume ratios in the active material that are expected from this technology could make a strong impact in defense-related applications.

Results and Accomplishments

We have developed novel methods for the chemical modification of lignin precursors for energy storage applications. Our team has developed conversion methods to fabricate 3D architectures of lignin-based carbon fibers that dually function as current collector and active material in lithium ion batteries. Only low-cost scalable methods compatible with the carbon fiber pilot plant were investigated. The newly synthesized active materials are on par with the theoretical capacity of graphite. Fabrication of the 3D architecture does not require coating a complex slurry of active material, binder, and conductive additive onto a current collector that contributes additional inactive mass to the cell. Additionally conversion methods to render high columbic efficiency materials (near 100% efficiency) for over 150 cycles (cells are still cycling) with a low first-cycle irreversible capacity are investigated. Most interestingly we have found the highest capacity from seemingly amorphous materials. We are using neutron scattering on NOMAD to supply structural information to a molecular dynamics modeling effort. This LDRD project has also investigated the electrochemical performance LCF battery materials in an aggressive electrolyte ($LiPF_6$ in PC) and found high-capacity retention, a feat not possible in graphite. An unexpected discovery was made when carbon nanotubes (CNTs) were dispersed into the lignin precursor prior to spinning with the goals of enhancing electron transport. After conversion of the composite fibers we found that regions surrounding the CNTs formed a highly aligned graphitic structure suggesting that heterogeneous nucleation is a viable method to control the inherent turbostratic disorder that has plagued lignin in other applications. Although this has been demonstrated in polyacrylonitrile-based fibers, this is the first evidence of structural alignment in lignin carbon fibers. Significant work is still required to secure sufficient IP and show leadership in this new area.

Information Shared

This LDRD project has led to five invention disclosures:

1. Lignin-based Active Anode Materials Synthesized from Low-Cost Renewable Resources;

2. Functionalization of Precursors for High Capacity Lignin Carbon Fiber Anode Materials in Li-ion Batteries;
3. Synthesis and Activation Methods of Ultrahigh Surface Area (Activated Carbon) 3D Architectures for Supercapacitors;
4. Method for Controlling the Structural Alignment in Carbon Fibers with Naturally High Turbostratic Disorder Using Heterogeneous Nucleation; and
5. Lignin-based multifunctional high capacity composite anode materials.

Sufficient data have been generated on inventions 1 and 2 in order to file for a US patent application.

06172

Improving Energy Efficiency in Thermoelectric Materials by Integrating Neutron Scattering with Supercomputing and Modeling

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Project Description

The generation and transport of energy in materials is of great scientific and technological importance. Current and future energy technologies are dependent on our understanding of microscopic physical processes involved in the transport and conversion of energy. Better control and management of these processes will require new and more detailed understanding about energy materials. Yet, our current knowledge about phonon relaxation times (limiting heat conduction) and coupling of phonons to the electronic structure (limiting electrical transport) could be drastically improved if quantitative information could be made available to benchmark models and theories. We leverage the unprecedented flux of the Spallation Neutron Source (SNS), the power of supercomputers at the National Center for Computational Sciences (NCCS), and state-of-the-art solid-state theory simulations to shed light on microscopic processes of energy transport in energy materials, focusing on thermoelectrics.

Mission Relevance

This project models the large four-dimensional scattering datasets produced by inelastic neutron scattering experiments at the SNS in order to reliably extract the fundamental physical quantities (phonon linewidths) and provide keys to a better understanding of microscopic energy transport. Our integrated approach will extract new scientific insights, and will advance our current knowledge of microscopic phonon transport. These insights will be fed back into designing better materials, with improved energy efficiency. We emphasize that no other experimental technique is presently capable of accessing phonon linewidths throughout the Brillouin zone, and the SNS thus offers a unique opportunity for scientific breakthroughs, with potential high impact for energy technologies. This work will enable major scientific advances and provide solutions to the DOE's critical missions in Scientific Discovery and Innovation and Clean Energy. Our project complements current research programs at ORNL investigating thermoelectric and other energy materials [Physic al Sciences Directorate/High-Temperature Materials Laboratory (PSD/HTML), Materials Science and Technology Division/Correlated Materials Group (MSTD/CEMG), etc.].

Scientific/Technical Accomplishments

1. Neutron scattering measurements:

We have performed measurements of phonons in single-crystalline samples of thermoelectric materials SnTe and Ge-doped PbTe using both the HB3 and CTAX triple-axis spectrometers at the High Flux

Isotope Reactor (HFIR) (IPTS-6448, IPTS-6470) and on the Cold Neutron Chopper (CNCS) and Wide-Angle Chopper Spectrometer (ARCS) time-of-flight spectrometers at SNS (IPTS-5293, IPTS-6683). The thermoelectric single crystals were synthesized in the Correlated Electrons Group (B. Sales) at ORNL. The phonon measurements show that the ferroelectric transverse optic (TO) mode has a pronounced softening at the zone center, characteristic of the nearness to the ferroelectric transition. The temperature dependence of the TO mode was studied and revealed a soft-mode behavior, as well as a strong broadening of the phonon linewidth with increasing temperature. This behavior indicates a strong anharmonicity of TO phonons in SnTe and Ge-doped PbTe, similar to PbTe. Linewidths of acoustic modes near the zone center were measured using the cold-neutron triple-axis spectrometer CTAX at HFIR. Modeling of triple-axis and time-of-flight data is under way.

A bcc Nb single-crystal was measured on ARCS in order to obtain a calibration dataset for our modeling methods (Fig. 1). The Nb dataset is of extremely high quality, and systematically shows the Kohn anomalies (dips and kinks) in the phonon dispersions, which arise because of the coupling with the Fermi surface. We are taking advantage of this scientific opportunity to extend our four-dimensional S(**Q**,E) phonon measurements to extract information about the topology of the Fermi surface, and the strength of the electron-phonon coupling.

2. First-principles simulations of microscopic phonon dynamics with density functional theory:
First-principles calculations of phonon dispersions and their pressure dependence were performed for SnTe. As part of this, we did benchmark calculations for several different exchange-correlation functionals. We find the best results with the standard local density approximation. The results show a strong pressure dependence of the soft transverse optic branch similar to what was earlier reported for PbTe. In the case of PbTe, this indicates a longitudinal acoustic–transverse optic coupling that is also seen in experiment, and is important for the low lattice thermal conductivity and unusual dynamics in that material. The present results suggest that unusual dynamics can also be anticipated in SnTe.

We also initiated finite displacement calculations to begin directly addressing the anharmonic couplings and anisotropy of the temperature dependent mean square displacements. So far, we find strong anharmonicity for the transverse optic branch, as expected for a soft mode.

Additional ab initio molecular dynamics simulations of SnTe have been performed, and results are being compared with measurements of atomic mean-square displacements (measurements with Powgen).

3. Algorithms for optimizing dynamics models and fitting neutron scattering data to extract accurate dynamical structure factors (for general systems):
We have written software to perform calculations of S(Q,E), and we are leveraging existing open-source codes to establish an interface between first-principles calculations of phonon-related quantities (interatomic force-constants and dispersions/eigenvectors) and the measured neutron scattering intensities. We have also initiated efforts to leverage the parallel-optimization package Dakota to optimize parameters in lattice dynamics models to best fit neutron scattering measurements. Work was initiated to rewrite our codes on GPGPU for better performance. Codes and test datasets are centralized on a group-shared SVN repository with Trac management ("PhononLinewidths" repository on the flathead server at SNS), which allows access to all LDRD members.

06175
Template-Assisted Bicontinuous 3D Electrode Architecture for Energy Storage Materials

J. Nanda, S. Pannala, J.C. Idrobo, S. Dai

Project Description

We propose to develop and demonstrate novel 3D battery electrode architectures that eliminate the current capacity, rate (transport), and life cycle limitations associated with today's intercalation-based batteries. A template-driven bicontinuous 3D electrode structure is proposed where the electrochemical active material layer is sandwiched between highly conducting electron and ion conducting interconnected pathways. The bicontinuous (two continuous electron and ion conductive channels) electrode enables (a) facile transport of ions through the interconnected pore network, (b) short solid state diffusion length for ion transport, (c) high electronic conductive pathway, and (d) large effective surface area for electrochemical activity/incorporation. The central focus of this proposal is to utilize the above mentioned 3D conducting scaffold or a carbonaceous fiber-based approach for incorporating high-capacity multi-electron (and multi-valent) electrode chemistries and enabling alternate electrochemical storage mechanisms based on conversion and displacement type reactions. The template approach offers the flexibility to vary the pore diameter and create gradient structures of the interconnected network to facilitate both the energy density as well as the power density. The proposed research will provide a proof of principle for the development of novel 3D electrode architecture that targets the DOE scientific roadmap (goals) for these materials and of 3D structures for electrochemical energy storage (EES) and will position ORNL to respond to calls for proposals from various DOE offices including DOE-BES (either core programs or proposed Energy Storage hub), the Energy Storage Program of the DOE-EERE-OVT, ARPA-E, and DARPA.

Mission Relevance

The proposed research, and the strategic partnership with Prof. Braun that it would foster, will strengthen ORNL's capabilities in proposing a BES energy storage hub and in seeking substantial follow-on funding from EERE, particularly since the research on high energy electrodes is a high priority of the Office of Vehicle Technologies. Apart from high impact publication and IP the proposed unique 3D architecture approach for energy storage is very timely as no other competing national laboratories are actively pursuing this area at present and hence, would position ORNL in to this important emerging subtopic. In addition to DOE, BES and EERE offices, we will be positioned well to approach DOD and ARPA-E for the follow on funding.

Results and Accomplishments

The proposal has three main objectives: (i) demonstrating multi-electron capacity in conversion compounds such as iron fluorides and oxyfluorides; (ii) developing 3D electrode architecture and underlying framework for hosting multivalent cathodes for achieving higher energy density and cycle-life performance; and (iii) understanding capacity-limiting mechanisms using materials characterization and 3D multi-scale modeling. We have made significant progress towards accomplishing each of these goals. We demonstrated reversible multi-electron capacity in iron fluoride (FeF_3 and FeF_2) conversion compounds by synthesizing Fe (II&III) fluoride –multilayer graphene (MLG) composite electrodes. Almost theoretical capacity of 700 mAh/g and 550 mAh/g is reported for FeF_3 and the FeF_2 composite electrode, respectively, for the first few cycles, but the samples show significant capacity fade and very high hysteresis (> 2V). The capacity retention and hysteresis are significantly improved by incorporating the FeF_3-MLG on a carbon-fiber-based 3D architecture. This is achieved by using a carbonaceous binder that binds the FeF_3-MLG onto the interconnecting fiber network. This resulted in significant improvement of cycle life with a concomitant reduction of hysteresis to 1 V. Further, electrochemical cycling at 60°C improved the reaction kinetics to obtain almost theoretical capacity (710 mAh/g) for > 40 charge-discharge cycles. This is the best data ever reported so far for this particular conversion chemistry. In order to facilitate ionic transport across the electrode length scale, we fabricated bicontinuous inverse opal 3D structures (in collaboration with Prof. Paul Braun's group at University of Illinois) having macrospheres in the range of 250–300 nm. Each macrosphere is connected to four adjacent spheres through micro-channels having a width of 50 nm. Such ordered electrode structure tends to reduce the ionic tortuosity and therefore improves capacity retention by facilitating electrochemical transport. Fe_2O_3 nanoparticles were then electrodeposited on 3D inverse opal electrodes. The electrochemical test results showed much improved capacity and cycle life performance. We also performed detailed high-resolution electron microscopy studies on pristine and cycled FeF_3 and Fe_3O_4 electrodes to map out various intermediate phases formed as a part of conversion reaction. Our results showed particle coarsening when FeF_3 electrodes are cycled. Furthermore, the FeF_3 sample showed significant electron beam damage because of the fluorine content in the sample. Our conclusions were further validated by performing similar experiments on iron oxide samples. Electrode modeling and electrochemical transport simulation studies of conversion-based compounds are currently under progress.

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06233

Development of the Neutron-Based Biomembranes Initiative at NScD

J. Katsaras

Project Description

This proposal outlines a science plan to establish the Neutron-Based Biomembranes Initiative (NBBI) within the Neutron Sciences Directorate (NScD) and ORNL. In broad terms, NBBI will be comprised of two major thrusts: (1) the elucidation of structure and its relation to the function of biological membranes— this will be accomplished through the use of biologically relevant membrane systems (both model and real) and the unique characterization capabilities offered by thermal and cold neutrons (e.g., contrast variation)—and (2) the development and fabrication of systems with utility to the pharmaceutical and medical industries (e.g., liposomal-based targeted drug delivery and imaging systems). Ancillary aims and benefits will include the development of novel techniques, samples, and sample environments, especially those that will exploit the capabilities of the SNS. Both thrusts will involve collaborators from NScD and other organizations within ORNL, and from outside of ORNL (i.e., universities, government agencies, and industry). The science described in this proposal will have a significant strategic impact on neutron scattering at ORNL. It will not only act as a nucleus for leading-edge science within ORNL, and the training of highly qualified personnel (HQP), but will also provide a critical "point of entry" and interface that will make neutron scattering visible and accessible to the biomembranes communities located at universities, DOE and other government labs, and industry. The goal is that NBBI will become an international center of excellence for biomembranes.

Mission Relevance

Throughout the biological world cell membranes are crucial to the existence of individual cells. In animal cells the plasma membrane is a selectively permeable barrier composed primarily of proteins and lipids, which separates the cytosol from the extracellular environment. Membranes also surround the various cell organelles (e.g., mitochondria, endoplasmic reticulum, Golgi apparatus, etc.), enabling them to maintain their characteristic differences from the cytosol. In addition to its barrier function, the plasma membrane acts as an anchor for the cytoskeleton, a cellular network of fibers contained within the cytoplasm that imparts , structure, shape, and movement to the cell.

With the diverse and in-depth expertise offered by the various groups at ORNL, including the nanomaterial characterization and fabrication resources available at the Center for Nanophase Materials Sciences (CNMS) and the modeling and computing capabilities at the Center for Molecular Biophysics, NBBI will have a significant strategic impact on neutron scattering at ORNL and beyond. This will position the NBBI team to pursue and successfully compete for continued support from agencies DOE (BER: especially Genomic Science, Bioenergy, Structural Biology and Subsurface Biogeochemistry programs; BES: especially User Facilities, Physical Biosciences, Biomolecular Materials and Chemical Physics areas), NIH (research on, for example, biofilms, antibiotics, microbiomes, infectious disease), DoD (biodefense, sensors, corrosion), and DHS (biodefense). In addition, and equally important, the capabilities developed by NBBI will become part of a suite of approaches available to NSSD's user community.

Results and Accomplishments

The goal of this LDRD is to build a neutron-based biological membranes science program that will not only establish itself as world leading but also one that will attract some of the top external scientists as collaborators and users. In establishing the program, in the past 24 months the NBBI has attracted postdoctoral fellows Fred A. Heberle (Cornell University) and Jianjun Pan (Carnegie-Mellon University) and PhD graduate student Paul Drazba (University of Tennessee, Physics) (supervisor, J. Katsaras).

Over the past 12 months the NBBI has undertaken a series of scientific developments, which have aided NBBI on its quest to establish itself as a leading-edge biological membranes science program. Some of these developments are as follows.

In recent years, the observation of phase-separated lateral domains in lipid bilayers has received considerable attention, especially in connection to "lipid raft" phenomena in cells. Rafts are believed to play a central role in an array of cellular processes, notably those involving signal transduction. While micron-size domains can readily be observed in model membranes with a light microscope, rafts that are much smaller than 100 nm are now thought to exist, both in vitro and in vivo. Structures of this size are inaccessible to optical microscopy and many biophysical methods. In collaboration with G.W. Feigenson's group (Cornell University), postdoctoral fellow Fred Heberle (NBBI) carried out small-angle neutron scattering (SANS) to measure the size of nanoscopic membrane domains in a model lipid bilayer mixture with unprecedented accuracy—using facilities at HFIR and SNS. They discovered a direct correlation between domain size and the mismatch in bilayer thickness between the coexisting liquid phases, suggesting a dominant role for line tension in controlling raft size. While this result is expected from line tension theories, the neutrons provided the first experimental verification in freestanding bilayers. These results suggest how the size of functional domains in homeothermic cells may be regulated through changes in lipid composition. (The manuscript has been submitted to the *Journal of the American Chemical Society*.)

Postdoctoral fellow Jianjun Pan has recently managed to develop a sample environment and data analysis software that enabled the Time-of-Flight (TOF) Liquids Reflectometer [located at the Spallation Neutron Source (SNS)] to carry-out diffraction experiments on aligned stacks of lipid bilayers. In a paper published in the *Journal of Applied Crystallography* [**45,** 1219–1227 (2012)], details are given regarding the instrumental setup, data collection and reduction, structure factor determination, and the reconstruction of the membrane's one-dimensional (1D) neutron scattering length density (NSLD) profile. The validity of using TOF measurements to determine the (1D) NSLD profile was demonstrated by reproducing the results of two well-known lipid bilayer structures. The method was then applied to show how an antimicrobial peptide affects membranes with and without cholesterol. This new capability will significantly broaden the user community that can make use of the SNS Liquids Reflectometer.

At the Joint Institute for Neutron Sciences (JINS), the NBBI in collaboration with the University of Tennessee (M. Dadmun and T. Egami) are continuing to develop physical characterization and sample preparation laboratories (A-110, B-107, and B-111) that will help the neutron scattering community to prepare neutron appropriate samples and to characterize them prior to interrogation by neutrons. The suite of instruments presently includes differential and isothermal titration calorimetries; time-domain fluorescence; static and dynamic light scattering; Langmuir-Blodgett troughs; densitometry; GC-Mass spectrometry. Over the span of the LDRD, 15 refereed publications were produced, with postdoctoral fellows Heberle and Pan figuring prominently.

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06241

High-Energy Rechargeable Magnesium Batteries Based on Nanostructured Materials

S. Dai and X.-G. Sun

Project Description

Magnesium is light (density 1.74 g/cc), inexpensive, and available, being the eighth most abundant element in the Earth’s crust. Unlike lithium, magnesium is stable in wet environments and has a high melting point (650°C vs. 178°C for lithium). However, there are two major obstacles to the development of a practical rechargeable magnesium battery: (1) slow magnesium intercalation kinetics into cathode materials and instability of the crystal structure of the cathode materials during repeated cycling and (2) passivation of magnesium in common electrolytes and low magnesium dissolution/plating efficiency. The goal of this project is to reduce the intercalation length of the magnesium into the cathode and improve the insertion kinetics by developing a magnesium battery that utilizes ultra-thin vanadium oxide and other oxide films grown on mesoporous carbon frameworks. A surface sol-gel synthesis or other conformal deposition methods will be used to controllably deposit vanadium oxide or other oxide films on the carbon material. In addition, novel electrolytes based on magnesium imide salts in ionic liquids will be explored to enable reversibility at the magnesium anode. The proposed battery is expected to have a practical energy density greater than 900 Wh/kg, be capable of operating over a wide temperature range, and provide long cycle life and safety. The results from this project can be used directly in preparation of external proposals for Advanced Research Projects Agency-Energy (ARPA-E) and other DOE Offices.

Mission Relevance

Electrochemical energy storage (EES) is one of the most important technologies for a sustainable energy future. The development of transformational EES systems is central to the DOE mission. Any future EES system must possess the following essential characteristics: (1) high energy density, (2) sufficient power, (3) reasonable cost, and (4) optimized safe operation and minimum environmental impacts (see J. B.

Goodenough, H. D. Abruña, and M. V. Buchanan, Basic Research Needs for Electrical Energy Storage, DOE Office of Basic Energy Sciences, July 2007). In addition to DOE, EES is also the key to many other funding agencies outside DOE. For example, the U.S. Army Office of Research and Defense Advanced Research Projects Agency (DARPA) have a continuing interest in the development of advanced batteries.

Results and Accomplishments

Our first target is to identify suitable electrolytes that can support reversible magnesium deposition and stripping. We have successfully synthesized two magnesium aluminate compounds, $Mg(BuEtAlCl_2)_2$ and $Mg(BuAlCl_3)_2$. The electrolytes based on the two salts in THF showed reversible magnesium deposition and stripping with good cyclability up to 100 cycles. One drawback of using a Grignard reagent as an electrolyte is its high sensitivity to moisture, which reacts vigorously with water and has to be handled inside an inert gas-filled glove box. This causes safety concerns for practical applications, even though there is less concern regarding the use of magnesium metal as compared to lithium metal. To solve this issue, we have tried to use other magnesium salts such as magnesium trifluoromethanesulfonate, $Mg(SO_3CF_3)_2$, and magnesium perchlorate, $Mg(ClO_4)_2$. It is found that $Mg(SO_3CF_3)_2$ is difficult to dissolve in common solvents such as accausetonitrile (AN), dimethylsulfoxide (DMSO), and dimethoxyethane (DME) while $Mg(ClO_4)_2$ can be easily dissolved up to 0.5 molar in those solvents. Unfortunately, CV showed that no reversible magnesium deposition/stripping were observed. In all these electrolyte systems, a pronounced electrolyte decomposition peak between 0 and 1.0V versus Mg^{2+}/Mg was observed, confirming that it is difficult for a magnesium ion to pass through the SEI layer for reversible magnesium deposition/stripping.

The successful magnesium deposition/stripping in the electrolyte of 0.25 M $Mg(BuEtAlCl_2)_2$/ THF suggests that THF is suitable as solvent for magnesium battery. Since both $Mg(SO_3CF_3)_2$ and $Mg(ClO_4)_2$ cannot be dissolved in THF, new magnesium salt is needed. Bis(trifluoromethane sulfonyl)imide (TFSI) is a highly delocalized anion, which makes its salt soluable in most organic solvents. Therefore, we have synthesized magnesium bis(trifluoromethanesulfonyl)imide ($Mg(TFSI)_2$) by reacting hydrogen bis(trifluoromethanesulfonyl)imide with high-purity magnesium hydroxide. A 0.25 M $Mg(TFSI)_2$/THF solution was made inside the glovebox. The CV test shows that there is magnesium deposition peak below 0 V and a magnesium stripping peak around 1.0 V versus Mg^{2+}/Mg. Another alternative magnesium electrolyte developed that is based on ionic liquid, methylpropylpyrrolidinium bis(trifluoromethanesulfonyl)imide (MPPY.TFSI) and $Mg(TFSI)_2$. The CV based on 0.25 M $Mg(TFSI)_2$/MPPY.TFSI on platinum working electrode shows that the electrolyte starts decomposition at 1.0 V, and its maximum decomposition peak occurs at -0.2 V versus Mg^{2+}/Mg. Correspondingly, there is an onset oxidation peak starting at 0 V. In the following cycles the current of electrolyte decomposition decreases and a distinct magnesium deposition peak occurs at -1.0 V, while a magnesium stripping peak occurs at 1.0V versus Mg^{2+}/Mg. The above facts indicate that the ionic liquid-based electrolyte can support reversible magnesium deposition/stripping, even though there is initial electrolyte decomposition. However, it should be mentioned that the separation between deposition peak and stripping peak is very large, around 2.0 V, which might be related to the high viscosity of the ionic liquid electrolyte and slow magnesium diffusion. Nevertheless, the SEI layer formed on the magnesium electrode by this ionic liquid electrolyte is not too densely packed to prevent the passing of a magnesium ion for deposition and stripping. In the future we will conduct the test at high temperatures to alleviate the viscosity effect.

In addition to focus on developing safe electrolytes for a magnesium battery, we also tried to synthesize and characterize new anode and cathode materials. Recently, $Li_4Ti_5O_{12}$, which is an anode material for a lithium ion battery, has been successfully used for a sodium ion battery and showed good reversible capacities. Considering that a magnesium ion is similar to sodium ion, we tried to use $Li_4Ti_5O_{12}$ as an anode for a magnesium battery and tested it in $Li_4Ti_5O_{12}||Mg$ half-cell. The result using 0.25 M $Mg(BuEtAlCl_2)_2$/THF as an electrolyte shows that indeed magnesium ion can be reversibly intercalated/de-intercalated into $Li_4Ti_5O_{12}$. However, the capacity is relatively low, partially due to the slow diffusion of magnesium ion within the electrode material. In order to improve the overall capacity, the electrode structure needs to be optimized. $MgMnSiO_4$ was synthesized as potential cathode for magnesium battery. The half-cell test using 0.25 M $Mg(BuEtAlCl_2)_2$/THF showed a nice plateau at 1.2 V. Unfortunately, the battery also showed low capacity and poor cycle ability, which are all due to the slow diffusivity of magnesium ion within the cathode material. Further optimization of the electrode structure is needed.

In the coming year, we will try to solve the slow diffusion kinetics of magnesium by depositing a thin layer of active material on the current collector. In the original proposal it was proposed that can be accomplished using an ALD technique. A newly acquired ALD machine has been installed in our lab and now is in the process of parameter optimization for ALD coating. This will be the focus of the final year of this project. Another interesting topic worth exploring is using magnesium as an anode and sulfur as a cathode. The theory capacity of this battery is 4000 Wh l^{-1}, which is twice of the capacity of lithium ion battery based on graphite as an anode and $LiCoO_2$ as a cathode. To test this possibility, a Grignard reagent–based electrolyte cannot be used due to its nucleophilic character, so we will use the neutral ionic liquid–based electrolyte for this task.

06242

Reengineering Xylanase

P. Langan, D. Graham, L. Coates, Q. Wan, S. Hamilton-Brehm

Project Description

This project aims to pioneer the use of neutron crystallography in combination with molecular biology mutagenesis and in silico design to guide the reengineering of the enzyme xylanase to allow for the more efficient hydrolysis of hemicellulose to xylose over a broader range of conditions. Five-carbon sugars such as xylose from hemicellulose represent up to 30% of lignocellulosic biomass, and their efficient hydrolysis is important for cost-efficient production of biofuels and other bioproducts. We expect that our innovative multidisciplinary approach will be readily applicable to other bioengineering problems of industrial importance and will position ORNL with unique capabilities and expertise to attract programmatic funding.

Mission Relevance

The results will provide fundamental scientific insights into an enzyme with important applications in DOE science and energy resources missions. An improved enzyme is expected to have an impact on the cost and efficiency of the production of biofuels. Biofuels are of direct relevance to DOE missions in renewable energy. The impact of this mission on our energy security and environment is widely appreciated. This proposal will broaden the science and capabilities of the DOE-funded Center for Structural Molecular Biology by adding a new crystallography component to its present capabilities in deuteration and small-angle neutron scattering. The approach and capabilities developed here will be applicable to other bioengineering and synthetic biology problems, some of which may be of interest to the National Institutes of Health (NIH) when applied to enzymes of biomedical importance. The DOE missions in renewable energy are also of interest to the US Department of Agriculture (USDA). The USDA and DOE jointly fund programs in this area.

Results and Accomplishments

We developed an enzyme expression and activity assay pipeline for xylanase at the Bioscience Division after trials with several different hosts (*Clostridium cellulolyticum, Trichoderma reesei*, and *E. coli*) and different assays (measuring reducing sugars released by the hydrolysis of Birch tree xylan and a continuous spectrophotometric assay, using the soluble, chromogenic substrate 4-nitrophenyl-beta-xylobioside). In parallel we developed a crystallization and structure analysis pipeline at the Center for Structural Molecular Biology. Using these pipelines, we have expressed, assayed, crystallized, and determined the X-ray structures of several rationally designed mutants of xylanase. The results provide new information on the catalytic mechanism of the enzyme and indicate further mutations that will lead to improved performance. These preliminary results are being reported in two publications; one already submitted and the other is to be submitted within a month. From these X-ray structures we selected four protein targets for probing deeper with neutrons. Large crystals of these targets have been prepared, and neutron data collection beam time has been awarded and scheduled over the next 5 months at neutron sources throughout the world (include BioDIFF in Munich and the PCS at Los Alamos). One crystal has already been examined at the new IMAGINE neutron beam line at HFIR, and as IMAGIBE completes its commissioning, we expect it to be the main experimental facility for completing this work. The results of these neutron studies will lead to high-impact publications and mechanistic information to guide the rational design of improved industrial xylanases.

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06268

Perception-Driven Decision Support in Medical Imaging

G. Tourassi

Project Description

A vast amount of digital medical image data is generated for diagnostic interpretation on a daily basis. In the past two decades great efforts have been made to develop computer-assisted decision (CAD) support systems to help radiologists read medical images efficiently while reducing medical errors. However, several critical challenges remain. Conventional CAD systems provide the same decision support to all users. To achieve high sensitivity, the systems operate at a clinically undesirable low specificity. It is also recognized that radiologists respond differently to CAD cues, often disregarding correct ones while accepting wrong ones. The aim of the proposed research is to develop the framework for a personalized CAD system that supports the individual needs of each radiologist. The framework will be based on locally adaptive image analysis and decision making components driven by contextual information provided by the individual radiologist's visual search characteristics for the specific case under review. We will achieve this by integrating eye-tracking technology into a conventional CAD system to provide real-time, personalized decision support that complements the individual radiologist's perceptual and cognitive pattern. The personalized context-sensitive CAD system will be developed and pilot tested in mammography for breast cancer detection.

Mission Relevance

One of DOE's stated strategic goals is to support science that leads to improved US economic competitiveness and quality of life through innovations in science and technology. The proposed research involves technology development to improve health care (earlier cancer detection, thus better patient outcomes). The proposed decision support technology has a wide international market, and the underlying scientific concepts can be easily extended to other clinical applications that involve visual interpretation of medical images.

Results and Accomplishments

In the first year, research activities were focused on data collection and development of specialized data analytics algorithms to facilitate knowledge discovery for better understanding of the radiologists' perceptual and cognitive errors when they interpret screening mammograms. The scientific accomplishments were as follows. (1) Data Collection: Three separate institutional review board (IRB) protocols were established in collaboration with the Breast Imaging Division at the University of Tennessee Medical Center at Knoxville. Anonymized clinical cases were collected under these protocols as well as eye-tracking data from radiologists who participated in medical image interpretation studies. (2) Data Analytics: Using the collected data, localized texture image analysis and various machine learning decision algorithms were explored as a means to predict radiologists' eye-gazing behavior and diagnostic errors (both perceptual and cognitive).

The results of those experiments confirmed that radiologists of similar expertise *have diverse perceptual and cognitive patterns* when performing medical image interpretation. Commercial decision support systems in mammography are optimized to detect as many cancers as possible, ignoring the radiologist's specific reading needs and behavior. The scientific outcomes of the past year serve as proof of concept to support the need for a human-centered approach to designing decision support systems for medical imaging.

The work performed on this project has resulted in a 4-year grant application submitted to the National Institutes of Health on October 5, 2012. The application is entitled "Human-CAD Collaborative Decision Support in Radiology via Eye-Tracking Analytics" (PI: Tourassi). Also, two invention disclosures were filed in the past year based on work performed on this project: (1) Invention Disclosure Number 201202917, Georgia Tourassi, inventor, and (2) Invention Disclosure Number 201202916, Songhua Xu, Georgia Tourassi, James Kress, inventors.

Information Shared

S. Xu and G.D. Tourassi, "A novel local learning based approach with application to breast cancer diagnosis", 2012 SPIE Medical Imaging Conference Proceedings (Proc. SPIE 8315, 83151Y), 2012.

S. Xu, K. Hudson, and G.D. Tourassi, "Predictive modeling of human perception subjectivity: feasibility study of mammographic lesion similarity," 2012 SPIE Medical Imaging Conference Proceedings (Proc. SPIE 8318, 83180M), 2012.

G.D. Tourassi and V. Paquit, "Towards Human-Centered Decision Support in Mammography," accepted at the 2012 Biomedical Engineering Society (BMES) 2012 Annual Meeting, October 24–27, 2012, Atlanta, GA.

G.D. Tourassi and M.M. Mazurowski, "Case-Based CAD Systems in Breast Imaging", invited book chapter accepted for publication in *Computer-aided Detection and Diagnosis in Medical Imaging*, editors Q. Li and R.M. Nishikawa, Taylor & Francis Publishers (to be published in 2013).

A.C. Williams, A. Hitt, S. Voisin, and G.D. Tourassi, "Automated assessment of bilateral breast volume asymmetry as a breast cancer biomarker during mammographic screening," accepted for oral presentation at the 2013 SPIE Medical Imaging Conference, 2013.

F. Pinto, S. Voisin, S. Xu, and G.D. Tourassi, "Investigating the association of eye gaze pattern and diagnostic error in mammography", accepted for oral presentation at the 2013 SPIE Medical Imaging Conference, 2013.
J. Kress, S. Xu, and G.D. Tourassi, "A novel graphical user interface for high-efficacy modeling of human perceptual similarity opinions," accepted for oral presentation at the 2013 SPIE Medical Imaging Conference, 2013.

06271

New Capabilities for Neutron-Based Biomembrane Research at ORNL

R.F. Standaert and J. Katsaras

Project Description

This project will develop unique reagents and capabilities that will help establish ORNL as a leading-edge biomembrane research center, particularly through the use of neutron-scattering techniques. A topic of great interest is the role of unsaturated lipids in biomembranes. Neutron scattering is ideally suited to the study of the biomembrane model systems and, in conjunction with other techniques, has the potential to deliver groundbreaking advances. For this potential to be realized, new reagents and capabilities at the Spallation Neutron Source (SNS) are required. In particular, novel isotopically labeled lipids are needed to exploit the powerful isotopic contrast offered by neutron scattering. Furthermore, biomimetic membrane model systems must be improved and implemented. This project will build the requisite capabilities and provide immediate scientific impact through proof-of-principle experiments. In this way, it will lay the cornerstone of a permanent biomembrane research center and enhance the user program with a suite of capabilities unique to ORNL.

Mission Relevance

This project will advance the missions of the Office of Science Basic Energy Sciences program (BES) and the Biological and Environmental Research program (BER). For BES, it will greatly enhance the capabilities of the SNS user program, and it is directly aligned with the thrust areas of the Biomolecular Materials Core Research Area. For BER, it will support a wide range of basic energy and environmental research where cell–cell and cell–environment interactions are central, such as biofilms, bioremediation, and plant–microbe interactions. It will also support applied research, such as the development of fuel-tolerant microbes for biofuel production, where alterations in biomembrane composition and chemistry are important.

The National Institutes of Health (NIH) has great interest in biomembrane research due to the role of the membrane and unsaturated lipids in biomedical imaging, implanted devices, drug delivery, aging, and numerous diseases. Membrane research is also relevant to agencies such as the Department of Homeland Security (DHS) and the Department of Defense (DOD) due to the role of biomembrane processes in areas such as biothreats (detection and infectivity) and surface biofouling (sensors, ships, etc.). The proposed work will make advanced membrane models and novel, isotopically labeled lipids available to these agencies through the Neutron Sciences user program and through Work-for-Others projects.

Results and Accomplishments

A number of accomplishments were realized. The first of these was to establish the biophysical characterization laboratories at the UT–ORNL Joint Institute for Neutron Sciences (JINS). These laboratories contain specialized equipment for biomembrane studies. The main technical objective for the year was the production of perdeuterated sterols for use in neutron scattering studies. Sterols, the best known example of which is cholesterol, are essential components of the cellular membrane that serve to regulate fluidity, stiffness, and organization. To get the most sensitivity and information from scattering experiments, sterols highly enriched in the hydrogen isotope deuterium are required. We successfully prepared a fully deuterated version of the yeast sterol ergosterol, which is very similar to cholesterol. The deuterated ergosterol was used to study the rate of sterol desorption from model membranes using small-angle neutron scattering (SANS). Importantly, this study allowed the determination of desorption rates under native, equilibrium conditions without chemical modifications to the structure of the sterol. Additional initiatives started during the year include chemical conversion of ergosterol to cholesterol chemo-enzymatic desaturation of stearate to oleate for the production of perdeuterated lipids.

Information Shared

F.A. Heberle et al., "Model-based approaches for the determination of lipid bilayer structure from small-angle neutron and X-ray scattering data," *European Biophysics Journal*, **41**, 875–890 (2012).

06347

Quantum Monte Carlo Development and Applications in Materials Science

J. Kim

Project Description

The project aims to develop a new distinctive capability in computational science centered about the quantum Monte Carlo (QMC) method. This will include the development and implementation of efficient new algorithms to take advantage of leadership and emergent computing architectures. This work will act as a synergistic interface between the Computing and Computational Sciences and Physical Sciences Directorates at ORNL and allow new capabilities for highly accurate materials and chemical simulations/predictions. The goal is to adequately develop QMC methods such that they can become a key part of ORNL materials simulation portfolio, complementing and supporting existing methods and resources. This will place ORNL into a leading position for simulation and modeling of materials that include strong correlation and potentially excited states that are currently considered among the "grand challenges."

Mission Relevance

Oak Ridge National Laboratory is committed to a broad, integrated science and technology program devoted to discovery and development of materials and processes needed to revolutionize energy storage, conversion, and utilization. A significant part of this effort concerns the theory, modeling, and simulation of materials. In order to enable the rapid discovery of new materials and processes, as well as to further optimize already identified materials, theory involving first-principles many-body methods is required. These methods must be implemented efficiently on the Laboratory's leadership computing facilities and upcoming emergent computing platforms. Quantum Monte Carlo (QMC) methods, the focus of this proposal, have broad applicability across the ORNL materials portfolio, while satisfying the computational requirements. In addition to offering greater accuracy than other approximate methods, QMC methods can compute many-body properties inaccessible to single-particle, mean-field techniques such as density functional theory (DFT). QMC can therefore become a key method for projects in the Materials Science and Technology and the Computer Science and Mathematics divisions.

Results and Accomplishments

The PI led the development of computational scheme that allows the quick and efficient evaluation of multi-determinant expansions in QMC calculations and its application to benchmark first row dimers and the 55 molecules of the G1 test set. The potential of these wavefunctions to systematically reduce the fixed-node error in the QMC calculations has been demonstrated in almost all cases studied. When compared to traditional methods in quantum chemistry, the results show a marked improvement over MP2, CCSD(T), and DFT with various functionals; in fact, the only method able to produce better results is the explicitly correlated CCSD(T) method, extrapolated to the infinite basis set limit. A new method to represent a quantum energy density for use in QMC calculations is developed, allowing computation of formation energies of defects with much improved statistical errors at the same computational cost and providing microscopic description of correlation effects. All the newly developed methods and new capabilities are fully implemented in QMCPACK and are utilized to study defects in bulk silicon and germanium, metal-insulator transition at the low-density atomic hydrogen, and lithium diffusion in graphite. The PI has continued algorithmic development and improvement of QMCPACK on the HPC computers at the DOE leadership computing facilities. The performance enhancement to exploit new hardware and programming environment has resulted in 1.5–2× speedup for typical QMC workloads on both many-core and CPU/GPU hybrid systems.

Information Shared

J. Kim, K. P. Esler, J. McMinis, M. A. Morales, B. K. Clark, L. Shulenburger, and D. M. Ceperley, "Hybrid algorithms in quantum Monte Carlo", accepted for publication in the proceedings of conference on computational physics 2011, Gatlinburg, TN.

J. Kim, "QMCPACK: enabling breakthrough QMC simulations on leadership computing facilities," Accelerating Computational Science Symposium 2012, Washington, DC.

J. Kim, K. P. Esler, J. McMinis, M. A. Morales, B. K. Clark, L. Shulenburger and D. M. Ceperley, "Quantum Monte Carlo in the era of petascale computers," APS March Meeting 2012.

06349

Accelerating Data Acquisition, Reduction, and Analysis (ADARA) at SNS

G. Shipman, M. Hagen, S. Campbell, D. Dillow, M. Doucet, S. Hartman, J. Kohl, V. Lynch, R. Miller, S. Oral, P. Peterson, D. Reitz, S. Ren, D. Stansberry, C. Tang, S. Vazhkudai, F. Wang, K. White

Project Description

As the data sets generated by the increasingly powerful neutron scattering instruments at the Oak Ridge National Laboratory (ORNL) Spallation Neutron Source (SNS) grow ever more massive, the facility's users require significant advances in data reduction and analysis tools so they can cope. The SNS is the world's most intense pulsed, accelerator-based neutron source for scientific research and development. Funded by the US Department of Energy (DOE) Office of Basic Energy Sciences (BES), this national user facility hosts hundreds of scientists from all over the world every year, most of whom are engaged in materials science research. Through this LDRD, the SNS data specialists have teamed with ORNL's Computing and Computational Sciences Directorate to meet the neutron science users' next-generation requirements.

The result is ADARA—the Accelerating Data Acquisition, Reduction, and Analysis Collaboration project—which is composed of individuals from across ORNL. The collaboration between neutron sciences and supercomputing, two of ORNL's most high-powered research centers, has created a new data infrastructure that will enhance users' ability to reduce and analyze data as they are taken; create data files instantly after acquisition, regardless of size; reduce a data set in seconds after acquisition; and provide the resources for any user to do post-acquisition reduction, analysis, visualization, and modeling—not just on site—but literally from anywhere.

Mission Relevance

The capabilities we have developed will remove significant bottlenecks for SNS users and thereby greatly enhance the scientific productivity from SNS experiments in materials science, sustainable energy, and basic science. These capabilities enable a range of new technologies to be developed that can further enhance both the experimental capabilities of the SNS and also to allow for much greater integration with computational data analysis and visualization techniques. In integrating computation and neutron science, this work is of direct benefit to the BES and the Advanced Scientific Computing Research programs of the DOE Office of Science. Our work on ADARA has helped position ADARA, which helped facilitate ORNL's success in our funded proposal: "Center for Accelerating Materials Modeling from SNS Data" – $1M award from BES in FY 2013.

Results and Accomplishments

The ADARA project began in FY 2012, and in a remarkably short time the full system was architected, developed, and deployed in prototype form on the HYSPEC beam line at SNS. On August 29, 2012, the ADARA system was demonstated to BES reviewers live on HYSPEC with many positive comments by reviewers. ADARA is currently running on HYSPEC, providing near real-time access to result datasets (both raw event data and reduced data). Instrument scientists and users at HYSPEC can now obtain live feedback from their experiments. In FY 2013, ADARA will be deployed in production across a number of beam lines at SNS as the capabilities developed within ADARA are adopted by the SNS facility.

ADARA has provided a streaming data backplane, allowing scientists to go from experiment to data reduction to obtaining an energy spectrum or diffraction pattern nearly instantaneously, while the experiment is still running. Rather than the current approach of saving data in "buckets" and, once the bucket is full, handing the bucket off to the next process, ADARA uses a streaming approach. As data are being captured, translation is done concurrently. Every single event coming off a detector is translated live to a common data format. While doing translation, ADARA also does live data reduction, so as neutron events are coming off the detectors, that same data is reduced live into an energy spectrum or diffraction pattern. To accomplish this, the ADARA architecture leverages many of the techniques that are commonly used in HPC, as well as some of the techniques from more traditional, distributed computing.

The fundamental architecture for the streaming data system is built upon a high-performance publish/subscribe system. This system collects information from multiple feeds: from the neutron detectors, the experiment environment, such as temperature within the sample environment, and orientation of the sample. All of these data are "published" to the Stream Management Service, which then aggregates the data into a single, common network stream that can be sent to one or more downstream "subscribers." One of the downstream subscribers that has been developed has been dubbed the Streaming Translation Service, which translates the unified neutron event stream on the fly and creates NeXus files live, as the experiment is conducted. The instant an experiment is over, the full NeXus file is created. It does not matter if it is a terabyte. It does not matter if it is just a few megabytes. Another downstream subscriber that has been developed, known as the Streaming Reduction Service, which leverages the MANTID system, transforms the neutron event stream live from simple detector position and time of flight to an energy spectrum or diffraction pattern in real time. This provides scientists at SNS with real-time feedback from their experiment coupled with the Mantid reduction and analysis platform.

Although much of the work has focused on providing real-time feedback from an experiment, certain tasks in the data processing chain can be conducted only after the experiment is completed. To support this, the ADARA project has developed an automated workflow engine based on the Apache Active Message Queue system for post-stream processing. This workflow engine allows for coupling of an arbitrary number of tasks to the completion of an experiment, such as cataloging of the experiment data, additional data reduction and analysis, and archiving of the experiment data to our multi-petabyte archival storage system at the National Center for Computational Sciences. Once cataloged, these data are available for subsequent reanalysis and intercomparison with previous experiments. This post-processing step can be highly interactive in which users interact with their data through the Mantid software package or through other analysis tools and custom applications.

Information Shared

G. Shipman, "Accelerating Data Acquisition, Reduction and Analysis at the SNS," talk at a workshop organized by SNS and ESS, June 28–30, 2012.

M. Hagen, "Data Analysis at the Spallation Neutron Source," seminar at the European Spallation Neutron Source, Lund, Sweden, May 3, 2012.

D. Dillow, "ADARA – The Stream Management Service," talk at a workshop organized by SNS and ESS, June 28–30, 2012.

J. Kohl, "ADARA – The Streaming Translation Service," talk at a workshop organized by SNS and ESS, June 28–30, 2012.

S. Campbell, "ADARA – The Streaming Reduction Service," talk at a workshop organized by SNS and ESS, June 28–30, 2012.

G. Shipman, "Integration of Experiment and Simulation at DOE Facilities," talk at ASCR Networking Requirements Workshop, October 4, 2012.

M. Hagen, "Data Analysis at the Spallation Neutron Source," seminar at Niels Bohr Institute, Copenhagen, Denmark, May 4, 2012.

M. Doucet, "The Mantid Project for Data Reduction and Analysis," invited talk at the American Conference on Neutron Scattering, Georgetown University, June 27, 2012.

M. Hagen, "Accelerating Neutron Data Analysis," talk at a workshop organized by SNS and ESS, June 28–30, 2012.

M. Hagen, "The Center for Accelerating Materials Modeling at the SNS," Nanoporous Materials Genome Center Kick-off Meeting, University of Minnesota- Minneapolis, November 17–18, 2012.

S.X. Ren, P.F. Peterson, A. Huq, A.T. Savici, and M. Douce, "Automated data processing using Mantid at the SNS," poster at the NOBUGS Workshop, Rutherford Appleton Laboratory, Rutherford, England, September 2012.

R. Miller, "Using Moab Web Services to Provide a Simple Interface to a Compute Cluster," presentation at MoabCon, April 9–12, 2012.

S.I. Campbell, N. Draper, J.L. Zikovsky, R.J. Taylor, R. Miller, "Streaming and processing of data in real time," poster at the NOBUGS Workshop, Rutherford Appleton Laboratory, Rutherford, England, September 2012.

J.C. Bilheux, J.M. Borreguerro, S.I. Campbell, M. Doucet, V.E. Lynch, D.H. Mikkelson, R.L. Mikkelson, P.F. Peterson, S.X. Ren, M.A. Reuter, A.T. Savici, R.J. Taylor, W. Zhou, and J.L. Zikovsky, "Mantid data reduction and visualization at SNS and HFIR," poster at the NOBUGS Workshop, Rutherford Appleton Laboratory, Rutherford, England, September 2012.

06353
Secondary Coordination Sphere Effects in Catalyst Design

D.A. Lutterman

Project Description

There is interest in utilizing waste CO_2 for the production of fuels, but there are serious scientific challenges that need to be overcome including the large catalytic overpotentials or potentials in excess of the thermodynamic potential for CO_2 reduction and control over product selectivity. The goal of this proposal is to design and construct modified interfaces which use ligands in the secondary coordination environment to assist in catalysis and lower the overpotential for CO_2 reduction. Reduction of CO_2 to CO and H_2O is a complex reaction involving not only CO_2 and reductants but also protons. Investigations in water, where the proton deliver system is the solvent and protons are in a large excess, will provide pseudo-bimolecular reaction conditions. This will allow us to not only simplify this complex problem but also allows flexibility in controlling the system in a very modular way, such as independent regulation of the catalyst and substrate concentrations, buffer character, and solution pH. From these guiding principles, can we then develop simple architectures that can lower the catalytic overpotential in the absence of water where there is not an overwhelming supply of protons? Such a system would better match the environmental demands on catalysis in CO_2 waste streams and facilitate lower overpotentials via the constructed architecture to deliver protons efficiently. Successful completion of these goals will provide the foundation for new catalyst designs for the efficient reduction of CO_2 into more useful commodities.

Mission Relevance

The development of novel spectroscopic techniques and structural probes for in situ characterization of catalytic processes such that phenomenological catalysis can evolve into predictive catalysis has been identified as an area of interest by the Catalysis Science research area in the Basic Energy Science (BES) program of the Department of Energy. As such, it is expected that successful pursuit of the research described above will be highly desirable for future funding by this research area in the BES program. Also the office of Energy Efficiency and Renewable Energy (EERE) invests in clean energy technologies that strengthen the economy, protect the environment, and reduce dependence on foreign oil. Furthermore, $42 million in the President's budget is designated for "developing the next generation of materials, chemicals, and game-changing processes" for clean energy through "the nanoscale and to the mesoscale." This was highlighted in Harriet Kung's recent presentation on Feburary 23, 2012, th the Basic Energy Sciences Advisory Committee (BESAC). The BES says this will be the next major call, and this LDRD will prepare us for a submission when the call comes out.

Results and Accomplishments

A long-term goal of this project is to graft these types of catalysts onto structured electrodes because of the steady supply of electrons required by catalysts capable of reducing CO_2. The chosen rhenium-based catalysts are useful in that they can be activated both electrochemically and photochemically. Thus, in the nonconductive environment of the mesoporous silicas, these catalysts can still be activated in the presence of a sacrificial electron donor to probe the environmental effects of confinement. These catalysts were grafted onto the interior surface of mesoporous silicas via copper-catalyzed azide alkyne cycloaddition. The information gained from these studies on mesoporous silica (SBA-15) can then be used in soft-templated mesoporous carbons that have been synthesized with the same precursors. I have been working with Sheng Dai and members in the Nanomaterials Chemistry Group on designing techniques that will translate well between the mesoporous silicas and carbons.

While samples are being prepared, a parallel effort is being put forth in setting up and installing instrumentation for both steady state and transient characterization. Initial characterization of these materials will be to determine the steady state catalytic conversion of CO_2 to CO. To accomplish this, a photolysis system was set up in A202 of Building 4100. Here a 1000W Xe arc lamp is focused into a monochromator to produce small bandpass ranges to irradiate samples. Initial samples are being irradiated in solution under 1 atm CO_2, and conversion will be monitored via gas chromatography–mass spectrometry (GC-MS) and in real time with a Dwyer DW-USB-5 Data logger in a home-built system. Sample stability has been monitored by the new 8453 UV/vis spectrometer (Agilent Technologies) and Fluorocube (Jobin Yvon) fluorimeter also set up in this lab space. In addition, to characterize the homogeneous samples electrochemically in the steady state and transiently, a 760D bipotentiostat was purchased from CHInstruments and installed.

Lastly, in addition to the internal ORNL collaborations that are developing both in the Chemical Sciences Division and at the SNS mentioned above, it should be pointed out that external collaborations with scientist of similar interests are also being made. A collaboration with Professor Joel Rosenthal's research group of the University of Delaware has been forged because of his parallel interest in CO_2 reduction and talents as a synthetic inorganic chemist. His research group has synthesized a series of rhenium-based catalysts capable of CO_2 reduction with tethered photosensitizers enhancing the visible-light-absorbing ability of these complexes. The similar goals and complementary skills of this research group to my own will enhance productivity towards the end goal.

Information Shared

D.A. Lutterman, M.K. Kidder, J.M. Teesdale, Y. Ma, and J. Rosenthal, "New Rhenium-based Constructs for CO_2 Reduction Catalysis," Gordon Research Conference on Electron Donor-Acceptor Interactions, Newport, RI, August 5–10, 2012.

06576

Emergent Quasi-Particles and Their Detection through Neutron Scattering

C.L. Broholm

Project Description

A consequence of symmetry breaking, phonons and spin waves were established as the quintessential quasi-particles of condensed matter physics in seminal neutron scattering experiments on the first generation of sources and instruments.

It now appears correlated states of matter that break no symmetry also can support quasi-particles – distinguishable as topological defects. "Spinons" in one-dimensional spin chains are a case in point, but recent theory brings a rich variety of emergent quasi-particles into view. Relevant models include corner-linked tetrahedra with quantum spins and quasi-two-dimensional magnets near criticality. The novel instrumentation at the Spallation Neutron Source (SNS) and the High Flux Isotope Reactor (HFIR) offers an opportunity to profoundly advance this research. By linking a vigorous program of materials discovery and synthesis at the Institute for Quantum Matter with the SNS and HFIR, this project shall expose and characterize emergent quasi-particles in strongly correlated condensed matter. The research project will leverage a multifaceted program contributing to an enhanced scientific profile for the SNS.

Mission Relevance

Understanding and controlling materials with a very broad range of properties is central to the DOE mission. While most electronic materials used in the energy and information technology sectors at this time can be understood within the conventional framework of symmetry breaking and linear response, an exciting new class of materials beyond this framework is emerging. These strongly correlated dynamic states of matter offer new forms of magnetism and charge transport, and they exhibit chemical sensitivity rivaling semiconductors. Applications for information storage and processing are foreseen, and because superconductivity can result from strong electronic correlations, energy conversion, storage, and transport can also benefit from this research.

By developing new ways to probe hard condensed matter through scattering, this project advances the technique and the science. By funding a postdoc and a student located at ORNL, the project contributes to development of critical human resources.

Results and Accomplishments

In collaboration with Takeshi Egami, Meiyun Chang-Smith, Stephen Nagler, and others, Collin Broholm has developed and taught a graduate course on the use of neutron scattering in hard condensed-matter physics. The course is co-taught by six professors (Collin Broholm, Johns Hopkins University; Takeshi Egami, UTK; Stephen Nagler, UTK; Roger Pynn, Indiana University; Seunghun Lee, University of Virginia; and Young Lee, MIT). Lectures covering the full range of the subject matter have been given online and remain accessible in an archived format to registrants. Neutron scattering experiments have been conducted on materials with a potential to display emergent magnetic phenomena. These include a material that may realize magnetic monopoles with quantum spin dynamics. The Angular-Ranger Chopper Spectrometer (ARCS) the SNS played an important role in establishing the model for the individual rare-earth magnetic moments. A paper on this work is in review at *Nature Communications*. Invited talks highlighting this work were given at the 2012 international conference on highly frustrated magnetism at McMaster University in Canada and at the international workshop on frustrated magnetism and quantum spin liquids at the Kavli Institute for Theoretical Physics at UCSB. Powder diffraction experiments were conducted on the POWGEN instrument to solve the magnetic structure of a novel low-dimensional magnetic material related to iron superconductors. The corresponding paper, now in review at *Physics Review B*, showcases to the physics community how the excellent resolution of that instrument can contribute to resolving complex magnetic structures. A comprehensive search identified an outstanding postdoc, Dr. Jon Leiner. He recently graduated from the University of Notre Dame and will start on this project in February 2013.

06581

High-Throughput, Energy-Efficient System for Obtaining Highly Textured, Large-Crystal Materials

B.M. Evans III, O. Rios, R. Kisner, C. Parish, N. Kulkarni, G. Ludtka, and B. Radhakrishnan

Project Description

A recent breakthrough by ORNL researchers discovered that high magnetic fields allow the rapid production of a steel alloy with a highly oriented grain structure. This processing approach allows the rapid growth of large crystals and/or near-perfect texturing between crystals. Typically, single-crystal materials are grown at very slow solidification rates by applying specific thermal gradients which require high energy demands. We have demonstrated the ability to produce large single crystals at cooling rates ranging from 30–400°C/min. This technique allows the unique properties of single-crystal materials to be applied to a much broader range of applications than ever before, and has major implications on energy consumption, throughput, and material properties. This method will revolutionize the properties of structural materials and drastically improve production techniques for functional materials including semiconductors. In this project, we will examine a method and apparatus to produce structural materials for high-temperature automotive and aerospace applications by investigating nickel-based superalloys. This phenomenon will be further examined by adapting existing Monte Carlo and phase-field solidification codes to predict the solidification structures produced by high-magnetic-field solidification and solution heat treatment. ***The ability to rapidly produce single-crystal materials using energy-efficient, scalable technology will be transformational to material science and manufacturing. ORNL has the opportunity to lead this extraordinary field.***

Mission Relevance

Magnetic material processing techniques have been shown to reduce the time and temperature required for heat treating materials, resulting in substantial energy savings. The proposed methods have the added benefit of greater control of phase diagram location, which will allow higher operating temperatures for nickel-based superalloys. Higher operating temperatures translate to increased turbine energy efficiency and lower emissions for aerospace and power-generating turbine engines. Therefore the goals of this project are aligned with the Department of Energy's mission to increase energy efficiency in the United States and with the interests of the Fossil Energy Program.

Results and Accomplishments

This is an off-cycle LDRD that began in Aprilof 2012. Since the project beginning, we have installed the 9 Telsa, 5 in. bore vertical magnet in Building 5500, which will be primarily used for this project. All electric and cooling facilities have been installed on this system, and the cryostat has been evacuated to high vacuum. The manufacturer has been scheduled to complete the final step of filing the cryostat with liquid helium and commission the superconducting magnet system in October of 2012.

Previous magnetic processing research at ORNL has primarily been performed on horizontal bore magnets and has been limited to thermal/magnetic treatment of solid materials. We have designed a system capable heating nickel-aluminum alloys beyond the melting point (1500°C) inside the vertical bore magnet, and all components have been fabricated and assembled. The apparatus contains an inductive heating system, inert atmosphere, sample crucible holder, and cooling capability for components whose melting point is under 1500°C.

A system for Differential Scanning Calorimetry (DSC) under high magnetic field was designed in conjunction with the melt processing system and is currently in fabrication. The ability to examine changes in structural transition temperatures will allow the research team to characterize changes in the phase diagram that occur under high magnetic field and develop fundamental understanding of the effects of thermal processing under high magnetic field. An experimental matrix has been specified and materials have been ordered and received for the experiments. We will begin casting materials in November of 2012.

Information Shared

Two invention disclosures (IDs 2716 and 2731) have been submitted to technology transfer regarding this research. These have been elected and forwarded to patent attorneys for filing.

06584

Elucidating and Developing Spillover Catalysis: A New Paradigm for Predictive Catalysis

A. Savara

Project Description

Spillover is the phenomenon of adsorbed molecules migrating from one solid surface to an adjacent solid surface. The goal of this project is to measure spillover kinetics between catalytically relevant surfaces and to unravel the factors that govern spillover. Such measurements will lead to improved models for catalyst kinetics and new generations of catalysts by design. An existing ultra-high-vacuum apparatus is being modified in order to conduct spatially defined measurements (millimeter scale) by mass spectrometry and infrared spectrometry. An effusive molecular beam is being added to enable quantitative molecular gas flux exposures with millimeter-scale precision. Kinetic data will be obtained for spillover processes, and activation energies and pre-exponential factors will be extracted for spillover between catalytically relevant materials. Concurrently, theoretical derivations and computer simulations will be performed to predict the activity of molecules in spillover, particularly with regards to the influence of the configurational energy terms. From systematic measurements, fundamental insights regarding spillover and catalysis kinetics will be gained, enabling a priori predictions for spillover, and catalysis by design. The systems studied will include single-crystal surfaces but may include complex materials such as supported particles and molecular organic frameworks. In the long run, better microkinetic models and new types of catalysts will be developed from this work.

Mission Relevance

More accurate microkinetics for catalytic processes is one current goal for DOE Basic Energy Sciences. This research is in line with that goal and presents a new paradigm in the design of heterogeneous catalysts. Spillover processes play a role in environmental processes and energy production processes. Studying spillover will benefit the Basic Energy Sciences mission of DOE by enabling the rational design of new kinds of catalysts for energy applications (i.e., using CO_2 as a feedstock for renewable fuels) and may also provide insights into methods for optimizing more conventional and emerging catalysts (e.g., for catalytic degradation of lignin).

Results and Accomplishments

The design and physical construction of the new instrument has been completed. The most crucial aspect of this equipment modification is that accurate and precise spatial exposures are required to show unambiguously that the reactant was introduced solely to the first surface and detected on the second surface. The next step towards spillover measurements will be writing a custom Labview code to run the instrument, and then studying real systems.

During delays in the manufacture and installation of pieces of equipment, extra focus was put onto the theory side of the project. As a result, more progress was made on the theory side than expected during FY 2012. A specialized kinetic Monte Carlo simulation software package called "kmos" was successfully installed, and a custom simulation code has been written to run within the kmos framework. The first test simulations of spillover suggest that configurational entropy promotes spillover more strongly than expected. Getting this software operational was an important achievement for the present study and will have great benefits in the long run not only for this project but for other catalysis projects in the future. Several theoretical papers regarding the entropy and enthalpy of adsorption have been written and are currently undergoing internal review prior to submission to scientific journals.

Information Shared

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GLOBAL SECURITY SCIENCE AND TECHNOLOGY

05487

Biological Signature Identification and Threat Evaluation System (BioSITES)

R.W. Cottingham

Project Description

The United States has a well-established and accomplished multiagency process dedicated to nuclear forensics; there is no parallel process for biological forensics, underpinned by state-of the-art science. BioWatch, the current standard in deployed biothreat detection, cannot detect genetically engineered threats. There is a pressing need for a new system leveraging recent scientific advances to improve threat detection. A new system called BioSITES was developed that prototypes integration of systems biology knowledge repositories with new data collection technologies such as high-throughput sequencing. This approach enables the construction of better detectors and provides a basis for mitigation, response, protection, and forensics and therefore a path for future development of BioSITES and biodefense.

Newly funded initiatives are establishing ORNL as a leader in knowledgebase development for systems biology research. Further, ORNL projects such as the BioEnergy Science Center were awarded in recognition of the resident expertise in systems biology research and management of such large-scale biological projects. This project leverages these core competencies toward the development of a new kind of biodefense system required to respond to upcoming threats of the 21st century. The BioSITES prototype demonstrates capabilities that go beyond current deployed systems.

Mission Relevance

This research supports the mission of the laboratory in enhancing national security by developing methodology to be applied for biosurveillance in defense of our military and civilian populations.

Results and Accomplishments

The techniques of Scenario Driven Development (SDD) and Scenario Driven Data Modeling (SDDM) were developed for this project and provide the capability rapidly and accurately develop the software system components and methods for integrating diverse sources of data and data streams in ways that support the real-time performance and system scaling for a biodefense application. An Ontology for Scenarios was prototyped to demonstrate linking concepts across ontologies leveraging the power of existing ontologies. These capabilities are highlighted in the SDDM process published in *BMC Bioinformatics*. As a result of all of these developments, BioSITES is capable of implementing any scenario that involves screening biological sequence and relevant data, geographic location, and time.

A scenario was developed based on the recent naturally occurring threat of the NDM-1 gene. NDM-1 confers resistance to multiple antibiotics. SDDM was used to fully refine this scenario into a Semantic Knowledgebase representing NDM-1 as a public health threat. As part of the development of this scenario, sensors were created that look for the NDM-1 gene in a stream of sequence data, and a new kind of detector was developed for streaming ProMED articles that extracts content from representative ProMED articles describing NDM-1 that are preprocessed into a semantic representation. This exercise demonstrates how BioSITES could be rapidly configured and performs detection of a real-world threat.

Information Shared

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05599

Portable Water Reclamation from Diesel Exhaust by Inorganic Membranes

M.M. DeBusk, J. Klett, B.L. Bischoff, C.S. Daw

Project Description

The goal of our project is to develop and demonstrate enabling technologies for a small footprint, high-efficiency water-reclamation system. At present, water generated during fuel combustion, at a rate of 1 gallon per gallon of fuel consumed in vehicle engines or stationary generators, is discharged with exhaust. Water recovered from exhaust will help alleviate the military's logistical problem associated with water management in combat and national/global disaster areas. Fifty percent of the military's logistical burden is related to delivering water (predominately bottled water) to forward locations, increasing troop vulnerability and limiting tactical use, making it the Department of Defense (DoD) #2 priority for logistics solutions.

The primary enabling technology for our water-reclamation system is based on inorganic membranes and facilitates increased potable water recovery, while requiring less energy and space than conventional condensation recovery methods. We plan to maximize both the overall system energy efficiency and the level of water recovery from vehicle/generator exhaust by tailoring and improving the properties of inorganic membranes (pore size, flux) and integrating the membrane with a small, lightweight advance cooling system.

Mission Relevance

This project aims to develop and demonstrate enabling technologies for a small-footprint, high-efficiency inorganic-membrane-based water-reclamation system that can be used in diesel/JP8 engine exhaust applications. A device capable of reclaiming potable water at the point-of-use from currently wasted water vapor in engine exhaust will advance both our national and energy security. Producing water from available sources, such as diesel exhaust, will reduce the burdens associated with water transport in combat zones and is DoD's #2 priority for logistics solutions. Reducing the logistical burden will also reduce the military's current energy consumption associated with bottled water transport. The successful demonstration of this membrane reclamation system's potential will position us to request funds from the Army, Marine Corp., and other active branches of DoD for full-scale demonstration and testing.

Results and Accomplishments

In the first year of the project, lab-scale water recovery tests were performed to study how various system parameters affect the water recovery efficiency of a single-membrane water recovery system. The water reclamation efficiencies of four membranes with different median pore sizes were evaluated as a function of flow rate, membrane temperature control, inlet gas temperature, and feed-gas water-vapor content. Efficiency decreased as flow rate or water jacket set point increased. Little efficiency change was observed as a function of inlet temperature when the water jacket set point was held constant. As theory predicts, greater efficiency was obtained as the concentration of water vapor increased. The results of the first year created the following set of baseline test conditions to be used for testing on a stationary generator (GenSet) in year 2 of the project: 8.2nm membrane, 250°C inlet temperature, 2 L/min exhaust flow, 25°C water jacket, chiller set-point, ~150 torr water displacement vacuum.

In the second year of the project, the same 8.2 nm membrane tested in year 1 was tested on a slip-stream of a GenSet exhaust treated upstream by an OEM DOC and catalyzed-diesel particulate filter (DPF) under the baseline condition set forth in year 1. Exhaust from both diesel (ULSD) and JP8 fuels were evaluated, and reproducible water recovery efficiencies for each type of exhaust were obtained, 50.7±0.14% and 55.3±0.71%, respectively, and in good agreement with the comparable lab-scale efficiency of 59.11%. CFD modeling results suggest that increasing the membrane length will help reach upper limits for exhaust/membrane contact time, allowing maximum efficiency at higher flow rates. Water quality testing was impeded by contamination caused by new treatment to graphite foam used for heat transfer. However, results show lower water acidity was achieved as a result of the membrane-based water recovery system and that no trace fuel components were seen in the reclaimed water.

Information Shared

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M. Moses-DeBusk, B. Bischoff, J. Klett, J. Hunter, and D. Adcock, "Water Separation from Gas Streams Using Inorganic Membranes," American Chemical Society National Conference, Anaheim, California, 2011.

05623

Functionally Graded and Geometrically Ordered Titanium Composite Armor Materials

S.D. Nunn, R.R. Dehoff, S. Simunovic

Project Description

Titanium and its alloys have many superior characteristics which make them desirable for use in defense systems. Among these are high strength, light weight, and corrosion resistance. Ti-6Al-4V provides more efficient ballistic protection than conventional steel armor, but it is far less efficient than state-of-the-art ceramic armor. The ceramics exhibit high compressive strength, very high hardness, and light weight. The increased availability of recently developed low-cost titanium powders to fabricate structural components using solid state powder metallurgy processing technology provides an unprecedented opportunity to engineer advanced composite armor structures which combine titanium and ceramic materials. This project will investigate two types of composites: (1) Functionally Graded Composites, which consist of two or more blended phases where the ratios can be continuously graded or locally varied and (2) Layered Hybrid Composites, which consist of discrete regions or strata of different materials. Throughout the project, computer modeling will be used to assist in the design of composite structures, choice of materials, and prediction of ballistic performance.

The goal of this project is to design, fabricate, model, and test new composites of titanium and ceramics having unique properties and performance capabilities for use in critical defense applications. Demonstration of titanium-based composite materials with improved protective properties would generate immediate interest for further development and utilization of these materials over a broad range of land, air, and naval systems.

Mission Relevance

This project supports DOE's mission to develop new materials and new material processing methods that will benefit US government agencies in accomplishing their goals related to national security, energy conservation, and US competitiveness. The development of advanced titanium composite materials will enhance the performance of ballistic armor for both military and homeland security applications. Simultaneously, it has the potential to substantially reduce the weight of vehicles and systems, which will result in significant fuel savings. The processing methods being proposed utilize low-cost titanium materials and eliminate most of the manufacturing waste (often greater than 90%) that is typically associated with conventional processing, thus conserving a critical resource.

Variations of the technology that focus on reduction in wear, friction, and galling between mating components will result in lower energy requirements, reduced maintenance, and conservation of vital raw materials in both government and civilian applications. The project benefits a broad spectrum of programs for the Department of Defense (DoD) and The Department of Homeland Security (DHS), and supports the Department of Energy's Energy Efficiency and Renewable Energy (EERE) program.

Results and Accomplishments

Functionally graded titanium composite armor tiles were formed by incorporating a ceramic compound in a titanium matrix. Two ceramics were found to work well for forming the composite: titanium diboride (TiB_2) and boron carbide (B_4C). When powder blends of Ti-6Al-4V (Ti64) alloy and one of these ceramics were compacted and heated, the ceramic reacted with the titanium to produce TiB, in the case of TiB_2 additions, or TiB + TiC, in the case of B_4C additions. In either case, the resulting Ti/ceramic composite exhibited modified properties when compared to Ti64. The extent to which the properties were changed depended on the ratio of the metal and ceramic powders. Properties such as the elastic modulus, hardness, and acoustic velocity could be varied over a wide range of values by adjusting the composite composition. Graded armor tiles were formed by varying the amount of ceramic through the thickness of the tile. In ballistic tests, the graded armor tiles were shown to have improved penetration resistance. The ballistic mass efficiency was increased by as much as 28% when compared to conventional Ti64 armor plates.

The same Ti/ceramic composite blends were used to form layered hybrid composite armor structures. Rather than using simple parallel layers having planar interfaces, direct manufacturing methods were utilized as part of a fabrication process to produce layered structures with controlled, complex geometric interfaces. Ti64 components were produced directly from a CAD file drawing using electron beam fusion of metal powder. Then, a predetermined quantity of the Ti/ceramic composite powder was sandwiched between the Ti64 components in a die and consolidated in a hot press using heat and pressure to form a layered hybrid composite armor tile. The complex interfaces of the hybrid composite operate on two levels to defeat a ballistic projectile: mechanically and acoustically. Mechanically, the geometry of the interfaces can act to alter the path of a penetrator. Acoustically, the impedance mismatch between the materials, combined with the complex geometry of the interfaces, can interact with stress waves and alter the wave propagation through the tile. The ballistic mass efficiency of the layered hybrid composites was increased by up to 31% when compared to conventional Ti64 armor plates.

Computational simulations were used to investigate and evaluate the performance of new armor configurations that can be produced using advanced manufacturing techniques, such as additive manufacturing. These new manufacturing methods can be used to develop new projectile defeating mechanisms that are difficult or impossible to produce by conventional manufacturing methods. With direct manufacturing, the number of possibilities and the design space is enormous, so that it is more efficient for the armor designer to evaluate different concepts and materials using computational simulations, rather than using prototypes and tests. We used three-dimensional FEM models and high-velocity projectile penetration simulations to explore new armor configurations. The same CAD models that were used in the additive manufacturing process were also used to develop the FEM models for the armor. A detailed model for an armor-piercing bullet was developed and used as a penetrator at different impact locations relative to the geometric design. The simulations indicate that complex geometrical features produced by using additive manufacturing can significantly improve the armor's resistance to ballistic penetration. This was confirmed in the ballistic tests. Results from the project can be viewed at the project's web site: http://thyme.ornl.gov/Armor.

05698

Quantum Lightwave Circuits

P.G. Evans, R.S. Bennink, D.D. Earl, W.P. Grice, T.S. Humble, R.C. Pooser

Project Description

Quantum Information Science (QIS) is an innovative and enormously promising new field comprising the creation, storage, manipulation, secure transfer, and use of information encoded in the quantum states of particles or light. Applications of QIS relevant to global security include secure communications, quantum sensing, and quantum computing. Of the many physical implementations of QIS, the photonic approach is the most mature, yet deployment of photonic QIS systems outside of the laboratory has been hampered by scaling, power requirements, and stability issues. We propose development of integrated quantum lightwave circuits to advance the capabilities, and accelerate the transfer, of this nascent technology from research to the applications domain. Our approach will take advantage of new techniques for fabricating polarization-manipulating and phase-modulating circuit elements on silicon-on-insulator (SOI) waveguide platforms. Our goal is to demonstrate dynamic, multi-photon integrated quantum lightwave circuits that outperform their bulky and delicate lab brethren in terms of size, stability, and tunability. In addition, the ability to integrate quantum lightwave circuitry with ORNL's existing telecom-band multi-photon entangled sources will provide ORNL with a unique capability that highlights excellent fundamental science-to-global security applications in a highly flexible, reproducible, and affordable package.

Mission Relevance

Quantum information science (QIS) will continue to shape the global security landscape in the next decade. Global security areas that benefit under QIS development include completely secure communications; quantum sensing for nuclear safeguards and nonproliferation; and quantum computing for advanced materials simulation and support to our intelligence community.

To date, QIS proof-of-principle demonstrations have mostly been lab based, in which bulk optical equipment is precisely aligned on large tables in environmentally stable laboratories. This approach does not lend itself favorably to being deployed on a naval vessel, on a surveillance satellite, in a soldier's backpack, or even on a computer user's desk. Advances in technology and engineering are required to take QIS out of the lab and bridge it to real-life global security problems. We propose the quantum lightwave circuit – a quantum optical equivalent to the electronic integrated circuit – as an enabling technology to fill this need.

The DOE is likely to benefit both directly through the NA-22 program with quantum sensors and indirectly through Work for Others programs with the Defense Advanced Research Projects Agency (DARPA), the Department of Homeland Security (DHS), the Army Research Office (ARO), and the intelligence community.

Results and Accomplishments

All basic optical circuit elements have been designed and modeled and exceed initial performance metrics. A user proposal to fabricate QLCs at the Center for Nanophase Materials Sciences (CNMS) nanofabrication facility was granted with positive external reviewer comments.

Fabrication of various QLCs at the CNMS has been successful and is currently ongoing under the existing CNMS user proposal. Prior to the QLC project, ORNL had no silicon photonics fabrication capability, but now we have developed a robust silicon photonics capability at ORNL with the existing tools at the CNMS. Fabrication of QLC elements has proved challenging and required novel processes to be developed. For example, the dielectric outer-core structures crucial to the functionality of the fiber-waveguide couplers and polarization rotating elements have been realized by electron beam lithography of SU-8 polymer.

Complex integrated optical circuits have been designed, fabricated, and tested using the individual elements mentioned above. We have developed circuits for 2- and 4-photon polarization entangling devices – where bi-photons generated externally from a non-linear optical process are entangled on-chip before being output. We have also attracted external funding from the DARPA InPho program to design, develop, and characterize a novel optical communications circuit referred to as a "Green Machine" in collaboration with Raytheon-BBN Technologies and MIT.

We have developed methodologies and design tools to ensure circuit designs are path-matched, that is, that the propagation delay experienced by photons traveling in different paths along a complex circuit are made equal. We have developed a way of implementing a so-called anti-symmetric beam-splitter – crucial to many quantum photonic information protocols – using built-in phase shifting elements. We have also begun developing a process that will allow a highly efficient optical non-linear material – potassium titanyl phosphate (KTP) – to be integrated within the silicon photonics platform. If successful, this would allow direct generation of bi-photons on-chip, together with other applications arising from a strong second-order non-linearity such as second harmonic generation, sum-frequency generation, and optical squeezing.

We are currently in the process of filing intellectual property rights on all designs and processes developed throughout this work. Other opportunities have arisen with such potential future collaborations as the National Institute of Standards and Technology (NIST), Vanderbilt University, and several commercial companies.

Our long-term goal for the quantum lightwave circuits platform is that of a fully integrated, compact, and scalable source of single- and entangled-photon states for a variety of quantum information applications.

Thanks to the LDRD funding of this project, we have developed the necessary foundations for this nascent technology to be carried forth at ORNL.

Information Shared

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05770

Quantum Imaging by Compressive Sampling for Enhanced Surveillance and Real-Time Monitoring

R. Pooser, P. Evans, W. Grice, T. Humble, D.D. Earl, R. Bennink

Project Description

Quantum imaging, which involves manipulation of images stored in quantum mechanical systems, is a rapidly growing field that promises increases in the information capacity of images. This increase in information capacity yields improvement in image resolution and information content that is expected to subsequently impact the performance of many imaging applications. Remote sensing, pattern recognition, position measurements, image amplification, and surveillance are a few specific applications that can benefit from quantum imaging methods. Current efforts in quantum imaging require expensive CCD cameras, however, and they are based on designs limited to detecting very low light levels. We propose a method of quantum imaging whereby the CCD camera is replaced with a more economical compressive measurement apparatus. The proposed method allows for more efficient detectors to acquire the images and reduces overall integration time. This fundamental speed-up in quantum imaging acquisition time would enable applications of "quantum monitoring" or "quantum surveillance," where changing quantum images are monitored in real time. We propose to develop and demonstrate a system that is capable of producing and measuring real-time changes in quantum images by using multiple-spatial-mode quantum optics alongside compressive sampling. This will enable the development of new quantum imaging applications. This proposal leverages existing ORNL expertise to design and demonstrate the first real-time quantum imaging device.

Mission Relevance

Quantum information science is part of ORNL's cyber security program, and thus the project supports ORNL's and DOE's broader mission of information security. While most of the research proposed here is fundamental science, it will lead to a new capability at ORNL: "compressive quantum imaging." The Defense Advanced Research Projects Agency (DARPA) has shown interest in compressive sampling due to the potential to increase the speed of communications in both classical and quantum contexts, specifically citing quantum imaging in the BAA for its "InPho" program. The results of this program have also attracted attention from the Special Cyber Operations Research and Engineering (SCORE) Committee, which coordinates cyber security research among government agencies. Follow-on seed funding was secured for application of compressive imaging to microchip characterization, which is important for malware and counterfeit detection. A follow-up to this seed funding is currently in review with the committee.

Results and Accomplishments

We achieved all of the project milestones (we expect to have a demonstration of real-time imaging published in one month). We have designed and built a nonlinear optics system based on four wave mixing in rubidium. We observe 6.0 decibels (dB) of quantum noise reduction (~10 dB inferred), making it state of the art. Using our spatial light modulator (SLM) imaging apparatus we can imprint images onto our probe beam for use in image amplification and quantum imaging. We have measured quantum noise reduction in an array of images of almost arbitrary type, and we have demonstrated the ability to control the input spatial modes and measure quantum noise reduction on changing images in real time. Our detectors also successfully run compressive imaging algorithms. We use two digital mirror display devices which we can control via software and perform differential compressive imaging (a first for macroscopic quantum light sources) to characterize the twin image carrying beams. We have adopted the gradient projection and total variation minimization approaches for reconstruction. We developed a new sampling matrix for compressive algorithms, inspired by the use of sparse matrices in a publication on image reconstruction, for use in compressive quantum imaging and compressive beam profiling. We have also successfully used this sampling matrix to image chip-scale structures produced at ORNL's Center for Nanophase Materials Sciences (CNMS). This project resulted in an invention disclosure on the subject of fast beam profiling of extremely low light levels (single photons) using specialized sampling matrices (subsequent patent application is under construction). This project resulted in follow-on funding from the SCORE committee on cyber security. A report on the results of that funding was submitted to the committee in support of additional follow-on funding for a chip-scale imaging program.

Information Shared

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05986

A Scalable Framework for Timely Discovery and Situational Understanding of Cyber Attacks

J.R. Goodall and E.M. Ferragut

Project Description

Rapidly discovering novel and sophisticated cyber attacks from masses of heterogeneous data and providing situational understanding to analysts are ongoing problems in cyber defense. We will meet the challenges of knowledge discovery and extraction from security events in large data sets through the integration of anomaly detection, event classification, real-time information visualization, and a context-aware learning feedback loop between users and algorithms.

Security analysts maintain continually evolving mental models that allow them to differentiate malicious and benign traffic. However, current systems do not exploit this knowledge. This effort addresses three pressing challenges in knowledge discovery for cyber defense: (1) incorporation of previously unused domain knowledge, (2) scalability of architecture and algorithms, and (3) timeliness of discovery. The results of the effort will enable more accurate and timely attack discovery than current systems, enabling analysts to find more complex attacks hidden in voluminous, high-dimensional, streaming data sets in cyber defense, as well as laying a foundation for other domains, such as intelligence analysis and infrastructure cyber protection.

Mission Relevance

This research makes a significant contribution to cyber security and situational understanding, and as such aligns with DOE's mission of scientific discovery and innovation. DOE's Office of the Chief Information Officer (CIO) lists one the cyber security objectives as "Promote real-time cyber security situational awareness." This research directly addresses this objective.

Recent funding and stated priorities from DOE for situational awareness data collection, analysis, and visualization for increasing cyber security for energy delivery systems, Department of Homeland Security science and technology (DHS S&T) for solutions in network data visualization for information assurance for the United States Computer Emergency Readiness Team (US-CERT), and the Department of Defense (DoD) for the analysis of large data sets, cyber science and technology, and human-machine interfaces all point to problems and open research areas that our effort addresses.

Results and Accomplishments

Major accomplishments to date include the following:

(1) acquired test data from multiple sources,

(2) developed tools for collecting and streaming log data,

(3) defined the architectures and data flows for the system,

(4) defined an organizing framework for anomaly detection comprised of a concise language for defining position (where), time (when) and value (what),

(5) defined a general construct for grouping log events at multiple scales,

(6) designed and implemented streamlined probabilistic algorithms for anomaly detection,

(7) designed and implemented a scalable method for event classification, and

(8) designed and prototyped initial user interfaces and visualizations.

Information Shared

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06001

Biosurveillance Data Analysis and Decision Support

T. Brettin

Project Description

Protecting our military and civilian population from biological threats requires making the most effective and efficient use of all biological information available. This proposal focuses on the dynamic, rapid collection and integration of critical biosurveillance information using Internet data sources, along with the identification of information gaps. The integration and automated computational analysis and reporting of this information will improve the ability to identify and respond to biological threats with better situation awareness and confidence. Our research hypothesis is that it is possible to advance automatic identification while increasing the relevance of biological threat-related information from the Internet, including social media, and do so with better performance, thereby enabling more effective decision-making. We propose to address this hypothesis through the development of biological threat critical information requirements, methods to fulfill those requirements using information adaptively collected from the Internet, benchmarks for assessing Internet data sources, credibility models for investigating information tractability, biothreat ontology for concept unification, and performance and effectiveness analysis of these capabilities. Through establishment of this multidisciplinary team, we bring together strengths in computational biosciences and knowledge discovery resident at ORNL to discover critical information through passive monitoring of existing data streams for biological threat decision support.

Mission Relevance

This reseach supports the mission of the laboratory in enhancing national security by developing methodlogy to be applied for biosurveillance in defense of our military and civilian populations.

Results and Accomplishments

We have developed a list of information requirements in close collaboration with three federal organizations. In collaboration with the staff at the National Center for Medical Intelligence, we elicited and documented information requirements central to their mission. These were elicited during several meetings with one of their analysts and focused primarily on obtaining information on influenza outbreaks in countries that are traditionally hard to collect information from using public sources.

We developed a list of information requirements in close collaboration with the Centers for Disease Control (CDC). For Aim 2, our progress on this has been aided significantly through our collaboration with staff at the National Center for Medical Intelligence. The current status is a collection of relevant terms compiled by staff at NCMI has been used by web crawlers developed under Aim 3 (described below). Additionally, we have internalized both the Bio2RDF and WordNet databases. Bio2RDF is a Biological database using the Semantic web technologies to provide interlinked life science data. We have developed a Smart Web Crawler that takes a list of terms of interest (for instance, the set of NCMI relevant terms) as a basis for crawling the Web. The crawler returns data from sites it identifies as relevant to the terms provided. Initial tests using the 49,088 NMCI terms resulted in 1,010,084 data documents retrieved with a total size of 97GB. We use Support Vector Machines (SVM) to classify the text data fetched from Social Media websites, such as Twitter. In Year 1 of the project, we proved that SVM is suitable for classifying the messages retrieved from Social Media. The SVM classification method can separate the social media dataset into two categories: relevant and non-relevant to the bio-threat topics. We have implemented the SVM classification algorithm and software platform and trained the algorithm, using manually selected keywords, so that the trained SVM algorithm can accurately predict unknown data (i.e., data fetched from social websites).

06041

Fully Virtualized Computational Energy Infrastructure Model for Improved Cyber Resilience

T. Kuruganti, J. Nutaro, G. Allgood, I. Patterson, D. Fugate, R. Sawhney

Project Description

Multiple interdependent energy foundations, comprising energy generation, transmission, and end use, serve as critical infrastructure for ORNL. These infrastructures are driven by multi-level control systems that observe the state of the system and respond to attain a local stable operating point. Cyber threats to these control systems are a pressing concern. Current guidance on securing these systems is prescriptive and does not take into account the impact of security technologies on the resilience of the system. A comprehensive understanding of the risks posed by cyber attacks to the ORNL infrastructure can only be achieved by analyzing component behavior in the context of the whole campus. This understanding requires a comprehensive computational model of interdependent installations and usage to analyze the whole-campus resilience due to cyber attacks. The purpose of the project is to develop a cyber-centric infrastructure modeling and simulation tool that facilitates simultaneous simulation of multiple energy foundations and associated control systems. A detailed sensitivity analysis provides the fidelity required to capture the behavior at a level suitable for characterizing risks posed by cyber attacks. The end result is a simulation framework to analyze the resiliency of the campus that can be scaled to include regional- and national-level infrastructure modeling.

Mission Relevance

This research is aligned with reliable energy delivery, which is the primary mission of the DOE Office of Electricity (OE). The proposed research effort is particularly relevant to the DOE/OE Control Systems Security Program. The proposed research can support DOE to assess the impact of new technologies on energy infrastructure resilience. The proposed research effort focuses on developing a capability to assist rapid deployment of resilient cyber infrastructure. This is also relevant to the DOE Energy Efficiency and Renewable Energy program. In addition, the Department of Homeland Security (DHS) Cyber Security Division's Control System Security Program is focused on reducing the industrial control system risks within and across all critical infrastructures. The Department of Defense (DoD) is interested in understanding the resilience of microgrid environments at mission-critical locations. The ability to conduct large-scale evaluations of proposed smart grid technologies is of interest to electric utilities as they build infrastructure to incorporate new sources of generation, load, and other components.

Results and Accomplishments

In the first year of LDRD we have reached all the major technical goals set forward in the project proposal. Specific accomplishments included (1) risk-based resilience analysis method for developing secure control systems with in critical infrastructure (we completed proof of concept demonstration for supercomputing chiller system and preliminary demonstration for ORNL Electric Distribution); (2) a method for model-based optimization of investment strategies for protecting critical infrastructure against cybersecurity threats; (3) a method for vulnerability identification using state transition diagrams. Additionally the team is currently performing sensitivity analysis of the ORNL infrastructure models created so far. Most work on cybersecurity emphasizes methods and technology for prevention, detection, or mitigation. We focus on how the effectiveness of each method along with dynamics of the physical system to determine the likelihood of an undesired outcome and how this information may be used to set requirements for the performance of security functions. We follow an approach with the purpose of quantifying the relationship between performance (therefore, cost) of a security system and the likelihood of an undesired outcome. A framework for designing secure controllers and validating existing control software is developed. Small-scale experimental-based validation of the simulation framework is currently in progress. Components of the simulation technology are carefully chosen to demonstrate geographic and computational scalability of the simulator. The team also had several significant program development activities during Year I including DOE Office of Electricity, Software Engineering Institute, National Institute of Standards and Technology, Pacific Northwest National Laboratory, UtiliSec, and California Energy Commission.

Information Shared

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06055
Automated Software Tools for Engineering Quantum Computers (ASTEQC)

R. Bennink, T. Humble, M. Pleszkoch, E. Ferragut, A. Bishop, K. Sayre

Project Description

Quantum Computing (QC) is a revolutionary new computing paradigm that, if developed into a feasible technology, will have significant ramifications for national security. QC development is held back in part by a lack of tools for designing and analyzing complex quantum devices. We propose to address this problem by developing the initial components of an envisioned software toolkit for the design, programming, and analysis of application-specific quantum information systems. Specifically, we will deliver (1) a system description language for specifying the detailed physical and operational characteristics of quantum information systems and (2) a software tool for inputting and visualizing design information. Methods for design analysis will also be researched.

Mission Relevance

Aspects of this project are classified and are not reported here.

Results and Accomplishments

Development of a Design Framework. We have developed a novel approach to the design of quantum information systems based on the principles of model-based design. We have developed a preliminary language for describing a quantum information system as a specification tightly integrated with a model. A system is defined hierarchically in terms of typed components, which include both state and process aspects and may be composed spatially and/or temporally. Design requirements and operational constraints are formally expressed as predicates on design elements. A novel type abstraction relationship among components allows the system to be described and analyzed at varying levels of abstraction and from multiple perspectives. We have identified three main levels of abstraction (algorithmic, computational, and physical) and the kinds of design inputs needed at each level. We plan to implement this language as an extension of SysML to take advantage of existing SysML design resources.

Development of a Formalism for Analysis. We have developed a mathematical formalism that rigorously defines model semantics and supports both simulation and formal analysis. This formalism, which we call a quantum-analog-digital (QuAD) system, may be seen as an extension of piecewise deterministic Markov processes to incorporate quantum states and quantum dynamics. This formalism can express both quantum and classical continuous evolution ("flow") as well as discrete state changes ("jumps"). In practical terms, it can express ideal or noisy quantum physical dynamics, ideal or noisy classical physical dynamics, and algorithmic control. We have developed a programming language for expressing QuADs and begun development of an associated logic based on interval temporal logic (ITL).

06068

Data-Driven Threat Radar for Local-to-Regional Energy Grid Stability

M. Shankar, J. Beaver, C. Briere, S. Chinthavali, A. Dimitrovski, S. Fernandez, J. Hubbs, B. Jewell, J. Nutaro, A. Ramanathan, M. Starke, R. Sukumar

Project Description

Using real data obtained from the field over the past 3 years, we are constructing a data-driven threat radar for the electric grid. Our threat radar takes into account distribution outages, transmission outages, and incipient cyber vulnerabilities. The goal is to combine signals of cyber incursions along threat vectors applicable to electric grid SCADA (Supervisory Control and Data Acquisition) systems with tracked behaviors in the electric grid. Our aim is to first enable detections at a fine-grained resolution within a facility – a local cyber-to-SCADA impacts model. We couple this with regionally detected behaviors – distribution and transmission outages – which can suggest an evolving attack. We distinguish our capability by using a one-of-a-kind grid awareness dataset available only at ORNL. By also representing the grid topology as a graph, we perform large-scale and high-speed cyber/grid infrastructure analytics together.

Mission Relevance

DOE's various program offices [Office of Electricity Delivery and Energy Efficiency (OE), Office of Energy Efficiency and Renewable Energy (EERE), Office of Science, Office of Intelligence (IN)] are deeply concerned about the security of the energy grid. We have proposed to create, based on grounded data, a cyber-threat detection and alerting viewer for the electric grid. No such system exists that relates control systems threats and outage indicators on the wider area electric grid. We take the vital first step to create a principled methodology going from detecting local to regional to wide-area cyber threats against the electric grids to ultimately enable rapid response.

Results and Accomplishments

1(a) Cyber Attack Parameters – We have developed the technology to automatically acquire and aggregate near-real-time alerts of cyber security data, and expanded our ingest mechanisms of power system data.

We have constructed a Cyber Attack Modeling and Early Outcomes (CAMEO) database based on an existing Common Attack Pattern Enumeration and Classification (CAPEC) taxonomy in use by the Department of Homeland Security (DHS). Control system attack profiles that we address include the prominent Stuxnet, Duqu, and Night Dragon control system attacks. Approximately 300 vulnerabilities from the Common Vulnerabilities and Exposure Database (CVE) have been incorporated into the CAMEO structure.

1(b) Cyber threat scenario catalog and case-study – Hurricane Irene. We are cataloging SCADA Descriptions for substation resources across utility sector.

2(a) SCADA Control Attack Scenario. We have developed a Matlab Simulink-based model of the electric grid and have shown how a load manipulation cyber-attack (on the Simulink model) can potentially destabilize SCADA systems (unstable oscillating frequency with increasing amplitude).

2(b) We have developed prototype software to perform preliminary correlation of Cyber and SCADA incursions.

Information Shared

Mallikarjun Shankar and Supriya Chinthavali, "An Information Overlay for Grid Stability Alerts," CIGRE-CA, Montreal, Canada, October 1–4, 2012.

06217

High-Throughput Transcriptomics for Microbial Bioforensic Analysis

L. Hauser, A. Gorin, D. Pelletier, S. Brown, R. Stouder

Project Description

We propose to develop a new approach for bio-threat and bio-forensic analysis of bacterial samples based on the ability of High-Throughput Transcriptomics (RNAseq) to create a unique Transcriptome Profile (TP) for any sample. This technology has significantly superior specificity and sensitivity when compared to shot-gun proteomics, making it an optimum "orthogonal" technology to DNA sequencing as part of any future comprehensive bio-forensic and bio-threat analysis system. We will develop a robust automated analysis pipeline that will identify all significant differences between any two TPs, and will calculate the degree of relatedness between any two TPs as well as determine the probability of any new TP having been derived from one already known. Thus, the TP of a bacterial pathogen isolated from a crime scene could be compared with a database of TPs, just as human fingerprints or DNA fingerprints are used today. We propose that if the proof-of-principle work in this proposal is successful, the TPs of virtually every bacterial pathogenic strain can be used as a barcode or fingerprint. Eventually, this technology could be expanded to fungal and viral pathogens.

Mission Relevance

RNAseq technology is rapidly becoming one of the prominent tools of systems biology, and ORNL and all of DOE will also need this technology to fully implement any full systems biology projects. The Department of Homeland Security's current bio-threat detection, response, and forensic programs are continually funding new methods and capabilities. A similar version of this grant was submitted to a Department of Homeland Security (DHS) call requesting forensic technology orthogonal to DNA sequencing was rejected solely because it was too preliminary. Recent Defense Threat Reduction Agency (DTRA) calls were looking for projects involved in "threat agent science" and "system biology and bioinformatics" and specifically characterization of cultured versus natural isolates of *Burkholderias*. RNAseq Transcriptome Profiling would be ideal as part of this characterization.

Results and Accomplishments

This project has three main objectives. The first is to determine the reproducibility of the technology by comparing numerous replicates of the TP of one or more bacterial strains. The second is to test whether the TP of one strain is sufficiently different from the TP of a second closely related strain, and that difference can be detected in a consistent and reproducible manner. The third is to create a slight modification of one strain by adding a plasmid and be able to clearly differentiate the modified strain from its parent. We identified and acquired two strains of *Bacillus thuringiensis*, a close relative of *Bacillus anthracis* which causes anthrax, that are >99.8% identical to each other but can be grown safely using standard laboratory practices. The two strains are *B. thuringiensis* ATCC 10792 and *B. thuringiensis* chinensis CT-43. Initially we grew 16 samples of each strain in batches of four biological replicates on four separate occasions and different batches of growth media. These samples were used to determine the best methods for isolating and sequencing the RNA to create the TP. An additional 16 samples have been grown, processed, and sequenced. The statistical analysis of this data is still in progress. A plasmid containing an antibiotic-resistant gene has been added to one strain and will be grown and TP determined in the near future.

LAUNCH

06282

Nano-Textured, Optically Transparent, Durable Superhydrophobic Thin Film Coatings

T. Aytug and J.T. Simpson

Project Description

Using today’s technologies, it is extremely challenging to obtain a superhydrophobic coating with high-quality optical transparency and robust mechanical properties, fabricated over large scale with good uniformity. Generally, superhydrophobic coatings are soft in nature, with a Teflon-like surface chemistry, which results in reduced adhesion and durability, and hence are not suitable for most commercial applications. This project aims to develop atomically bonded, optically transparent superhydrophobic thin film coatings that will achieve very high levels of mechanical, thermal, and environmental stability, along with anti-reflective and UV blocking functionality, while relying on manufacturing processes that are inherently scalable and cost-effective. By establishing these key features, this project will open new coating markets for residential windows, vehicle windshields, optical lenses / lens filters, goggles, eyeglasses, cover glasses for photovoltaics, optical instruments, and optical components in weapon systems for US Army and accelerate the adoption of anti-fouling coatings.

Mission Relevance

The ultimate implementation of the ORNL superhydrophobic technology would combine optical transparency and mechanically/environmentally durable coating whose performance will have revolutionary impact on our daily lives. This proposal specifically addresses these two key performance needs voiced by the marketplace and will greatly benefit the energy missions of the Department of Energy (DOE). For example, keeping optical windows, displays, and solar cell cover glasses cleaner and clearer will greatly reduce maintenance cost. In addition, coated photovoltaic cell covers will also provide increased cell efficiency due to inherent anti-reflective functionality of the coating, addressing one of the primary goals of DOE Office of Energy Efficiency and Renewable Energy (EERE) solar energy program. Further, it supplements and enhances DOE EERE’s water power program where antifouling and flow surface alteration with advanced coatings are of high interest as cost-reduction and/or performance-enhancing pathways for both hydropower and marine energy devices.

Results and Accomplishments

Met all deliverables and milestones stated in the Year-1 proposal. First year accomplishments include (1) achievement of world’s first atomically bonded, optically transparent superhydrophobic coating on fused silica; (2) demonstration of superhydrophobic performance with a droplet contact angle >170^{o}, optical transparency comparable to or better than the underlying substrate along with UV-blocking functionality;

(3) durability assessment of the coatings to cracking or fracture and scratch, where the coated samples showed no tendency toward delamination or brittle fragmentation and exhibited scratch resistance similar to that of the underlying substrate material. Complementary to the mechanical testing described above, we assessed the mechanical stability and adhesion of the sputtered films to the underlying substrates by a standard adhesive tape pull and by Al_2O_3 abrasion tests. Samples showed similar superhydrophobic behavior before and after both tests, substantiating excellent adherence of the coatings. Based on technical accomplishments, one US patent application has been filed, and two new invention disclosures have been submitted.

Information Shared

One US patent application has been filed, and two new invention disclosures have been submitted. Presented technical results to companies and industry leaders at an Industry Symposium hosted on September 5, 2012 at ORNL.

06285

One-Stop Information Shop: Personalized Content Recommendations

S. Xu

Project Description

We propose a novel personalized information service based on our previously developed advanced information management technology. The technology detects users’ personal information needs and accordingly recommends comprehensive high-value content, optimized for individual users’ preferences. Enabled by a set of intelligent user interfaces, a wide spectrum of implicit user feedbacks is first captured. By collaboratively mining semantic concepts, a personalized user information interest profile is inferred. With this refined profile coupled with collaborative filtering, we can comprehensively recommend high-value personalized content. This technology will (i) vastly enhance individuals’ capability to stay on top of content with critical personal values in today’s information explosion, (ii) significantly reduce personal effort and time in harvesting relevant information, and (iii) considerably empower users’ knowledge competitiveness. Technology readiness level (TRL): 7 (achieved after Year 1), 9 (anticipated after Year 2). Invention Disclosure #: 201102746.

Mission Relevance

The primary research on this project will focus on developing advanced image and text search models, ultimately merging unique techniques into a powerful software environment for data access and mining. This work is of strategic interest to the Department of Energy (DOE) and in an area of growing science focus at ORNL: Knowledge Discovery. This research area is the science agenda thrust of the Computational Sciences and Engineering Division and has direct relevance to DOE interests in national security, energy assurance, and basic science. The successful achievement of this research will also result in direct impact across several directorates at ORNL, with important practical applications to the National Institutes of Health (NIH) and the Department of Defense (DoD).

Results and Accomplishments

We proposed a personalized webpage re-ranking algorithm by exploring a user’s dwell times in his/her previous readings over individual documents. The algorithm first models concept word level user dwell times. In order to understand a user’s personal interest, according to the estimated concept word level user dwell times, the algorithm then infers a user's potential dwell time over a new document. Based on the inference results, the algorithm can re-rank webpage search results in a personalized way. Rankings produced by this algorithm were compared with rankings generated by popular commercial search engines and a recently proposed personalized ranking algorithm. The results clearly show the superiority of this method.

There are several ideas that contributed to methods we used to determine an image's relevance to a user. The first idea is that if a researcher talks about something in his paper, he is likely interested in it. Unfortunately, however, sometimes it is not always that simple in academic research papers. Sometimes an author only contributes to certain parts of a research project, while the other authors contribute the rest. This can cause a problem for computer algorithms because they cannot detect which contributions came from which author. To remedy this, we must gather many documents from the author so that we are able to determine more precisely what the author's specific interests are. With a large enough sample size, the interests of the author converge onto several main topics, while the topics that occur infrequently become less important. However, since most researchers do not have enough publications to fulfill the law of large numbers, we must use additional indicators to more precisely narrow the authors' interests.

The second idea that guides the determination of an author's interests is that they are most often interested in the same things their coauthors are. Using the coauthor relation defined in the following section, we can lend more significance to topics that occur often in the author's documents as well as their coauthor's documents. This enables the system to locate topics that will be of interest to the author, even though they may not have written much about them themselves. This social aspect of research fosters interdisciplinary research by locating topics outside of the author's direct field of research that may still be of interest to them.

Third is the idea that images in a document relate closely to the content of the document. This allows a simple mapping from the relevance of a document to the relevance of an image, though it cannot differentiate between different images in the same document. Additionally, grouping the images by the document in which they appear gives the user a more context-sensitive view of the image. If a user is truly interested in an image, it will likely lead to reading the context of the image to learn more about it, so if the user is able to see all of the images that are in the same context (i.e., in the same document), they can better gauge their interest.

06304

Active Composite Material for the Prevention and Treatment of Fouled Surfaces

M.J. Doktycz, S.T. Retterer, D.P. Allison, S.L. Allman

Project Description

Microbial fouling and antibiotic-resistant bacteria are ubiquitous medical and industrial problems. The advancement of an active composite material for the prevention and treatment of fouled surfaces is proposed. The composite material can be directly, or remotely, activated to physically or chemically alter its surface, thus preventing microbial colonization and/or destabilizing the fouling substance. The proposed technology is intended for biomedical applications, where implanted devices are routinely used but often contaminated with microbial biofilms. More specifically, an improved vascular catheter is sought. Demonstrating the efficacy of the proposed technology for preventing or reducing bacterial contamination is the experimental goal of the proposed efforts.

Mission Relevance

Fundamental aspects of microbial colonization and how they are enhanced or eliminated are relevant to several programs carried out by the DOE Office of Science, Office of Biological and Environmental Research. Further, the proposed efforts are pertinent to the Department of Energy (DOE) programs related to nanoscience and to ORNL’s Center for Nanophase Materials Sciences. The technology also addresses research needs in national security as a countermeasure to pathogens. Also, the biomedical focus of this work fits the research needs of the National Institutes of Health (NIH). The NIH funds both fundamental and applied studies in interfacing nanomaterials to biological systems and to reducing the effects of infectious diseases. Additionally, this research is relevant to several agencies, including the Department of Defense (DoD), the Defense Advanced Research Projects Agency (ARPA) and the Department of Homeland Security (DHS), that fund research on biological countermeasures.

Results and Accomplishments

Our first year efforts focused on (1) preparing and optimizing a composite material comprised of nanoparticles and polymer; (2) measuring physical activation of the composite material; and (3) measuring the effect of the activated composite material on bacterial adhesion. Nanomaterials comprised of gold were prepared. Various sizes of gold or gold shell nanoparticles were synthesized and characterized. Incorporation of these materials into polyurethane was demonstrated, and physical activation of the material was measured. Evaluations of the composite material to reduce or prevent bacterial adhesion were carried out using a colorimetric bioassay and imaging. Iterative optimizations of the system were carried out.

06308

Real-Time In Situ Water (and Air) Field Monitor

D.B. Watson, T.L. Mehlhorn, S. Cheng, W.B. Whitten, J. Xu

Project Description

We have developed a transformational prototype sensor technology, Membrane-Extraction Ion-Mobility Spectroscopy (ME-IMS), which will revolutionize and greatly reduce the cost of monitoring volatile organic compounds (VOCs) in water and air. Lab testing showed that a prototype sensor is capable of uniquely identifying over 115 VOCs, including the most common environmental contaminants, trichloroethylene (TCE) and tetrachloroethylene (PCE). The limit of detection for TCE is 0.5 ppb, well below regulatory limits. ME-IMS technology eliminates the need for collecting and shipping samples, and expensive offsite lab analysis. The Department of Defense (DoD) has estimated that the cost of sampling per location is $2,500/event. Costs for using our sensor may be only <$250/event. Preliminarily tests at Y-12 National Security Complex and the NASA Stennis Space Center confirmed our ability to detect, identify, and quantify VOCs in the field. After resolving several technical issues identified during field testing, our technology will be ready for commercialization and deployment for environmental and industrial purposes. Technology readiness is TRL 6. A patent was filed in 2010.

Mission Relevance

Substantial economic and societal benefits will result when the ME-IMS technology becomes commercially available. Development of the ME-IMS sensor has direct application to DOE’s environmental cleanup mission. If the ME-IMS sensor is used in place of existing expensive sampling and analysis technologies, DOE could save 100’s of millions of dollars. Expenditures currently directed toward routine annual monitoring costs could be shifted to conducting remediation efforts which would help to accelerate site cleanup, reducing costs further. The technology could also be used for national security purposes through monitoring of our nation’s water supplies and airborne contaminants. There is also the potential to use the ME-IMS for monitoring VOC (and other contaminant) releases related to energy production.

Results and Accomplishments

Major technical accomplishments were achieved that will help lead to proof-of-principle of the ME-IMS. Laboratory studies were conducted to quantify impacts of temperature and pressure changes on the membrane and VOC peak intensity. To overcome temperature and pressure impacts on the quantification of VOCs, an equilibrium mode, passive membrane extraction system was designed and a prototype unit constructed. Commercially available silica ceramic coatings were identified that can be use on sampling components to reduce sorption, reactivity, corrosion, etc., of canisters (e.g., equilibration chamber), tubing, and fittings. For our new instrument configuration, it was important to understand instrument response for a range of vapor-phase concentrations. Gas standards were prepared and used to quantify instrument response (peak areas) and develop calibration curves for key VOCs (e.g., PCE and TCE). A computer program was developed to estimate the concentration of VOCs in water based on the measured concentrations of VOCs in equilibrated vapor at different temperatures and pressure. The program also predicts vapor-phase concentration if a water concentration is known. To show technological proof of principle, surrogate membranes were deployed in VOC-contaminated groundwater wells, retrieved and analyzed for dissolved gases. The concentration of VOCs in groundwater was estimated using our software program. New media types were identified and incorporated into the ME-IMS sensor that will trap vinyl chloride, significantly increasing commercial value of the ME-IMS sensor because vinyl chloride is a toxic contaminant of interest at many sites.

Information Shared

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06324

Low-Cost Nanomaterials for PV Devices

C. Duty, T. Phelps, L. Love, J.-W. Moon, P. Joshi, B. Armstrong, G. Jellison, I. Ivanov, A. Rondinone

Project Description

NanoFermentation (NF) is a biologically based synthesis route for the manufacturing of advanced nanoparticle materials. This technology offers an environmentally friendly, scalable, low-cost alternative to manufacturing high-quality materials typically used in such areas as photovoltaics, solid state lighting, and thin film batteries. This project focuses on the production of nontoxic and earth-abundant materials to be used in solar cells, potentially bringing the cost of solar energy well below that of conventional energy sources (~$0.07/kWh). The goal of the project is to demonstrate scaled production of nanoparticle materials that are shaping the future of the solar energy sector, namely, zinc sulfide (ZnS) and copper zinc tin sulfide (CZTS). These materials are similar to the current champion-efficiency material for thin film solar cells (copper-indium-gallium-selenium, CIGS), but they are significantly more attractive because they are also earth abundant and nontoxic.

Mission Relevance

In order for US industry to realize the potential of nanomaterials and nanotechnology, key technical challenges related to synthesis, scalability, reliability, and dispersion must be overcome. NanoFermentation (NF) represents a novel approach for synthesizing nanomaterials that addresses these challenges while potentially representing major cost savings and using earth-abundant materials. The rapidly growing solar energy market is in need of a low-cost approach to nanomaterials in order to become competitive with traditional energy sources ($0.07/kWh). The Department of Energy has recognized this need and launched the SunShot Initiative to reduce the cost of solar energy by about 75% by the end of this decade. By combining NF synthesis of CZTS nanoparticles thin film consolidation, it will be possible to produce kesterite-based thin film PV cells of moderate efficiency (~ 10%) at an extremely low production cost of <$0.40 per watt, exceeding DOE goals of $0.50 per watt module costs.

Results and Accomplishments

The overall goal of the project has been to demonstrate the feasibility of the NF process for producing large volumes of nanoparticles that are commercially relevant for use in solar cell production. The research plan for the first year included two primary tasks: (1) the synthesis of ZnS and CZTS nanoparticles and (2) characterization and qualification of the nanoparticles. The critical milestone for the first year effort was to demonstrate a production rate of >25 g/month for both materials.

The team was able to achieve the production of high-quality ZnS nanoparticles within the first few months of the project. A protocol was developed to scale production in a 24 L parallel reactor system to produce ~0.5g/L over the course of 7 days. This resulted in a production rate of ~50g/month with a controlled and repeatable synthesis protocol.

Since CZTS is a quaternary compound, the synthesis of a single-phase material was much more challenging than the binary ZnS compound. The focus during this first year has been to develop the appropriate synthesis protocol for production of end-member stoichiometry CZTS, namely, Cu_2ZnSnS_4, by adjusting the concentration of input materials. Our team was able to achieve single-phase CZTS nanoparticle production and scaled-up production in a 40 L dual parallel reactor to demonstrate a production rate of >75g/month.

Information Shared

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SCIENTIFIC DISCOVERY AND INNOVATION

05481

Novel Zeolitic Carbon Support for Catalytic Bioethanol Production

D.-E. Jiang, S.-H. Chai, M. Kidder, Z. Wu, J.Y. Howe, S.H. Overbury, S. Dai

Project Description

One of the key challenges in the thermochemical conversion of biomass to ethanol is controlling the catalytic transformation of biomass-derived syngas ($CO + H_2$) to obtain high ethanol selectivity with high CO conversion. The most promising catalysts for conversion of syngas to ethanol are based on Rh. Recently, it has been shown that confinement of the Rh catalyst inside carbon nanotubes greatly enhances yield and selectivity, although the origin of this enhancement is unclear. By understanding and controlling confinement effects, significant advances could be made in ethanol formation and other reactions such as Fischer-Tropsch synthesis and formation of longer chain alcohols. The overarching goal of this project is to understand and control the confinement effects on catalysis by transition-metal nanoclusters confined in porous supports. We will pursue three specific aims. First, how can we achieve and control the confinement where the monodisperse catalytic particles are confined in a well-defined porous environment? Second, how does the confinement by the porosity of the support affect activity and selectivity of the metal nanoclusters to catalytically convert syngas to ethanol? Third, how can we control the catalyst's performance to achieve desirable targets of activity and selectivity of syngas to ethanol? The knowledge generated from this project will help achieve high-yield ethanol formation from syngas and benefit other energy-relevant reactions, thereby attracting applied funding sources such as the DOE-EERE Biomass Program and the joint DOE-USDA program on biofuels.

Mission Relevance

Catalysis is core to DOE's missions. The proof-of-principle study of this LDRD project could potentially attract future funding from DOE's highly successful catalysis program. The novel method to prepare the support and the confinement effect by the hybrid support will increase the knowledge base of heterogeneous catalysis for studying other energy-relevant reactions such as Fischer-Tropsch synthesis and the formation of longer chain alcohols. Therefore, this project will position us to attract new funding from DOE such as the Office of Energy Efficiency and Renewable Energy Biomass Program. For example, President Barack Obama announced on May 5 that DOE plans to invest $786.5 million in Recovery Act Funds in biofuels, including $130 million in biofuels research and development. Moreover, several funding agencies have current and future programs to fund biofuels research. For example, the US Department of Agriculture (USDA) has a joint program with the Department of Energy (DOE) to fund biofuels research (Biomass Research and Development Initiative, DE-PS36-09GO99016, issued on 1/30/2009, program funding: $25 million). The catalyst developed in this project is promising for the thermochemical route of converting biomass-derived syngas to ethanol, thereby benefiting this program.

Results and Accomplishments

Graphitic mesoporous carbon (GMC) was found in our FY 2011 year's work to be a promising support of precious Rh-based catalysts for synthesis gas conversion to ethanol. However, the high cost and limited availability of Rh metal make it unattractive for practical application. In FY 2012, we instead explored cheaper molybdenum carbide (β-Mo_2C) catalysts, which were synthesized in situ on the GMC support by carbothermal hydrogen reduction of supported MoO_3 precursor. The areal specific rate over the β-Mo_2C catalysts decreases, independent of the carbon supports, linearly with increasing the carbide particle size. GMC appears to be a preferable support of β-Mo_2C to traditional activated charcoal and carbon black, because smaller carbide particles form on the GMC and consequently result in higher catalytic activity. The addition of a minor amount of K_2CO_3 into β-Mo_2C/GMC considerably promotes the formation of higher alcohols (C_{2+}–OH, mainly ethanol and 1-propanol), leading to a maximum space time yield (STY) for C_{2+}–OH at molar K/Mo ratio of 0.1. Compared with typical Rh/GMC catalyst promoted triply with Mn, Li, and Fe oxides, K_2CO_3/β-Mo_2C/GMC (K/Mo = 0.1) shows higher C_{2+}–OH selectivity (30 vs. 25 mol-C% on CO_2-free basis) and STY (71 vs. 46 mg $(h\ g_{cat})^{-1}$) at a CO conversion of ~2 % under the reaction conditions of 573 K, 3.0 MPa, and molar H_2/CO = 2.

Information Shared

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05501

Enabling Plant Systems Biology Investigations for Carbon Cycling and Biosequestration Research

U. Kalluri, H. Bilheux, S. Gleason, G. Fann

Project Description

Plant systems biology studies that complement high-resolution molecular profiling (-omics) approaches with insightful phenotypic profiling and modeling methods can provide a powerful capability to study fundamental plant processes such as carbon fixation, transport, and fate. However, there is a dearth of suitable approaches to study plant growth and response mechanisms in vivo. Towards enabling such an approach, we propose to (1) adapt x-ray micro-CT and neutron imaging technologies to studying living plant systems, (2) generate experimental data using in vivo as well as ex situ molecular and phenotype profiling methods, and (3) develop an initial modeling framework to assess, correlate, and predict as to which spatiotemporal changes in system dynamics are key to predicting emergent properties of the system.

Mission Relevance

The project sought to demonstrate a new cross-disciplinary investigative approach that has also been recently advocated in the recent National Academy of Sciences report on "New Biology." The combined capabilities of in vivo and ex situ molecular and phenotype profiling methods can provide a powerful approach to study the fundamental processes underlying plant physiology as well as to help model plant growth and development. Proposed efforts are expected to complement and further strengthen ORNL's position to pursue future funding opportunities related to the declared grand research challenges within the DOE Biological and Environmental Research programs in feedstock genomics, climate change, and plant-microbe science areas.

Results and Accomplishments

The project successfully adapted x-ray micro-CT technology to carry out in vivo imaging of plant structure and neutron imaging technology to carry out in vivo chemical imaging using *Populus*, a model bioenergy crop. Progress towards developing CT-imaging technique to study live plants included optimization of sample preparation, achieving a spatial resolution of ~ 50–100 µm, successful live whole plant scanning at 512 × 512 × 512 voxels in under 30 minutes, whole plant reconstruction, refining the image output using suitable algorithms to filter noise and application of newly developed techniques to genetically modified plants. We also undertook conventional histochemistry of the same plant stems followed by the use of automated cell counting algorithms to further inform the coarse grain in vivo imaging output. We adapted neutron imaging capabilities at CG1D to study plants, achieved a ~70 µm resolution, increased understanding of conducting dynamic studies, and acquired neutron CT images from water phantom samples that could quantitatively inform water uptake in plants. The labeling, growth, delivery, and imaging experiments (boron-labeled sucrose transport and water transport in auxin mutants) were undertaken successfully, and real-time imaging data was employed in 3-D image reconstruction. Neutron imaging was used successfully to demonstrate water transport defects in auxin mutant plants (manuscript in preparation). Furthermore, we have implemented a coupled partial differential equation model, one equation for the water movement in the soil and another for water movement in the plant roots, in MADNESS (2011 R&D winner), a high-level environment for the solution of integral and differential equations.

Information Shared

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05565

Engineered Chemical Nanomanufacturing of Quantum Dot Nanocrystals—Meeting the Energy Technology Demands

M.Z. Hu, T. Zhu, D.W. DePaoli, G.E. Jellison, Jr.

Project Description

The objective of this project is to develop a core chemical nanomanufacturing capability that can fulfill the large-quantity demands of high-quality, molecularly tailored quantum dots (QDs) for energy applications. Oak Ridge National Laboratory (ORNL) and the Department of Energy (DOE) have been strategically investing in scientific studies of QDs because of great potential in several important energy applications such as solid-state lighting, solar cells, and photoelectrochemical devices for water splitting. However, current methods for producing QDs are primarily suitable for small-quantity R&D samples and for medical and biological labeling and imaging. The project focused on employing our recent breakthrough in chemical synthesis of QD nanocrystals by a newly discovered thermodynamically driven noninjection process (TD-NIP) to develop industrially viable QD production methods. This approach is well suited to process scale-up because of its simplicity and its potential for high reproducibility of produced QDs between batches. The effort collected engineering data on thermodynamic equilibria, chemical reaction kinetics, and nanocrystal nucleation and growth needed to understand the process parameters for tailored production of QDs in various compositions and demonstrate a scalable and reproducible process. Successful development of this innovative technology will enable further R&D focused on specific energy applications of a new class of nanocrystals.

Mission Relevance

The project is directly relevant to the mission of the Advanced Manufacturing Office (AMO) of the DOE Office of Energy Efficiency and Renewable Energy (EERE), which is focused on the scale-up and commercialization of manufacturing technologies, including nanotechnologies, related to energy. The project is also applicable to other DOE EERE missions, including solid-state lighting and solar programs. The capability of producing QDs in large scale may also be applicable to programs in other federal agencies, such as the Department of Defense and the Department of Homeland Security.

Results and Accomplishments

Based on our discovery of a thermodynamic equilibrium-driven mechanism, we have demonstrated the use of microwave processing via a non-injection approach to produce a new class of nanocrystals, that is, magic-size/molecular-species quantum dots (MSQDs). With well-defined molecular features, MSQDs are drastically different from conventional, regular quantum dots (RQDs), in terms of their formation mechanism, particle characteristics, and properties. Microwave synthesis has been developed as an engineering scale-up methodology to produce nanocrystals in significant quantities and of high quality (i.e., with essentially identical size and precisely controlled numbers of atoms in each nanocrystal). The new scientific MSQD-formation phenomenon, so far achieved with cadmium-containing systems (CdSe, CdS, CdTe, or CdSeTe), could be further developed as an innovative green process technology for creating various new environmentally friendly material systems (such as $CuInS_2$, $CuInSe_2$, PbSe) with high impacts on energy and many other applications.

We have successfully met project goals and have made new discoveries that we expect to lead to significant opportunities for future funding. Highlights of past progress include the following.

- Developed a microwave-processing methodology for engineering development
  - Demonstrated for the first time that MSQDs can be produced via microwave processing
  - In contrast to the conventional heating, microwave synthesis has produced nanocrystals of lower defects with tailorable trap emission
  - Determined condition regimes of cluster (gel) formation and nanocrystal formation
  - Identified the need of co-solvent to tailor the microwave absorption efficiency
- Conducted small-angle neutron scattering (SANS) experiment using HFIR

- SANS study clarified the controversial scientific issue regarding MSQD morphology by supporting the existence of nanosheet structure in colloidal solutions.
- Analysis of SANS data, using a unified model, for microwave-synthesized MSQDs has revealed the existence of two-dimensional scales of objects.

- Developed a potential pathway for producing MSQD of targeted composition (such CIS, CISe, PbSe) for energy applications and engineering methodology for next-year process technology development on large-throughput continuous synthesis.

Beyond the currently studied model CdSe system, the microwave-aided MSQD-forming phenomenon could be utilized for other targeted compositions of practical significance to energy and opto/electronics applications. Future considerations for engineering scale-up are also discussed, including the need of co-solvent addition to improve microwave absorption efficiency and continuous flow mode to reduce reactor volume while allowing large throughput production of nanocrystals.

This project has been successfully completed with follow-on funding from DOE NA-22 program (OR12WAVEDISCPD05) on making QDs-based optical materials for gamma/neutron detectors: $392K (FY 2012) and $546K (FY 2013).

Information Shared

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05594

Direct Catalytic Conversion of Ethanol to Hydrocarbons – A First-Principles Theoretical and Experimental Study

C.K. Narula, B.H. Davison, J.R. Mielenz, R.A. Geiger, E.M. Casbeer

Project Description

The goal of this project is to explore direct catalytic conversion of ethanol to hydrocarbons for use as transportation fuel and as raw materials for the chemical industry. Our preliminary studies indicate that dilute ethanol streams can be catalytically converted to olefins. Guided by theoretical studies, we propose to develop catalysts that can selectively convert dilute aqueous ethanol streams and fermentation streams to hydrocarbons at low temperatures and pressure. The results of this project will lead to substantial intellectual property and publications that will establish the expertise of ORNL in the conversion of ethanol and other products such as bio-butanol to hydrocarbons. The results of this research will enable us to respond to the anticipated calls from DOE-OBP (Office of Biomass Program), Department of Defense (DoD), and the Advanced Research Projects Agency–Energy (ARPA-E). Further investigation and optimization of catalytic process and process development for commercialization of technology will be carried out under follow-on funding from these offices.

Mission Relevance

The results of this project will demonstrate that it is possible to convert dilute ethanol streams to C2+ hydrocarbons. This work is very well aligned with the missions of DOE-OBP. DOD and ARPA-E offices are also interested in this topic. A successful demonstration of catalytic process to convert ethanol streams to C2+ hydrocarbons will enable us to work with program managers to secure funding for the optimization of the catalytic process that employs fermentation streams to produce C2+ hydrocarbon streams that can be used as renewable chemical feedstock and can also be mixed with fuel (diesel, gasoline, or JP-*) in any ratio for transportation or power generation.

Results and Accomplishments

In FY 2012, we modified the catalyst and achieved full conversion at 350°C and atmospheric pressure with less than 10% ethylene. Our preliminary mechanistic studies rule out ethylene as the first step of ethanol conversion to hydrocarbons. We have shown that the catalyst is durable for over 80 h, and we expect to complete 200 h testing in November. The hydrocarbon mix as produced from ethanol is a mixture of 2.47% paraffins, 10.5% iso-paraffins, 9.65% olefins, 3.11% naphthalenes, and 74.26% aromatics. The average molecular weight of hydrocarbon mix is 97.86, the average specific gravity is 0.823, total hydrogen is 10.5, and the carbon-to-hydrogen ratio is 8.47.

The calculated research and motor octane numbers are 107.6 and 93.3, respectively. This blend-stock was used to run modified Sturman variable valve actuation engine with a ported fuel injection which can be warmed up using gasoline direct injection fueling system without consuming test fuel. Test fuel or certification gasoline is then introduced, and performance data such as cylinder pressure and heat release rate as a function of crank angle are recorded. We found these parameters for an engine operating on our blend-stock to be identical to the parameters for an engine operating on certification gasoline. The emission data are also collected.

Fractional collection enables collection of 160–300ºC blend-stocks suitable for mixing with diesel or jet fuel.

For technoeconomic analysis, we started with our analysis of process design and economics for biochemical conversion of lignocellulosic biomass to ethanol. Our assumption are for a plant size of 2,200 dry US ton/day corn stover with 20% moisture content and ethanol yield of 79.0 gal/dry US ton feedstock. The feedstock cost is $58.5/dry ton, and the internal rate of return is 10%. The upgrading of ethanol yields 39.1% water, 15.6% ethylene, and the rest is hydrocarbon product. The upgrading conditions are 350ºC at LHSV of 4.6 h^{-1}. Taking into account the capital investment of $446 MM/year, variable operating cost of 68.6 MM/year and fixed operating cost of $11.4 MM/year, the selling price of blend-stock will be $3.06/gallon.

Information Shared

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05606

Characterization and Modeling of Permafrost Microbial Community Diversity and Metabolism during Simulated Global Warming

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Project Description

Carbon cycle models suggest that permafrost soils contain massive reservoirs of organic carbon, whose mineralization would substantially increase greenhouse gas (GHG) levels. Models simulating current GHG production and transport do not address permafrost thawing due to global warming, or the subsequent microbial mineralization of buried carbon. This project has measured GHG emissions from permafrost cores during controlled warming, and we have produced fundamental data for single point source models of GHG emissions. We are also developing a systems biology approach toward aiding in the development of more discreet and locally accurate models for predicting CH_4 and CO_2 generation and emissions from the release of trapped GHG due to enhanced microbial metabolism of buried nutrients. Our microcosm experiments at ORNL characterized perturbations in microbial metabolism and GHG production, and these data will help to focus future longer-term studies on specific controlling factors. This integrated effort supported the Earth System Modeling and Carbon Cycle Science thrust areas within the Climate Change Science Institute.

Mission Relevance

The US DOE has identified GHG release as the "non-linear tipping point" for global warming. Efforts are under way within the Climate and Environmental Sciences Division of the Office of Biological and Environmental Research (OBER) towards better understanding of these processes for more accurate predictive capabilities, and funding is expected to increase in the near term. Current GHG emission models estimate active layer gas release, and often underestimate biogenic CH_4 while assuming litter pools exist in upper soil layers. Decomposition rates are calculated from the soil top 40 cm, but it is spatially varied throughout the permafrost layer. Carbon distribution is not modeled, but the Climate Land Model (CLM4) does include soil temperature, moisture, and freeze/thaw status to >3 m depths. There are also no parameters for discreet depth discrimination, that is, surface, active or permafrost, nor is there a component for the effect of a changing pH. The work performed on this project aimed at accentuating the models predictive capabilities by providing environmentally relevant biogeochemical data derived from microbial community metabolism of warmed permafrost core material. We have been successful in generating that required data.

Results and Accomplishments

Year 1 deliverables were met within 8 months of funding, and the team exceeded the deliverables by month 12. This project also met all Year 2 deliverables. For Aim 1, we obtained four frozen core samples from Fairbanks, AK, to a depth of approximately 3 m. Sediment samples from three of the cores were removed from different depths and analyzed for pH, total nitrogen, and organic carbon, which all increased with depth. Organic carbon was >83% of the total carbon in all cases. Sediment microcosms were constructed from samples of the surface, active and permafrost layers of the Fairbanks cores, and incubated for 3 months at -2^{o}C, +3^{o}C, and +5^{o}C. Surface microcosms began aerobic, while all others were constructed in an anaerobic glove bag. While all frozen samples thawed during incubation, increased warming (-2^{o}C to +5^{o}C) did not significantly increase CO_2 or CH_4 generation and emission. Carbon dioxide increased to 14% (v/v) headspace gas in the surface sediments and up to 3% in the active and permafrost incubations. Methane was absent in the surface layers, up to 0.2% in the active sediments and highest in the permafrost incubations at 0.5%. The highest rates of CO_2 generation in the surface incubations (0.120 μmol/g sediment/month) were approximately 20 times faster than the highest CH_4 generation rates in the permafrost incubations (0.006 μmol/g sediment/month). These results indicate that anoxic conditions, more neutral pH, high water, and organic carbon contents of the thawed permafrost samples were most conducive to methanogenesis. After 6 months of incubation, the pH of almost all sediments dropped to below 5.8. At this acidic pH, CH_4 production declines substantially, and dissolved CO_2 will be volatilized, further increasing the CO_2 emission rates and yields. In Year 2, DNA extraction and phylotyping experiments were performed to identify changes in the microbial population that corresponded to organic matter mineralization and acidification during the microcosms' incubation. We have also provided samples to collaborators at the Lawrence Berkeley National Laboratory (LBNL)-JGI for DNA extraction and metagenome sequencing.

For Aim 2, in Year 1 we compared the effects of water saturation in microcosms and determined that high water content is secondary to anaerobiosis in controlling CH_4 and CO_2 emission profiles. In Year 2, we also established Fairbanks sediment microcosms in the presence of pH buffers to identify pH-dependent effects on organic matter mineralization during FY 2012. No buffers had any effect, but this may have been due to the experimental setup in delivering too low a volume of the buffers to homogeneously affect the sediments.

For Aim 3, we hired a new post-doctoral fellow and engaged him in parameterizing land models using the organic matter mineralization and greenhouse gas production rates we determined in the sample microcosms. In Year 2, the post-doc successfully generated new modules to encompass the experimental data.

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05641

Advanced Bioprocessing for Sustainable Biorefinery Technology Development

A.P. Borole, D. Pelletier, J. Mielenz, J. Elkins, and B. Davison

Project Description

Efficient production of fungible fuels and future bioproducts from mature biorefinery technologies will combine multiple biochemical and thermo-chemical processes. One such hybrid process includes biomass gasification to syngas, followed by a fermentative step to produce fungible fuels. Many limitations currently plague syngas transformation including mass transfer, biocatalyst issues, and product recovery. We are proposing a novel system to transform production of fuels from syngas. This includes two components: bioreactor development and pathway development. A bioreactor capable of high rates of mass transfer and conversion is described. A new and efficient pathway for incorporation of CO into fungible fuels via intermediate fermentation products is proposed. The performance of this bioreactor is expected to be significantly better than existing designs and will revolutionize the technology for conversion of syngas from biomass, which can be one of the most abundant, easily produced, and cheap energy source available today.

Mission Relevance

This LDRD seeks to develop solutions to two most pressing issues related to syngas conversion to biofuels and bioproducts. Demonstration of effective utilization of carbon monoxide can result in a major step forward in hybrid biochemical-thermochemical biorefinery process development. The reactor can potentially be used with other biocatalysts currently being used for ethanol/butanol production. The second component of this work, that is, pathway development opens doors to higher throughput and increased rates of conversion for fuels and chemicals production. Potential sponsors for follow-on funding include the Advanced Research Projects Agency–Energy (ARPA-E), which recently had a solicitation for breakthrough concepts of this nature, the DOE–US Department of Agriculture (USDA) Biomass R&D Initiative (which is now seeking innovative integrated projects), the Office of Energy Efficiency and Renewable Energy (EERE), as well as chemical companies like DuPont that are moving into the fuels market (DDCE JV). The results will be a drop-in fuel that meets the current infrastructure and vehicle requirements in this country.

Results and Accomplishments

Demonstrated conversion of CO to hydrogen under the control of redox potential.

Developed bioelectrochemical reactor (BER) and demonstrated ability to control redox potential of catalytic biofilm.

Demonstrated sorbitol production using 2-gene pathway in *E. coli* and *R. rubrum.* Activity of fructose-6-phosphate dehydrogenase was lower compared to the phosphatase enzyme.

Month 24. (a) Demonstrated expression of biosynthetic pathway in *R. rubrum*, (b) Completed assessment of carbon monoxide conversion in BER.

Information Shared

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Bioreactor for syngas bioconversion, patent application submitted 9/21/2011. Further work on demonstrating improvements in rate of hydrogen production from CO, testing of bioenergetics and mass transfer effects in BER is in progress.

05663

Nanoporous Inorganic Membranes for Selective Separations in High-Temperature Flow-Through Recycle Pretreatment of Lignocellulosic Biomass

R. Bhave, J. Mielenz, T. Tschaplinski, L. Lynd, X. Shao

Project Description

We propose to investigate a new concept for pretreating cellulosic biomass to make it amenable to bioconversion. Flow-through Recycle (FTR) pretreatment will offer radical reductions in the cost of overcoming the recalcitrance of cellulosic biomass, the major technical obstacle to cost-effective production of fuels and chemicals from these feedstocks, while also providing a unique approach to biomass fractionation for value-added co-products. We propose to test FTR pretreatment on a variety of feedstocks, generating solid and liquid fractions that will be characterized with respect to composition and fermentability. Nanoporous inorganic membranes with pore diameters in the range of 1 to 10 nm will be evaluated to determine the separation performance on solubilized fractions (lignin, sugars, and protein) at pretreatment conditions including temperatures up to 250˚C and operating pressures up to 550 psi. Successful demonstration of FTR pretreatment would enhance ORNL leadership in materials and separation technologies in what has emerged as a strategic need for this country, biomass-derived fuels and chemicals.

Mission Relevance

Separations are one of the key focus areas of the Department of Energy Energy Efficiency and Renewable Energy Industrial Technologies Program (DOE-EERE/ITP). Our novel pretreatment research initiative in lignocellulosic biomass processing using membranes can reduce the cost of overcoming biomass recalcitrance and deliver improved energy savings and reduce water use critically important to improve the energy efficiency of industrial processes. We anticipate significant benefits to DOE-EERE/ITP and Bioenergy Science Center programs resulting from this research that focus on development of novel approaches in selective separations and preferential inhibitor removal to increase the bioconversion yield to ethanol and co-products.

Results and Accomplishments

We have evaluated membrane separation on hydrolyzates prepared by high-temperature FTR pretreatment of several feedstocks such as bagasse, corn stover, poplar, and switchgrass (early and late cut) at temperatures in the range of 180–220˚C. We have demonstrated that FTR produces highly reactive solids compared to simultaneous saccharification and fermentation (SSF) and consolidated bioprocessing (CBP). Nanoporous inorganic membranes with 2–4 nm pore size showed quantitative carbohydrate retention with simultaneous selective removal of monolignols and phenolic acid/aldehyde inhibitors. We have also shown that membrane diafiltration (DF) enhanced hydrolyzate fermentation to further reduce the level of inhibitory compounds. FTR pretreatment without membrane DF inhibited fermentation (no cell growth). It was observed that relatively high membrane flux could be maintained (20–40 liter/hr-m^2), further demonstrating the potential for energy efficient cost-effective separations for large-scale lignocellulosic biomass processing. Membrane performance was fully restored with membrane cleaning using 0.5 wt % caustic solution at temperatures of 160–180˚C. Our results show that FTR pretreatment with membrane separation could substantially reduce biomass recalcitrance and play a critical in achieving high bioconversion efficiency.

Information Shared

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05684

Towards Full First-Principles Simulations of Correlated Electron Materials

T.A. Maier, G. Alvarez, M.S. Summers, T.C. Schulthess

Project Description

The goal of this project is to develop a capability for material-specific and predictive simulations of correlated electron materials. Two immediate aims will guide our research: (1) The development of many-body methods and simulation tools that will enable the computation of emergent properties of material specific models, which are generated from first principles by electronic structure techniques; (2) The integration of these many-body methods with state-of- the-art electronic structure techniques will form a robust and parameter-free first-principles framework for simulations of correlated electron systems. Our effort will be guided by the objective to develop robust procedures and simulation tools with predictive power, which can make use of future exascale computing architectures. As a proof of principle, we will use these tools to perform material-specific simulations of cuprate high-temperature superconductors. In particular we will focus on solving one of the most important questions at the forefront of condensed matter physics, the link between differences in the chemical composition and the critical temperature between different compounds. The concepts, procedures, and tools we will develop in this project will be applicable to a range of new materials and will allow the intelligent design of new complex materials with optimized properties.

Mission Relevance

This project is relevant to several DOE initiatives. The development of advanced computer algorithms and fast codes to treat many-particle systems and, in particular, the development of predictive models for the discovery of new materials with targeted properties are important aspects of the mission of the Division of Materials Sciences and Engineering in the Office of Basic Energy Sciences. The new tools that will be developed in this project will also be beneficial to the Center for Nanophase Materials Sciences (CNMS) by providing a new capability that will enable growth of the CNMS user community, an important goal of the CNMS. Furthermore, the project is also in line with the vision for computational science at the exascale at the DOE Office of Advanced Scientific Computing Research (ASCR).

Results and Accomplishments

Our work was focused on developing effective low-energy models for single-layer cuprate superconductors using a full-potential linear augmented plane wave (FP-LAPW) framework, implementing a state-of-the-art continuous-time auxiliary field quantum Monte Carlo (CT-QMC) solver for multi-orbital models within the dynamic cluster approximation DCA++ framework, and applying this methodology to calculate the superconducting transition temperature of a number of single-layer cuprate materials. Results and accomplishments can be summarized as follows: (1) We have applied an FP-LAPW framework combined with a random-phase approximation (RPA) to generate low-energy effective multi-band models of a selected set of single-layer cuprate superconductors. (2) We have extended the DCA++ framework to interface with the output of the FP-LAPW calculations and to support models with multiple orbitals. (3) We have developed a robust implementation of a state-of-the-art continuous time auxiliary field solver for the DCA++ cluster problem for multi-orbital Hubbard models. (4) We have started to develop a new solver based on the density matrix renormalization group (DMRG) approach to enable the direct calculation of dynamic quantities such as magnetic structure factors to support comparisons with neutron scattering experiments. (5) We have developed a new algorithm, DCA+, which incorporates a much more physical self-energy with continuous momentum dependence into the DCA algorithm and thus leads to much faster convergence with cluster size. (6) We have started to apply these new technologies to calculate the superconducting transition temperature T_c of a set of selected single-layer cuprate superconductors. Preliminary results indicate that the large variation of T_c between lanthanum-based and mercury-based compounds can be reproduced in these calculations. This opens the door for an additional analysis to obtain a fundamental understanding of the high-T_c pairing mechanism and of the factors that determine the transition temperature and its variation between different compounds.

Information Shared

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05685

Modeling Long-Term Population Resettlement under Climate Change Scenarios

B. Bhaduri, X. Cui, J. Schryver, B. Preston

Project Description

Changes in climate are expected to challenge the capacity of human settlements to adapt to a changing environment. Some of the predicted impacts include an increase in the duration of wildfires, an increase in the likelihood of flooding, more severe and longer heat waves, more intense hurricanes, desertification, an increase in snowstorms, and an increase in foodborne, airborne, and waterborne diseases, among others. The goal of this project is to develop a conceptual model of population dynamics covering displacement, migration, and resettlement as an interactive consequence of vulnerability to climate change and its impacts on social arrangements, political stability, economic prosperity, water resources, land cover, and land use. The climate-induced population dynamics conceptual model is unconventional and innovative in that it is not just a theoretical exercise to identify factors or variables that operate and interact in human and environmental systems. In contrast, we present an alternative dialectical approach that models human life as interactions among adaptive agents who influence one another in response to the influence they receive (a breakthrough in the social sciences and disaster studies). ORNL is strategically positioned to develop this spatio-temporal dialectic simulation of climate-induced population dynamics for the analysis of geopolitical and security analysis.

Mission Relevance

Developing new understanding of climate-change-induced human migration and resettlement has tremendous implications for the future of natural resources and geopolitical stability. This is relevant to Office of Advanced Scientific Computing Research and the Office of Biological and Environmental Research because of (1) the novel data and computational requirements including the representation of complex systems via high-performance computing and (2) the potential applications in the context of integrated assessment modeling, respectively. This project is also relevant to other federal agencies including the Department of Defense and United States Agency for International Development (USAID) due to the potential applications of the research with respect to identifying vulnerable populations and communities that may be adversely affected by climate change in the decades ahead, prompting humanitarian and/or security crises to which U.S. agencies may need to respond. In this context, this project can assist in preparedness and contingency planning for federal agencies.

Results and Accomplishments

We developed a conceptual framework utilizing scientific knowledge from close to 200 research articles on social impacts of climate change, social vulnerability, migration decision making, disasters and population displacement, forced migration, internal migration, transnational social networks, hazards and disasters in Bangladesh, and human adaptation to climate change. A hybrid migration decision model was developed by integrating reactive adaptation to climate change (RACC) and the multi-alternative decision field theory (MDFT) frameworks to integrate push and pull factors into a single quantitative model that conceptualizes migration decisions as a nonlinear process. The uniqueness of this hybrid decision-modeling framework is an integration of a human decision model adapted from the climate change migration literature and a quantitative sequential sampling decision model from the cognitive psychology literature. A destination matrix was used to determine the preferential strength of alternative destinations from their values on six attributes or decision criteria. An agent-based software and visualization platform was developed to simulate the relationship between the influence of climate change and human migration pattern in Bangladesh. Using demographic and socioeconomic data, a scenario-based platform made of households nested in a social system was developed to model agent decision intentions as a function of attitudes generated through interaction with others, demographic and socioeconomic characteristics, and of the perceived capacity of the social unit for adaption. Utilizing past cyclone incidence data, climate change scenarios are generated to simulate possible long-term outcomes of population migration that will be tested against known observations, isolating thresholds and triggers for migration.

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05699

Incorporating Molecular-Scale Mechanisms Stabilizing Soil Organic Carbon into Terrestrial Carbon Cycle Models

M. Mayes, W.M. Post III, H. Ambaye, L. Petridis, S. Jagadamma

Project Description

The top meter of soil contains 1500 Pg of carbon (C), and contemporary models often simulate C dynamics by determining pool sizes and turnover rates post hoc. This standard representation does not explicitly consider microbial activities, and this lack of quantification means that acclimation of the heterotrophic community and associated exo-enzyme activities to climate change are ignored. Our project produces a mechanistic model of cycling of organic C (OC) in soils. We hypothesize that attachment at the interface with soil minerals will determine the bioavailability of C to microbes, and thereby exert control over soil OC turnover. The relationship between attachment and stabilization for common OC compounds (aromatics, fatty acid, sugars, starch) will be determined in batch sorption and long-term incubation experiments using a global suite of soils. The mechanisms of attachment will be determined using a coupled application of neutron reflectometry and molecular dynamics simulation. The turnover of the OC compounds as they cycle through measurable pools (dissolved, mineral OC, particulate OC, and microbial biomass) will be modeled through the mechanism of enzyme-facilitated microbial degradation. The model framework will be developed and validated using published data, followed by application using our coupled sorption and degradation measurements on global soils. The ultimate outcome is a validated, realistic, globally relevant soil C model that is linkable into widely used global circulation models.

Mission Relevance

We seek to build a program providing a new theoretical and quantitative framework for systematic, mechanistically based terrestrial C cycling models. Our program will enhance the Energy and Environmental Sciences Directorate's existing strengths in ecological response to climate change, modeling global and terrestrial C, and in using molecular-scale techniques to study interfacial processes between contaminants, soils, and aquifer materials. We have obtained continued funding for the modeling portion of the work from the Climate and Environmental Sciences Division of Biological and Environmental Research (BER) through the Terrestrial Ecosystem Science Focus Area. Finally, new techniques developed through interdivisional collaborations using neutron reflectometry and supercomputer modeling will interrogate interfacial, molecular-scale adsorption processes in soils and subsurface media. These techniques will be applicable to the Subsurface Biogeochemical Research program at the Office of Biological and Environmental Research (BER) and many other areas.

Results and Accomplishments

This research provides comprehensive data and validated modeling to represent the turnover of major organic compounds found in a global suite of soils. In Objective 1, we determined relationships between attachment and stabilization for common OC compounds (aromatics, fatty acids, sugars, starch), added in batch sorption and long-term incubation experiments to soils obtained from artic, tropical, and temperate climates. The mineral fraction of surface soils has similar or greater sorption than that of subsurface soils for all compounds. Increased adsorption of the different OC compounds decreased their bioavailability, and we observed progression of the dissolved, sorbed, and biomass pools over 1 year coincident with CO_2 respiration. This suggests that sorption is a key process that inhibits the availability of OC for microbial decomposition. Carbon use efficiency (CUE) experiments found rapid turnover of glucose, while long-term experiments observed extensive ^{14}C residence times, possibly suggesting transformation of glucose to microbial by-products. For Objective 2, we investigated OC stabilization on pure minerals using a novel, coupled application of neutron reflectometry (NR) and molecular dynamics (MD) simulation. Experiments conducted at the Spallation Neutron Source (SNS) using OC-mineral systems prepared at Center for Nanophase Materials Sciences (CNMS) found the formation of stacked layers of OC on mineral surfaces with internal arrangements dictated by chemical character. For Objective 3, we created a mechanistic microbial model of enzymatic degradation of measureable pools of soil OC [mineral-associated OC (<53 µm), particulate OC (>53 µm), dissolved OC and sorbed dissolved OC, and microbial biomass)]. The activities of extracellular enzymes were considered through the Michaelis-Menten equation, and the model was parameterized by steady-state and dynamic analyses using kinetic parameter values and pool estimates gleaned from an extensive literature search. Model simulations found that CUE is a critical parameter, and when allowed to fluctuate according to temperature, substantial differences are observed compared to simulations using a constant CUE. Changes in microbial biomass and enzyme production accompany changes in temperature and directly influence the stabilization of soil OC, resulting in greater preservation of cellulosic over lignin substrates. The model is the first fully parameterized soil C cycling model to use measureable pools of soil C, and to explicitly consider decomposition via microbial enzymes and the influence of sorption of dissolved OC.

Information Shared

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05801

Unraveling the Molecular and Biochemical Basis of Crassulacean Acid Metabolism (CAM) in *Agave* for Sustainable Biofuel Production

X. Yang, D.J. Weston, H. Yin, S.D. Wullschleger, T.J. Tschaplinski

Project Description

As an emerging biofuel crop, *Agave* has high cellulose and sugar contents, along with high biomass yield. More importantly, it is one of the most water-use efficient plants in the world due to its crassulacean acid metabolism (CAM). The goal of this project is to establish CAM expertise at ORNL and characterize genes regulating CAM physiology. CAM has four phases: phase I, CO_2 fixation catalyzed by phosphoenolpyruvate carboxylase (PEPC) and accumulation of malate at night with the stomata open; phase II, CO_2 fixation shifted from PEPC fixation to Rubisco fixation after dawn; phase III, Rubisco refixation of CO_2 released from malate decarboxylation with the stomata closed in the late morning; and phase IV, direct CO_2 fixation by Rubisco with limited stomatal opening in the late afternoon. Two-dimensional aspects (diurnal 24-hour time course and developmental difference in CAM between young and mature leaves) will be explored using a systems biology approach integrating physiology, genomics, metabolomics, and computational biology. This research will discover the transcriptional and metabolic networks driving the four CAM phases, set the stage for genetic improvement of *Agave* to increase the magnitude of CAM expression, and consequently enhance biomass production.

Mission Relevance

Biofuel crops are currently envisioned to be generally planted on agricultural land, yet for many locations around the world, marginal lands represent a valuable resource that could prove to be a viable option. Crops will need to be tailored to such water-limited and degraded regions, as current biomass production systems using C3 and C4 plants are poorly suited for biomass production on such lands without irrigation. With the CAM pathway, Agave uses water and soil resources very efficiently. Some Agave cultivars possess high sugar and cellulose content. Furthermore, Agave is adapted to growth on marginal lands, making it an ideal feedstock by avoiding competition with food production. However, there is essentially no biochemical or genomics-based studies to inform improvement strategies for bioenergy purposes. The goal of the proposed research is to obtain a genomic and biochemical-based understanding of CAM in Agave necessary for its consideration as a biofuel feedstock. This project will aid our long-term mission in bioenergy research and enable ORNL to be a world leader in Agave biofuel research.

Results and Accomplishments

We have met and exceeded the deliverables for FY 2012. In Task 2A, the short-read sequencing of transcriptome in *A. americana* using Illumina HiSeq2000 has been completed. Forty-five samples (three biological replicates of 15 tissues) were sequenced, and a total of ~851 million high-quality reads were generated, with ~19 million reads per sample on average. The Illumina RNA-Seq reads were assembled into contigs. A high-quality *Agave* unigene set was generated by combining the Illumina contigs with the

Roche/454 sequencing reads obtained in the previous year (FY 2011). Quantitative expression data was obtained by mapping the RNA-Seq reads onto the unigenes. In Task 3, ~72,000 protein sequences of over 10 amino acids in length were predicted from the unigenes. Eighty-seven gene clusters were obtained by k-means clustering of the quantitative expression data. We finished Gene Ontology (GO) annotation of all the *Agave* protein sequences, and identified gene clusters that were over-represented with genes involved in biological process relevant to CAM regulation such as stomatal movement. Co-expression network was constructed. Protein domains and subcellular localization were predicted for all the proteins. We have made very good progress in comparative analysis of CAM species including *Agave* vs. non-CAM species. Furthermore, our bioinformatics analysis identified key *Agave* genes involved in light (i.e., red/far-red, blue light) signaling, circadian clock, and stomatal movement. Several clock genes were cloned and tested using protoplast transient expression system. The results from this LDRD have contributed significantly to the success of our $14.3 million DOE Biodesign (or synthetic biology) proposal.

Information Shared

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05893

Quantifying Economic Losses Associated with Climate Extremes under Conditions of Climatic and Socioeconomic Change

B.L. Preston, W.O. Shem, E.S. Parish, M.C. Maloney

Project Description

The economic costs of extreme weather events have increased markedly in recent decades, largely as a result of socioeconomic processes and trends; yet, quantitative understanding of the interactions between climatic and socioeconomic change on economic damages from climatic extremes is lacking. The parallel application of "top-down" and "bottom-up" analytical methods will be applied within a GIS environment to address this knowledge gap. The Hazards U.S. Multi-Hazard Model (HAZUS-MH) will be parameterized for a cross section of US case study communities as part of a "bottom-up" comparison of economic damages in response to simulated extreme events. Model sensitivity will be tested using a range of hazard event return periods and observed and synthetic development patterns. National Centers for Environmental Prediction (NCEP) reanalysis products as well global and regional climate modeling will be used to quantify changes in the spatiotemporal distribution of climatic extremes given anthropogenic climate change. To generalize simulation results across a range of spatial scales, empirical models of hazard losses will be developed based upon US county, state, and national data for historical losses as well as data for extreme event frequencies and socioeconomic conditions. These top-down models will then be perturbed with climate model projections of extremes and socioeconomic scenarios to estimate future economic losses.

Mission Relevance

The project seeks to improve the scientific basis for assessing the potential consequences of climatic change by linking global and regional modeling of climatic extremes to hazard models for the estimation of economic impacts. The proposed project also seeks to contribute to the development of more integrated assessment tools for estimating future impacts with a particular emphasis on integrating scenarios of alternative demographic and economic futures with information on climate variability and climate change. This work is most relevant to the Office of Biological and Environmental Research, particularly with respect to the development of methods for accounting for the costs of extreme weather events within integrated assessment models.

Results and Accomplishments

Over the course of FY 2012, the project achieved a number of milestones. Outputs from FY 2011 research were presented at an international climate change adaptation conference in May of 2012, and various research outputs have been submitted for publication to a range of journals in the environmental and atmospheric sciences. We have also taken advantage of invitations to collaborate on various publications pertaining to climate change adaptation. New research tasks in FY 2012 focused on developing new quantitative estimates of the relationship between changes in socioeconomic exposure and disaster losses as derived from observed disaster loss data for the years 2007–2011. This has resulted in the first analysis that we are aware of for a US scaling metric and associated uncertainties. This work is currently being prepared for publication. In addition, a significant number of analyses have been conducted focusing specifically on socioeconomic development and exposure in US coastal regions. We have developed a seamless high-resolution data product for US coastal exposure to storm surge inundation from tropical cyclones which has been used to interrogate multiple scenarios of future housing growth to project future changes in housing exposure. This work is also currently being prepared for publication. Finally, a second round of simulations with the Weather and Research Forecasting Model (WRF) was conducted on Jaguar to compare the joint effects of increases in radiative forcing from greenhouse gases and land use forcing from land use change on extreme rainfall events at different resolutions. This work is also being prepared for publication.

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05977

Bacterial Iron and Uranium Redox Cycling in the Contaminated Subsurface

F.E. Loeffler

Project Description

The incomplete understanding of the microbial processes affecting the flux of redox-active metals, including radionuclides such as uranium, in subsurface environments is a shortcoming to meaningfully predict long-term radionuclide mobility and fate. The proposed work will advance scientific understanding towards DOE goals by (i) obtaining oxidized metal-respiring bacterial isolates from contaminated DOE sites, (ii) performing comparative analyses of U(VI)-reducing bacteria to determine differences in reduction rates, mechanisms, growth yields, and response to fluctuating redox conditions, and (iii) identifying biomarkers to measure the presence and activity of relevant bacteria implicated in metal reduction. These efforts will provide relevant new information for monitoring and predicting the contributions of indigenous microbes for the long-term stability and the fate of contaminants.

Mission Relevance

Controlling and predicting the fate and the mobility of DOE-relevant contaminants in subsurface environments is a major challenge. Traditional site remedies are expensive, often without meeting cleanup criteria, and innovative, economically feasible technologies are needed. Knowledge of the microbial processes that affect contaminant transformation is crucial for predicting contaminant flux and longevity, and, if necessary, implementing bioremediation approaches as cost-effective corrective solutions. With increased knowledge of the microbial controls on uranium mobility, the long-term fate of uranium can be predicted with less uncertainty, and resource allocation can be directed towards sites where natural processes are insufficient to prevent uranium plumes from breaching compliance boundaries. At sites that require intervention, the new information generated will allow effective site management at reduced costs. The study of microbial metal cycling and associated carbon and nitrogen fluxes is a focus area of the DOE Office of Biological and Environmental Research (BER) research portfolio, and this project anticipates future funding from DOE BER.

Results and Accomplishments

Distinct bacterial isolates of the genera *Desulfovibrio*, *Anaeromyxobacter,* and *Geobacter* have been obtained from radionuclide-impacted DOE sites, including the 300 Area at the Pacific Northwest National Laboratory and the Oak Ridge Integrated Field Research Center (IFRC). *Anaeromyxobacter* spp. and *Geobacter* spp. reduce U(VI), and we demonstrated that *A.dehalogenans* strain 2CP-C grows with U(VI) as electron acceptor. Oxic-anoxic transition zones are hot spots for redox reactions and control the mobility of relevant metals (i.e., iron) and radionuclides (i.e., uranium). Hence, understanding how metal/radionuclide-reducing bacteria adapted to life in redox transition zones is crucial. Studies with strain 2CP-C suggested that these bacteria are microaerophiles that detoxify oxygen at atmospheric oxygen partial pressures but respire oxygen at lower partial pressures. These features indicate that *Anaeromyxobacter* spp. are uniquely adapted to conditions at oxic-anoxic interfaces where they affect metal redox chemistry, and hence uranium mobility. To monitor *Anaeromyxobacter* spp. activity, the *c*-type cytochromes of strain 2CP-C grown with different electron acceptors were characterized. Specific *c*-type cytochromes were expressed under different growth conditions, suggesting that these electron carrier proteins serve as activity biomarkers. Collaborative efforts with the University of Illinois explored the utility of high-precision uranium isotope fractionation measurements as a monitoring tool for U(VI) reduction. The results of this LDRD project indicate that process-specific biomarker and uranium isotope measurements characterize relevant microbial activities in the subsurface and oxic-anoxic transition zones, and generate new information about the microbiology and the environmental conditions that control contaminant fate and longevity.

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05982

Adaptive OFDM Radar Waveform Design for Target Detection

S. Sen

Project Description

We propose to develop efficient algorithms to detect and track a slowly moving target using an orthogonal frequency division multiplexing (OFDM) radar. The detection and tracking techniques are critical and challenging to the radar technologies used in both the military and civilian applications. We employ a wideband, multi-carrier OFDM signaling scheme that mitigates any possible signal-fading, effectively resolves the multipath reflections, and provides additional frequency diversity as different scattering centers of a target resonate at different frequencies. Moreover, we devise adaptive waveform design techniques to select the spectral parameters of the OFDM signal for further improving the detection and tracking performances. The rationale behind the adaptive waveform design (in a closed loop) is to enable better sensing performance by fitting the operational scenario, in contrast to the conventional open-loop systems.

Mission Relevance

This research has direct relevance to DOE's CESAR program, the Department of Defense, and the Department of Homeland Security. Conventional radar systems, which are designed to operate mainly in open environments, face significant difficulties when targets move in multipath scenarios. Such situations arise in diverse military and civilian applications, such as tracking of ground-moving vehicles or sea-skimmers from an airborne platform. Due to the existence of inherent multipath propagation, these systems encounter a number of demanding issues, such as the presence of significant multipath returns over multiple range cells, spreading of Doppler frequency, and sometimes even the absence of any line-of-sight (direct) path between the radar and target. Therefore, this project aims to address these complex problems as realistically as possible to develop an efficient detection and tracking procedure.

Results and Accomplishments

We employed an OFDM radar to detect a target using a sparsity-based space-time adaptive processing (STAP) technique. We discovered that the OFDM-STAP filter-weights were adaptable to the frequency variabilities of the target and interference responses, in addition to the spatio-temporal variabilities. The variations in the designed STAP-filter weights changed with respect to the target and interference variabilities in a "waterfilling" type approach – allowing easy target detectability along the subcarrier at which the target response was stronger, while simultaneously blocking the interfering signals along some other subcarriers at which the target response was weaker. Furthermore, we proposed a Pareto-optimal OFDM-waveform design technique to improve the STAP performance by better utilizing the frequency variabilities of the scenario. In addition to the standard approach of maximization of the output signal-to-interference-plus-noise ratio (SINR), we simultaneously minimized the Cramer-Rao bound (CRB) on the normalized Doppler frequency, calculated for the known spatial frequency, target response, and interference-plus-noise covariance. To solve the Pareto-optimization problem, we applied the well-known nondominated sorting genetic algorithm II (NSGA II), which belongs to the class of evolutionary algorithms.

To discuss the solutions of the multi-objective optimization problem and to demonstrate the performance improvement due to adaptive waveform design, we simulated several numerical examples. We found that although the optimal solutions of the individual objective functions were not the same, the nature of the objectives were not conflicting to each other and they converged to the Pareto-optimal solution very quickly. We showed a significant amount of improvement in STAP performance due to the use of Pareto-optimal waveform by computing the receiver operating characteristics and CRB on the Doppler frequency estimations.

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06008

Novel Covalent Organic Frameworks with Tailored Carbon Capture Functionality

R. Custelcean, D. Jiang, M. Kidder, E.W. Hagaman, S. Dai

Project Description

We seek to develop novel, robust covalent organic framework (COF) materials with tailored functionality for optimal CO_2 binding, release, and transport. COFs are a new class of materials with exceptional chemical stability and porosity that can provide a much-needed solution to the CO_2 capture problem. The key to COFs for optimal carbon capture is to custom-build their pores for specific CO_2 binding. To achieve this goal, we are asking three specific questions: (1) How can we introduce CO_2-phillic functionalities into COF materials? (2) How does CO_2 interact with these COFs? (3) How can we tune the pore functionality to achieve fast, selective, and reversible CO_2 capture? To address these questions, we will first design and synthesize a new class of COFs self-assembled from CO_2-phillic building blocks, and benchmark their CO_2 sorption. Next, the mechanism of CO_2 binding and transport will be interrogated by in situ vibrational and solid-state NMR spectroscopies, neutron scattering, and molecular simulations, to correlate the structure of the COFs with their carbon capture function. In the end, this research may lead to a new generation of functional COF materials exhibiting exceptional stability and water tolerance, high CO_2 capacity (>30 wt%), excellent selectivity (CO_2/N_2>100), optimal adsorption enthalpy (40–60 kJ/mol), and fast diffusion kinetics.

Mission Relevance

This interdisciplinary research, combining theory with innovative synthetic methods, will likely lead to major breakthroughs in carbon capture materials, thereby positioning ORNL at the forefront of this area of research. Our preliminary results put us in a great position to successfully respond to a much-anticipated BES call on *Carbon Capture*, that was recommended in the recent Basic Research Need document *Carbon Capture: Beyond 2020*. Furthermore, our *materials-by-design* approach is a cross-cutting theme for Office of Basic Energy Sciences (BES). Also, the White House has recently released the Materials Genome Initiative, which recommended the employment of computational tools to speed up the development of the next generation of advanced materials. This research is also relevant to Mesoscale Science; there is an anticipated DOE call on this topic next year, for the development of the next-generation materials from nanoscale to mesoscale, and carbon capture is specifically mentioned as a target.

Results and Accomplishments

Following on the proposed plan to functionalize the COFs with CO_2-phillic ether groups, we have performed extensive molecular modeling and theoretical calculations to evaluate the ability of these groups to capture CO_2 within THF-functionalized COFs (THF = tetrahydrofuran) with interpenetrated 3D diamondoid structures. Our calculations found that, with increasing level of interpenetration (from one- to five-fold), the porosity of the frameworks decreased, while their affinity for CO_2, expressed as the isosteric heat of adsorption (Q_{st}), increased. Thus, the five-fold interpenetrated framework was not only found to be the most stable in the series but also to display the strongest CO_2 binding (Q_{st} = 25.1 kJ/mol) and best CO_2 sorption capacity at 0.1 bar (≈0.5 mmol/g), due to its smaller pore size, resulting in higher density of the THF groups. Another COF system under consideration was based on a 2D hydrazone-linked framework with pores functionalized with polyethyleneoxide units. The question here is: how do the CO_2 sorption properties (i.e., Q_{st}, capacity, selectivity) change with the number of ether oxygens (n = 1–5)? We anticipate that beyond a threshold length, the pending ether groups may act as molecular gates, allowing selective permeation of CO_2 and potentially leading to membrane-based separations. We have recently synthesized one COF within this series (n = 3) and confirmed its structure by powder X-ray diffraction (PXRD). Porosity and CO_2 sorption measurements are currently under way; so is the synthesis of other members in the series.

06060
A Hierarchical Regional Modeling Framework for Decadal-Scale Hydro-Climatic Predictions and Impact Assessments

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Project Description

Probabilistic prediction of climate change at decadal scale, and quantification of its impacts on natural and human systems, is a great scientific challenge, and one that has significant potential to inform decision-making regarding the management of climate risk. Due to their policy relevance, eight to ten global modeling groups will undertake decadal-scale prediction experiments of the global climate as part of the Fifth Coupled Model Inter-comparison Project (CMIP5), whose results will be an integral part of the Fifth Assessment Report of the International Panel on Climate Change (IPCC-AR5). While a new generation of General Circulation Models (GCMs) has improved substantially in the simulation of the large-scale response to climate forcing, GCM resolution and accuracy are still inadequate to fully understand the response of regional-to-local-scale processes, particularly those governing hydro-climatic extremes. To improve on the limitations of GCMs, we will develop a hierarchical regional modeling framework to substantially enhance our ability in the quantitative understanding of the decadal-scale climate change at national and sub-national levels, and its potential implications for energy, water resources, and other sectors. This framework will use a suite of Earth system models and statistical techniques to downscale predictions from a multi-model ensemble of IPCC-AR5 global models to an ultra-high horizontal resolution of 4 km over the United States and South Asia.

Mission Relevance

ORNL has a strong presence in the GCM development community through its contribution in the development and maintenance of the Community Earth System Model; however, there has not been any formal effort to develop the capability in the regional hydro-climatic downscaling and modeling. Development and demonstrating of such capacity will enable ORNL to compete for the leading roles in the national and regional level climate change impact assessments. Moreover, the capability of regional hydro-climate modeling directly aligns with the strategic goals of Department of Energy (DOE) (under *Lead the National Conservation on Energy – Provide Sound Information on Energy Systems and Their Evolution*" and "*Science and Engineering Enterprise – Extend our Knowledge of Natural World*) to improve the accuracy and precision of climate predictions with a particular focus on the regional impacts and to pursue predictive climate models at the regional spatial scale and decadal time scale as part of the U.S. Global Change Research Program.

Results and Accomplishments

This project will provide ultra high-resolution climate projections for the need of climate change impact assessments through the implementation of Earth system models and analysis techniques over the continental United States and South Asia. In FY 2011, a considerable amount of time was invested in compiling and analyzing relevant datasets to develop capabilities and evaluation matrices that will assist in addressing several research questions proposed in the project. We describe these findings in two peer-reviewed studies. First, a manuscript describing the projections of snow-dependent hydrological extremes in multi-model ensemble of GCMs from CMIP5 has been accepted for publication in *Nature Climate Change*. Our results suggest that many snow-dependent regions of the northern hemisphere are likely to experience increasing stress from low snow years within the next three decades, and from extreme changes in snow-dominated water resources should global warming exceed 2°C. Second, a manuscript describing near-term hydrological changes in the western United States is in revision for the *Journal of*

Geophysical Research-Atmospheres. Our results show that an increase in greenhouse forcing results in an acceleration of decrease in spring snowpack and a transition to a substantially more liquid-dominated water resources regime over the next three decades that will have important implications for the availability of water for agriculture, hydropower and human consumption, as well as for the risk of wildfire, forest die-off, and loss of riparian habitat.

Information Shared

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06070

Synthetic Metabolic Pathways for Bioconversion of Lignin and Biomass Inhibitors

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Project Description

Economic conversion of lignocellulosic materials into sustainable biofuels is challenged by the recalcitrant nature of the carbohydrate-lignin matrix as well as toxic, organic by-products generated during the pretreatment process. These inhibitors include short-chain fatty acids, 5- and 6-carbon furans, and various substituted phenolic compounds. This LDRD project will pursue an innovative approach to utilize the lignin fraction of biomass for biofuel production while alleviating pretreatment toxicity by engineering organisms to directly catabolize and assimilate phenolic compounds and low-molecular-weight fatty acids. Cutting-edge tools in metabolic engineering, pathway modeling, and synthetic biology will be employed to develop a new class of advanced biofuel-producing microorganisms that have improved yield and productivity in the presence of otherwise toxic pretreatment inhibitors. Using *Escherichia coli* as a chassis, synthetic metabolic pathways will be engineered to produce advanced biofuels or bioproducts from lignin and other by-products while also allowing cleaner process water. In addition, this work will create a synthetic metabolic network involving uncoupled anabolic and catabolic pathways that will allow higher overall yields and productivities of biofuels beyond ethanol. Further, this project will improve advanced computational tools for genome annotation, especially for biofuel-relevant microbes.

Mission Relevance

Our proposal aims to engineer bacteria to convert lignin into biofuels. A top priority of the Department of Energy Office of Biological and Environmental Research (DOE BER) is to “develop biofuels as a major secure national energy resource.” Bioconversion of lignin into biofuels through our innovative process will help accelerate this development. We will also engineer bacteria to consume toxic compounds common in lignocellulosic feedstocks, such as acetate. Our link to the lignin and acetate in feedstocks therefore has major implications for long-term biofuel viability and rural development, which would be relevant for the DOE Office of Energy Efficiency and Renewable Energy (EERE), and the US Department of Agriculture (USDA), Biomass R&D Initiative. An additional goal of this project is to improve annotation of genes that are only annotated as hypothetical, especially in biofuels-producing organisms. Better annotation will enable improved metabolic models and enhanced metabolic engineering efforts.

Results and Accomplishments

We have designed a metabolic pathway for growth on a model compound that can be derived from lignin by utilizing catabolic genes from a soil bacterium. This pathway was synthesized and functionally expressed in *Escherichia coli*, resulting in cell growth with this compound as the sole carbon and energy source. This strain represents the first step in the engineering of *E. coli* to convert lignin into biofuels. Separately, we have engineered *E. coli* to convert the end product of this pathway into ethanol, albeit at low yield. These pathways will need to be combined to allow bioconversion of lignin derivatives into a liquid fuel. We have also created an *E. coli* strain that bioconverts toxic acetic acid that is present in plant biomass while fermenting glucose to ethanol. In this way, 2 mM acetic acid was consumed during growth on 10 mM glucose, with 95% conversion of glucose to ethanol. We have also developed scalable implementations of the required algorithm for the FROST supercomputer of 1000 cores with MPI and open–MPI libraries, constructed Protein Connectivity Networks for 8,000,000 protein data set, implemented and evaluated several metrics (graph traversing algorithms) for collecting functional assignments in *Clostridium thermocellum*, and developed an analytical approach for estimation false positive and false negative rates through computational means.

06195

Coupled Simulation of Surface-Subsurface Hydrologic Processes and Terrestrial Ecosystem and Climate Feedbacks: From Arctic Landscapes to the Continental United States

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Project Description

The representation of hydrologic processes in current-generation land surface models (LSMs) suffers from over-simplification or complete omission of physical processes. For example, most LSMs have a one-dimensional representation of subsurface flow and heat transport, a unidirectional flow from surface to subsurface, and no freeze-thaw dynamics. To enable study of several important aspects of climate change impacts on hydrology and associated feedbacks, this project aims to improve the state of the art by integrating detailed surface-subsurface thermal, hydrologic, and biogeochemical reaction models with comprehensive models of geophysical and land surface processes, using leadership-class supercomputers. We will develop models of rigorously coupled surface-subsurface hydrologic interactions and subsurface freeze-thaw dynamics, and integrate these into the massively parallel subsurface flow and reactive transport model PFLOTRAN. This extended PFLOTRAN model will be coupled with the Community Land Model (CLM), the land component of the Community Earth System Model (CESM), to enable novel studies, at field to regional scales, of the interactions between surface-subsurface hydrologic and biogeochemical processes and the terrestrial ecosystem and associated climate feedbacks, especially those related to hydrologically induced surface and subsurface carbon cycling. A particular motivation for this project comes from the desire to study permafrost degradation and the poorly understood yet potentially large carbon-climate feedbacks, but the novel capabilities of the new CLM-PFLOTRAN model will have broad utility.

Mission Relevance

Two of the four stated mission priorities for the Department of Energy’s Office of Biological and Environmental Research (BER) are to (1) "understand relationships between climate change and Earth’s ecosystems, and assess options for carbon sequestration" and (2) "predict fate and transport of subsurface contaminants." The proposed work will support and unite both of these priorities by enabling detailed simulations of the interactions between Earth surface and subsurface hydrologic and biogeochemical processes and the terrestrial ecosystem, and associated climate feedbacks. As an example of relevance to priority (1), this work will allow state-of-the-art simulation of landscape processes in permafrost regions, where increased thawing due to climate change has the potential to generate dramatic carbon-climate feedbacks due to increased microbial degradation of stored organic carbon and subsequent release of the greenhouse gases CO_2 and CH_4. These simulations will be of direct relevance to the Next Generation Ecosystem Experiment (NGEE) Arctic project being led by ORNL, a long-term field observation and modeling campaign to study warming in permafrost-affected regions.

Results and Accomplishments

As a necessary preliminary for most of the other aims of the project, we have greatly enhanced the unstructured grid capabilities in PFLOTRAN: the use of unstructured grids enables accurate representation of subsurface features in permafrost regions, allows detailed representation of complex drainage basin topography, and avoids disconnectedness between adjacent thin layers of the thin vadose zone (the below-ground region above the water table) in regional CLM-PFLOTRAN simulations due to stair-stepped representation of surface elevations required by structured grids. We have added a three-phase (liquid, gas, ice) ice model to PFLOTRAN and have verified that it correctly reproduces published observations of macroscale processes important in permafrost-affected soils such as freezing-induced water redistribution, or cryosuction. We have also added a surface water flow capability to the code that is coupled with the subsurface and have tested it in a series of benchmark problems against analytical solutions and also simulations conducted using other codes. Finally, we have developed a driver code to execute Community Land Model (CLM) simulations using PFLOTRAN subsurface hydrology and have verified its correctness in a series of benchmark problems. We have examined the effects of explicit representation of deep groundwater processes enabled by coupling with PFLOTRAN, and are currently running simulations at the watershed scale with the coupled model.

06232

Integrative Signaling Modules Guiding Plant Response to Environmental Stresses

J.-G. Chen

Project Description

As plants are sessile organisms that cannot relocate to escape biotic and abiotic stresses, they have evolved complicated yet precise mechanisms to respond to biological and environmental stimuli. An understanding of the associated signal transduction networks is critical for developing effective strategies for enhancing bioenergy sustainability and for crop improvement. Classical genetic screens have identified many components involved in signal transduction, but it remains unclear how these components interact with each other, how signals are integrated, how signal specificity and fidelity are achieved, and how the mechanism of signal transduction functions at the molecular level. In this project, molecular, cellular, genetic, biochemical, and bioinformatics approaches are being taken to address how the Receptor for Activated C Protein Kinase 1 (RACK1), a versatile scaffold protein, integrates input signals from diverse signal transduction pathways and facilitates the spatial and temporal regulation of signal transduction. The proposed research will develop signaling modules guiding plant response to environmental stresses. The platform established through the research will be an integral component of resources for facilitating the molecular and biochemical studies in both model organisms and bioenergy crops.

Mission Relevance

This project is highly relevant to DOE missions. Tools and technologies of functional genomics are of critical importance to many areas of interest to the DOE, such as bioenergy, carbon sequestration, global climate change, plant-microbe interactions, and biosystems design. Study of plant response to the changing environment and signal transduction is one of the major themes in DOE's Biological and Environmental Research programs and is one of the primary focuses of DOE's Genomic Science Program. This project will also benefit other federal agencies, such as The U.S. Department of Agriculture (USDA) and National Science Foundation (NSF). For example, study of the molecular mechanisms of plant stress responses is one of the primary focuses of USDA National Institute of Food and Agriculture Plant Sciences Program and of NSF Plant Genome Research Program. This project may also benefit the Energy for Sustainability Program launched by NSF.

Results and Accomplishments

The major objective of this project is to identify interacting partners for RACK1 and to characterize the molecular mechanism of action of the RACK1 signaling complex in plant stress responses. We conducted a global search for RACK1-interacting proteins through yeast two-hybrid (Y2H) screens and found that RACK1 is a component of G-protein interactome and that RACK1 interacts with a number proteins including protein kinases/phosphatases, nuclear transport factors, Ca^{2+}-binding proteins, transcription factors, as well as proteins with unknown function. This represents an unprecedented advance of our understanding of the molecular action of RACK1 and forms a foundation for the identification of RACK1-based stressosome. Among RACK1-interacting proteins, we selected With No lysine Kinases (WNK) serine-threonine protein kinases for further characterization because in mammalian cells, WNKs regulate ion homeostasis and other pathophysiological processes including cancer, hypertension, and renal ion transport, but the function of WNKs in plants is poorly understood. We confirmed the interaction using Y2H and bi-molecular fluorescence complementation assays. We demonstrated that WNK8 phosphorylates RACK1. The identification of WNKs as interacting partners for RACK1 and the identification of RACK1 as the substrate of WNKs shed new insight into the molecular mechanism of action of RACK1 signaling complex. We investigated the biological significance of the interaction between RACK1 and WNK8 by examining and comparing the phenotypic traits between *rack1* and *wnk8* single and double mutants. We discovered that RACK1-WNK8 complex regulates seed germination and seed production and is involved in abscisic acid (ABA, a key plant stress hormone) responses.

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06245

An Accurate and Efficicent Computational Methodology for Simulating Disordered Nanoscale Materials

M.G. Reuter

Project Description

Nanomaterials are often suggested as components in numerous next-generation devices, including batteries. Insights from computational studies of nanomaterials can guide the experimental design of these devices; however, nanomaterials are generally too large to simulate with ab initio quantum mechanical methods, especially when chemical defects are present. This limitation has forced the invocation of best-effort, yet often unvalidated, approximations when studying the fundamental effects of disorder on nanomaterials. As such, the principal objective of this proposal is to develop, implement, and apply a computational methodology that will accurately and efficiently simulate both pristine and disordered nanomaterials. A secondary goal is to assess the legitimacy of the aforementioned approximations, which become unnecessary in the proposed formalism. Finally, we aim to apply this framework to (i) determine the persistence of defect-induced effects in nanomaterials; (ii) probe the interplay of multiple defects; (iii) investigate how, and under what conditions, defects alter the flow of electric current through nanomaterials; and (iv) explore interactions, notably charge transfer, between nanomaterials and nearby molecules.

Mission Relevance

Proposed research will be useful in identifying fundamental roles of disorder on the electronic structure and response properties of nanomaterials. The ability to bridge length scales parallels some of the core research activities of the Materials Science and Engineering Division of the Basic Energy Sciences Program in the DOE's Office of Science. Also, the computer-aided design of nanomaterials benefits the construction of better batteries and solar cells (for examples), in line with the interests of the DOE Energy Efficiency & Renewable Energy (EERE) Program.

The development a general computational algorithm for simulating pristine and disordered nanomaterials of arbitrary size will likely be of interest to several Department of Defense (DoD) agencies.

Results and Accomplishments

Development of a Computational Method for Simulating Disordered Nanomaterials

Most of the effort over the last year has been focused on this task. As described in the original proposal, there were two key elements to this task, both of which are now complete.

First, obtaining the Green function for a particular nanomaterial—the key physical quantity containing information on static and dynamic properties—requires algorithms for inverting large matrices. For our applications, the matrices are block tridiagonal and nearly block Toeplitz, where the deviations from a true block Toeplitz structure are caused by disorder in the nanomaterial. Over the last year, we have developed a theory using matrix Moebius transformations for efficiently inverting these matrices. Our new method scales independently with the total size of the nanomaterial and linearly with the number of deviations from the true block Toeplitz structure. Such favorable scaling facilitates the simulation of large nanomaterials.

The second part of this task deals with obtaining the blocks of the matrix to be inverted. In short, we need a quantum chemistry code to calculate and output the Fock matrix for different segments of the system, for example, the bulk "nanomaterial" and any disordered regions. Owing to its favorable scalability and vibrant developer/user community, we chose NWChem for our quantum chemistry code; however, it needed some minor modifications to suit our purposes. For instance, the standard release of NWChem calculates, but does not output, the desired matrix blocks in a usable form. During the last year we have implemented all necessary modifications and installed the code on both the ORNL Institutional Cluster (OIC) and on Jaguar at the Oak Ridge Leadership Computing Facility (OLCF).

Ongoing work is merging these two parts together, which will enable the efficient simulation of large, disordered nanomaterials.

Applications of this Computational Method

We have had conversations with researchers at the Center for Nanophase Materials Sciences (CNMS) to identify possible systems of interest. One promising candidate is epoxy-type disorder in graphene nanoribbons. Besides demonstrating proof of concept of our method, this system can also be used to establish the (in)validity of previous approximations for simulating large, disordered nanomaterials. Items (i), (ii), and (iv), as listed above, will also be considered for this and other selected systems.

Understanding current pathways through disordered nanomaterials [item (iii) above] requires some theoretical development before application of our new computational method. Briefly, all existing current pathway theories are for two-terminal devices. Some nanomaterials, however, are best modeled as multi-terminal devices (more than two), and we have worked toward a theory for these cases over the last year.

While working with CNMS users to develop and validate this theory, several numerical problems arose relating to the non-orthogonality of the basis set. (Basis sets in quantum chemistry codes, including NWChem, are notoriously non-orthogonal.) Although these problems, termed "ghost transmission," have been previously reported [Herrmann et al. 2010. *Journal of Chemical Physics*. **132**, 024103], their cause remains a lamentable mystery. Furthermore, ghost transmission appears to be more insidious when looking at transport pathways than when considering more standard electron transport calculations.

As such, we have made a considerable effort to understand and "exorcise" this ghost transmission from our calculations. We have been able to show that ghost transmission is a numerical artifact caused by inconsistent system partitioning during the derivation of electron transport theory. We are presently finalizing a corrected theory and implementing it in NWChem; preliminary results are promising. Some of the matrix inversion results obtained in the development of our computational method were crucial to diagnosing the cause of ghost transmission.

With these numerical problems solved, we will return to transport pathways, which should be straightforward with the accomplished progress. A publication will be prepared once the theory is finished and substantiated.

Information Shared

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06267

A Generalized Mathematical and Computational Framework for Predictive Simulation of Complex Stochastic Systems

C. Webster

Project Description

Our ultimate aim is to develop novel enabling mathematical and computational methods for uncertainty quantification (UQ) in complex coupled systems. In particular, we will investigate a computational framework to represent and propagate uncertainty through complex system components based on a generalized stochastic Galerkin numerical approximation. Combining this approach with traditional adjoint-based techniques will allow computation of sensitivities of system output statistics with respect to random input distribution parameterizations for solving stochastic inverse, optimization, design, and stability problems. Another crucial component of this effort will be the ability to perform risk assessment studies for complex stochastic systems, for which we will introduce a novel adaptive generalized stochastic collocation (gSC) multi-resolution analysis (MRA) scheme based on hierarchical multi-scale piecewise basis functions constructed from both interpolating polynomials and wavelets. Finally, we will investigate the integration of nonlinear solution strategies and optimal model reduction for strongly coupled multi-component, mixed-fidelity, multi-scale stochastic systems geared to the stochastic representations described above.

Mission Relevance

This work will provide the mathematical and algorithmic foundations for the development of advanced multi-physics and multi-component system-level uncertainty assessment capabilities. Coupled systems with uncertainty represent some of the most challenging computational problems that must be solved to develop truly predictive science capabilities for emerging mission areas, including light water reactors (CASL), renewable energy technology, nuclear energy advanced modeling and simulation (NEAMS), climate modeling, science-based stockpile stewardship and disposal (ASCEM), as well as exascale computing. Substantial impact on scientific discovery, engineering technology, and decision-making processes will result from this effort. Predictive simulations are a critical component of many Department of Defense (DoD) missions including global tracking networks, public policy, and technologies for homeland security, and the importance of UQ to these missions cannot be overstated. Moreover, for predictive computational simulation to have impact on these missions, UQ of complex coupled systems is critically important.

Results and Accomplishments

Our work in FY 2012 has been focused on developing several novel mathematical and computational ORNL capabilities, including the following.

1. A multi-dimensional multi-resolution adaptive (MdMrA) sparse grid stochastic collocation (SC) method. This idea has resulted in an approach whose prescribed error tolerance is reached at the cost of just the optimum number of points (up to a constant) in a sparse grid adaptation process.

2. A scalable, parallel mechanism for stochastic identification/control that integrates an adjoint-based deterministic algorithm coupled with the MdMrA approach. The advantage of our technique is that it allows for the optimal identification of statistical moments (mean value, variance, covariance, etc.) or even the whole probability distribution of the input random fields, given the probability distribution of some responses of the system (quantities of physical interest).

3. A gradient-based model reduction approach for high-dimensional UQ. This approach uses information about the quantity of interest and its derivative from only a small number of samples, and we partition the uncertainty space into active and passive subspaces. We can then use high-order sampling methods but only over the low-dimensional active subspace. Unlike standard reduction methods, the error in our approximation can be analytically bounded. The rigorous bounds show very fast convergence rate.

4. The C++ implementation of the before mentioned algorithms in an advanced ORNL branded Toolkit for Adaptive Stochastic Modeling and Non-Intrusive ApproximatioN (TASMA- NIAN). The application of this effort to supersonic flow with shocks, stochastic turbulence, stochastic ground water flow, etc., has given the PI the opportunity to generate $1,450,000 in follow-on funding from several distinct program offices and industrial partnership (DOD- AFOSR, WFO-Caterpillar, DOE-CASL, DOE-ASCR Applied Mathematics).

Information Shared

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06655
Synthesis of the Heaviest Atomic Nuclei in Experiments Using Californium Targets

R.A. Boll, K. Felker, J. Ezold

Project Description

The objective of this proposal is to establish a new route for super-heavy element (SHE) research and a unique, vital, and enduring role for ORNL's signature capability in nuclear science and technology. The effort aims to exploit a unique californium product that is part of a limited inventory of materials, which could be strategic assets to the scientific community. The work will involve recovery of a californium product that is enriched in ^{251}Cf and demonstration of deposition methods for the preparation of targets for the synthesis of super-heavy nuclei. The initial focus will be the processing of old ^{252}Cf neutron sources, which offer the highest ratio of ^{251}Cf to ^{252}Cf. This will overcome a significant barrier to SHE research by providing feed material for experiments to access elements Z=118 and above that has sufficiently low radioactivity to enable safe target production and handling.

Mission Relevance

Success in this work will invigorate DOEs Nuclear Physics Isotope Program and position ORNL as a leader in SHE research through the development of unique materials and expertise required for target design and production for SHE experiments worldwide.

Results and Accomplishments

Work completed, during FY 2012, relevant to the recovery of ^{251}Cf material, included the following.

(1) The sources currently in the californium storage pool in Building 7930 were evaluated to determine which sources provide the best option for enriched ^{251}Cf recovery. Twelve ^{251}Cf sources, selected for this recovery, have been identified, located, and removed from the storage pool. (2) A tool (small jeweler's lathe) was obtained and modified for the cutting open of the ^{251}Cf capsules. The modifications addressed the safety concern of potential ignition of the zirconium filings. The lathe has a detachable shield to stop flying fragments, a removable collection container, and a sharp edge tool for cutting that will not produce fine power zirconium. The lathe was tested by cutting open simulated zirconium capsules at Building 3525 in an area that is equipped with safety equipment for ignitable materials. Electrical adaptation of the lathe for in-cell use was completed, and the lathe was installed in Cell D, 7930. (3) Cutting open the outer capsule the ^{251}Cf-Zr-encapsulated sources in Building 7930 hot cell began on September 26, 2012.

Work completed, during FY 2012, relevant to the development of electrodeposition method for titanium target production, included the following. (1) Purchased equipment (ultrasonic stirrer, high voltage power supply) for ^{251}Cf electrodeposition process. (2) Reviewed/completed Research Safety Summaries (RSS), Radiation Work Permits (RWP), and operating procedures to include high-voltage equipment and use of additional organic solvents and prepared isopropyl/isobutyl electrodeposition procedure documents. (3) Attended and consulted with experienced target production persons at International Nuclear Target Development Society (INTDS) conference in Germany. (4) Designed and fabricated the electrodeposition unit for the curved rectangular titanium foil sectors which are to be used to assemble an accelerator target wheel. (5) Designed shipping container for completed ^{251}Cf foils.

SUMMARIES OF PROJECTS SUPPORTED THROUGH THE SEED MONEY FUND

BIOLOGY AND SOFT MATTER DIVISION

06639

Detection and Characterization of Mesoscopic and Nanoscopic Bubbles on Patterned and Native Metal Surfaces Using Neutron Small-Angle Scattering and Reflectivity Techniques

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Project Description

Bubble formation on metal surfaces immersed in liquids plays a critical role in initiating boiling, an effective mode of heat transfer in a wide variety of natural and industrial processes. Developments in nuclear reactors, where exceedingly high heat quantities are generated in comparatively small volumes, focus attention on nucleate boiling as a mode of transferring heat at high rates at a constant temperature of the heat transfer surface. The key processes governing bubble nucleation occur on nanoscopic and mesoscopic scales, which are challenging to probe experimentally. To gain such insight, we propose to apply the small-angle neutron scattering (SANS) and neutron reflectometry (NR) techniques to detect the number, size, and shape of the meso- and nano-bubbles on model, nanopatterned as well as native metal surfaces. Co-PIs have extensive experience and expertise in applying SANS and NR to investigate the structure of nanoscopic and mesoscopic objects. We anticipate that these techniques can be successfully applied for detecting and in situ characterizing sub-micrometer bubbles formed at early stages of boiling. Demonstration of such capability will play to ORNL’s strengths and unique capabilities in neutron sciences and materials.

Mission Relevance

Successful completion of this project will have impact in many DOE applications, in particular thermal management of nuclear reactors, as well as in a broader range of power generating systems. Broader applications of highly efficient heat transfer systems based on super-nucleation phenomena include thermal management of high-power density electronics at the level of individual chips as well as at the system level. Furthermore, highly efficient heat transfer based on super-nucleate boiling and condensation is an enabling technology for thermal energy recycling with applications in unattended surveillance systems which are of interest to the Department of Defense (DOD) and the Department of Homeland Security (DHS). The targeted metrology of nano-cavitation will have broader implications in the areas, such as improved antifouling coatings and drag reduction in marine vessel technology [of interest to the Defense Advanced Research Projects Agency (DARPA) and the Office of Naval Research (ONR)] and nanofluids for biomedical applications [of interest to the National Institutes of Health (NIH) and DARPA]. The principal target source of follow-on funding will be the anticipated DOE Office of Basic Energy Sciences (BES) call for proposals in the general area of mesoscale science.

Results and Accomplishments

Execution of the project began on August 30, 2012. Since that time we have identified and manufactured a range of samples for initial scattering experiments. Three different types of nanostructured samples have been fabricated with a similar pore diameter (100 nm) and depth (150 nm) but different pitch of 400 qnd 200 nm. The surface of one of the samples remained hydrophilic, whereas surface of two other samples was hydrophobically modified. Three samples of “native” metals and alloys were prepared for experiments: Zircaloy, SiC, and stainless steel SS316. Beam time proposal for the VSANS instrument at FRM-II neutron scattering facility (Garching, Germany) was submitted and allocated 4 days of beam time. These initial experiments demonstrated a significant difference in neutron scattering from hydrophobic and hydrophilic samples with the same porosity and thus have confirmed the feasibility of the proposed experiments. Experiments were completed on Sept 20, and the data are being analyzed. A proposal for USANS beam time at the National Institute of Standards and Technology (NIST) has been submitted and allocated 3 days of beam time at the end of October. A proposal for SANS beam time (GP SANS instrument, HFIR) has been submitted. A preliminary design of the dedicated temperature controller and sample holders required to perform in situ boiling experiments was developed.

06644

Fabrication of Self-Assembled Superstructures of Opto-Electronic Polymers in Amphiphilic Block Polymeric Systems and Investigation of Their Structures by Small-Angle Neutron Scattering

C. Do, K. Hong, A.-P. Li, W. Heller, G.S. Smith

Project Description

In order to achieve optimized efficiency of organic photovoltaic solar cells (OPVs) based on opto-electronic conjugate polymers, it is critical to understand the relation between morphology and charge transportation property. However, such understanding has not been fully achieved yet due to the difficulty of controlling morphology parameters (e.g., the stacking distance) which determine the performance of these cells. In this work, we plan to understand the relation between the morphology of an opto-electronic conjugate polymer, $P3(EO)_4T$, and the charge transportation properties using a thermodynamically controlled polymeric system which can provide us morphology controllability with sub-nanometer precision. A neutron scattering technique, especially the EQ-SANS, with deuterated materials will enable us to uniquely identify the $P3(EO)_4T$ superstructures in polymeric systems at different phases. The unique contribution of this research lies not only in providing a knowledge of the relation between morphology and charge transportation of $P3(EO)_4T$ but also in establishing a novel method to fabricate ordered and thermoreversible superstructures of $P3(EO)_4Ts$ using polymeric solutions. In addition, the success of this project is expected to offer a new protocol for the design of polymer electronic devices with well-defined morphology and controllability.

Mission Relevance

Understanding of the relation between morphology and charge transportation property of opto-electronic polymers is a crucial step for the optimization of solar cell efficiency. This could provide an improved strategy of designing next-generation polymer-based solar cells. The proposed research develops a new method to fabricate and control the morphology of opto-electronic polymer ($P3(EO)_4T$) superstructures in sub-nanometer scale, which has not been shown before. Moreover, this method, once established, can be extended to design more general polymer electronics. Therefore, the goal of this project aligns well with the missions of BES DOE in search for renewable energy sources. In addition, since this project proposes to use ORNL's two major facilities: the Center for Nanophase Materials Sciences (CNMS) and the Spallation Neutron Source (SNS), we believe that this project can demonstrate the synergic effect of ORNL's capabilities.

Results and Accomplishments

In order to achieve the goal of the project, it is very critical to synthesize two molecules: partially deuterated L62 block copolymers ($(EO)_{10}$-$(PO)_{30}$-$(EO)_{10}$) and poly-thiophene with ethylene oxide side chains ($P3(EO)_4T$). In FY 2012 (project started from August 2012), we have purchased key materials such as deuterated ethylene oxides and thiophene molecules for polymer synthesis. The $P3(EO)_4T$ has been synthesized successfully and is currently undergoing a purification process. Partially deuterated L62 (deuterated ethylene oxide blocks with protonated propylene oxide block) was also synthesized and is currently undergoing a purification process.

We expect that the purified $P3(EO)_4T$ can be dissolved in water up to 20 wt % concentration, which would introduce measurable scattering signals if any kinds of ordered structures are formed when self-assembled with L62 block copolymers. Important feature of $P3(EO)_4T$ polymer is that the boundaries are defined by the distribution of water molecules; therefore, the interaction between $P3(EO)_4T$s can be tuned by controlling the local concentrations via self-assembly.

06667

Freeze Trapping of a Bound Reaction Intermediate Using Neutron Protein Crystallography

L. Coates, K. Weiss, S. Tomanicek, B. Standaert

Project Description

Neutron protein crystallography, which identifies active-site deuterium atomic positions, promises to revolutionize the precision of our understanding of enzymatic reaction mechanisms. However, to date no neutron protein crystal structure bound to a freeze-trapped reaction intermediate has ever been produced. In X-ray protein crystallography, studying protein crystal structures bound to a freeze-trapped reaction intermediates is commonplace. For neutron protein crystallography to advance and become a more widely used technique, a proof-of-principle experiment is needed. Several room temperature neutron protein inhibitor complex structures have been collected only to find the inhibitor is not bound and the neutron beam time has been wasted. Here, we propose to determine the neutron protein crystal structure of a β-lactamase enzyme bound to a mimic of its acylation transition state. This proposed research would utilize unique ORNL capabilities in protein perdeuteration, synthetic chemistry, and protein crystallography to produce world-class science that is only possible with neutrons.

Mission Relevance

This project pushes neutron protein crystallography into new areas and provides knowledge to enable studies on freeze-trapped intermediates from enzymes that are involved in biofuel production. Biofuels are of direct relevance to DOE missions in renewable energy. This proposal will broaden the science and capabilities of the DOE-funded Center for Structural Molecular Biology by adding a new key crystallography capability to study enzyme mechanism.

Results and Accomplishments

We were able to successfully collect cryogenic neutron diffraction data on perdeuterated Toho-1 β-lactamase crystals in complex with a perdeuterated inhibitor using perdeuterated trehalose as a cryoprotectant. During initial studies we identified several instrumental problems that led to icing of the sample; however, we were able to resolve those problems and collect a cryogenic dataset. During this experiment we learned several lessons that will make this sort of experiment possible at ORNL.

Information Shared

S.J. Tomanicek et al., "The active site protonation state of the Toho-1 β-lactamase complexed with an acylation transition state analog inhibitor determined by neutron and X-ray diffraction implicate a role for Glu166 as the general base in the acylation reaction," *FEBS Letters*, 585, 364–368 (January 2011).

BIOSCIENCES DIVISION

06616

High-Throughput Genetic System Development

A. Guss, S. Brown, R. Hettich, M. Leuze

Project Description

Genetic manipulation of microorganisms is a fundamental technology that greatly enhances our ability to understand and manipulate microorganisms. The difficulty in transforming novel bacterial isolates is a primary barrier to both fundamental and applied research. Current methods to transform previously untransformed bacteria rely on ad hoc and strictly empirical attempts, and thus often take from years to decades to develop. This SEED project develops the ability to stably introduce genetic material into previously untransformed organisms rapidly, systematically, and in an informed fashion. This novel approach, utilizing the world-class –omics capabilities at ORNL, has the potential to revolutionize many fields of microbiology where the lack of genetic tools hinders advancement. By understanding the organism-specific barriers to transformation, we expect to be able to develop the ability to transform new organisms within weeks to months. Thus, the ripples from this work would be felt in environmental, medical, and biotechnological microbiology.

Mission Relevance

The ability to rapidly develop genetic transformation methods for any new bacterial isolate will allow rapid advances in both biofuels and environmental (e.g., bioremediation) research performed within the purview of the Office of Biological and Environment Research (BER). For biofuels, new isolates with interesting properties for either fuel synthesis of plant material deconstruction could be rapidly studied and engineered. For environmental research, genetically tractable microcosms of natural environments could lead to better understanding of natural bioconversions of legacy toxins.

Results and Accomplishments

We have performed analyses on the DNA of multiple bacterial strains, including organisms relevant for biofuel production and for bioremediation, to better understand the barriers to bacterial uptake of heterologous DNA for metabolic engineering. Further, we have begun synthesizing the genes for enzymes that will allow us to circumvent these same barriers. We are also developing the technology to perform these same analyses in a more thorough fashion using high-performance LTQ-Orbitrap mass spectrometry. While this tool is still under development, we have demonstrated proof-of-principle analysis using model DNAs. We have begun constructing libraries of plasmids that will be used for our transformation pipeline, which will be integrated with knowledge from the above analyses to test the utility of our proposed pipeline for developing genetic systems in previously untransformed microbes.

06619

Strigolactones in the Woody Bioenergy Crop *Populus*

J.-G. Chen, T. Tschaplinski, W.Muchero

Project Description

Plants are constantly subjected to environmental challenges and have evolved complicated yet precise mechanisms to respond to these challenges. An understanding of the signal transduction system associated with plant-environment interaction is critical for developing effective strategies for cost-effective, sustainable production of plant biomass. One recent breakthrough in the field of plant biology is the discovery of strigolactones (SLs) as a new class of plant hormones controlling plant architecture. More importantly, the synthesis of SLs in plants is regulated by the nutrient availability in soil, and SLs exuded by roots serve as host recognition signals for symbiotic fungi. Therefore, SLs are viewed as integrative signaling molecules that couple nutrient availability and microbial symbiosis to control plant architecture and productivity. However, despite this important discovery, essentially nothing is known about this new class of plant hormones in the woody bioenergy crop *Populus*. Because plant architecture is a key determinant of carbon sequestration, allocation, and biomass production, this project takes an integrative approach using bioinformatics, metabolomics, physiology, and microbiology to define SL pathways and decipher its role in the regulation of plant architecture and plant-environment interactions in the woody bioenergy crop *Populus*.

Mission Relevance

This project is highly relevant to DOE missions. Understanding the regulatory mechanism underlying plant response to the changing environment is one of the major themes in DOE’s Biological and Environmental Research programs and is one of the primary focus areas of DOE’s Genomics Science Program. Furthermore, the proposed research may provide direct knowledge to inform genetic improvement of *Populus* trees maximizing biomass production per unit land area, thus achieving cost-effective and sustainable production of plant biomass, another major theme in DOE’s Biological and Environmental Research programs. This project will also benefit other federal agencies. Specifically, the study of the molecular mechanisms of plant-environment interaction is one of the primary focuses of the U.S. Department of Agriculture National Institute of Food and Agriculture Plant Sciences Program and Sustainable Bioenergy Competitive Grants Program, and of National Science Foundation Plant Genome Research Program and Sustainable Energy Pathways Program.

Results and Accomplishments

The major objective of this project is to identify SLs, their derivatives and biosynthetic intermediates, to identify key genes involved in SL biosynthesis and signaling, and to define SL-mediated physiological and microbial responses in *Populus*. In this reporting year, we have made progress in several areas. First, we have applied liquid chromatography–mass spectrometry (LC-MS/MS) to examine the existence of SLs and their derivatives in *Populus* roots. Preliminary analysis revealed that LC-MS/MS was able to detect synthetic SL analogs at concentrations that are within the range of endogenous SLs reported in other plant species. The detection limit of LC-MS/MS would enable us to examine the presence of native SLs in *Populus* samples. Second, we have identified seven *Populus* genes that are homologous to known key genes involved in SL biosynthesis and signaling, namely, *MORE AXILLARY GROWTH* 1 (*MAX1), MAX2*, *MAX3,* and *MAX4*. By using quantitative reverse transcription–polymerase chain reaction (RT-PCR), we have determined the expression patterns of these seven *Populus* genes across various tissues and organs. Third, we have cloned each of these seven *Populus* genes and transformed them into Arabidopsis *max* mutants to determine whether expression of these *Populus* genes can genetically complement the *max* mutant phenotypes. Finally, we have used gas chromatography–mass spectrometry (GC-MS) to examine the SL-responsive metabolome.

Information Shared

Jake Adcock, Olaf Czarnecki, Jay Chen, Identification of proteins interacting with MAX2, the key signaling component of the strigolactone pathway in plants, Department of Energy Summer Undergraduate Laboratory Internship Program, Oak Ridge, August 2012 (poster presentation).

06620

Biofuel Production from Multiple *Agave* Species

J. Mielenz, M. Rodriguez, T. Tschaplinski, X. Yang

Project Description

Agave is one of the most water-use efficient plants in the world due to its crassulacean acid metabolism (CAM). Surprisingly, initial testing of the leaves of five Agave species has determined that only one species can support fermentation to biofuel: *Agave tequilana*, a species restricted by the Mexican government. The overall goal is to determine the nature of the fermentative limitation in non-*A. tequilana* species to expand the potential of multiple *Agave* species for biofuels when coupled with the results from CAM genetics studies. Without determination of the cause of very poor fermentation, a majority of the *Agave* species may well have limited value for biomass-based biofuels until this problem is solved.

Mission Relevance

Biomass production is currently limited to areas of the United States that have significant rainfall. This leaves much of the US West unavailable for biomass production, as irrigation is too expensive. If the semi-arid (rainfall <31 in.) portions in the western half of the United States could be used to grow biomass for conversion to biofuels, additional sources of biofuels needed to displace petroleum could be produced from otherwise unproductive lands. *Agave* species could be grown as a source of biomass in these areas if the limitation we have identified can be overcome.

Results and Accomplishments

The bioconvertability of five *Agave* species has been investigated: *Agave americana* “Big Blue,” *Agave americana* marginata, *Agave americana* “Gainesville,” *Agave salmiana* “ferox,” *Agave tequilana,* and recently *Agave parryi truncate* and *Agave univittata* have been added as a low-temperature tolerant species. Tests are conducted on the whole plant (above ground) and not centered upon the core piñas, which is used for alcoholic beverage production with old 10+ year plant. We are using 2–3 year old plants. Experimentation is still ongoing for a project stated in February 2012. We have confirmed the poor performance of the first four non-tequilana species regarding fermentation of available sugars to biofuel such as ethanol. Test have included alteration of the fermentation approach such as simultaneous saccharification and fermentation versus separate hydrolysis and fermentation, use of classical detoxification methods such as overliming, removal of potential inhibitory constituents by granular activated carbon, anion and cation exchange resins, and hydrophobic membrane treatment. In addition, we have investigated the use of different enzymes for the breakdown of the complex carbohydrates, such as cellulases, hemicellulases, pectinases, beta-glucosidases, and other similar enzymes. This latter approach is providing improvement in the fermentability of the otherwise recalcitrant *Agave* species. Current experimentation centers on clarifying the role of these enzymes in the bioconversion process. A publication is planned and possibly a invention record, depending upon the status of our cuurent investigations.

06626

Biological Extraction and Sequestration of High-Value Rare Earth Elements

J.G. Elkins, J. Won Moon, K.A. Lowe, T.J. Phelps

Project Description

Due to their unique properties, the technological applications for rare earth elements (REEs) have steadily increased over the last several decades. For example, neodymium-iron-boron magnets are found in computer hard drives, electric vehicles, and wind turbines. The demand for REEs is set to dramatically rise, but the world market is controlled by a single, non-domestic source. Several government agencies seek to diversify the global supply chain and find multiple sources of parent material for REE extraction. This small SEED project will attempt to demonstrate that microorganisms can affect the relative concentrations of REEs in low-grade ore and sludge materials through mobilization or sequestration. Acidophilic iron- and sulfur-oxidizing bacteria will be applied to REE-bearing materials from a phosphate mining and processing facility. Changes in the relative concentration of individual REEs will be determined after incubating a series of microcosms under both mesophilic and thermophilic conditions. A second set of experiments, conducted in parallel, will test the potential for biomineralization of aqueous-phase REEs by coprecipitation and sequestration catalyzed by thermophilic, metal-reducing organisms. Successful proof of concept could facilitate future studies aimed at developing a “biomining” process specific for REE recovery.

Mission Relevance

The Department of Energy released a report in 2010 that identifies which REEs are most important to the clean energy sector while having the largest potential for market shortages. The DOE intends to direct policy and new research aimed at developing nonconventional sources and extraction technologies to circumvent REEs shortages in the short (0–5 years) and medium (5–15 years) time frames. This small SEED is very limited in scope but will allow a defined set of experiments to be conducted. We will test the hypothesis that REEs within low-grade waste materials from a large-scale mining operation can be mobilized or sequestered by using microorganisms. By documenting that REEs, including high-value dysprosium and terbium, can be extracted and enriched from waste material using microbes, we will be in a stronger position to propose larger efforts in future REE-focused research areas of need.

Results and Accomplishments

Acidithiobacillus ferrooxidans and *Metallosphaera sedula* were tested for their ability to solubilize REEs from phosphogypsum (PG), processed sludge (SL), and crushed ore samples. Growth of *M. sedula* was severely inhibited by each type of material when added at ca. 5% to 10% (*w/v*). The cause of growth inhibition could not be determined but was likely due to the solubilization of toxic compounds from the solid materials at higher temperatures. *A. ferrooxidans* grew well in sludge and ore-containing media, achieving cell densities of 2.6×10^6 cells/ml and 2.5×10^6 cells/ml, respectively, while the controls without added solids grew to 1.3×10^6 cells/ml. However, PG added to the growth medium was toxic with no growth occurring during the 14-day incubation period. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on duplicate cultures containing *A. ferrooxidans* and each type of

REE-bearing solid material. The concentrations of REEs La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were determined from the aqueous phase and compared against uninoculated controls. The data were reported as μg REE (released)/ g solids. The PG samples gave the highest release of REEs with Nd at 36.3 μg/ g PG, but this was not due to biological activity since no growth occurred in PG-containing tubes. Samples containing SL or ore actually showed a decrease in soluble REEs when *A. ferrooxidans* was present, suggesting that REEs are bound to other solid phases. Acid solubilization followed by selective precipitation or other separation methods may be an effective strategy for concentrating REEs from phosphogypsum.

06636

The Role of Geometric Structures and Hydrodynamics on Microbial Adhesion and Colonization

A. Kumar

Project Description

Microbial colonization and biofilm formation on medical devices have been recognized to be one of the most significant sources of recurrent infections. For example, infection through catheters alone accounts for hundreds of thousands of infections each year in the United States, which ultimately strains the healthcare system. Novel designs for anti-fouling surfaces are desperately needed, and they represent an active and growing area of interdisciplinary research today. While surface coatings and biomimetic designs have been explored, the role of fluid flow in countering biofouling is yet to be examined. In this project, we propose to investigate novel geometrical designs, which resist fouling by microbes by affecting fluid flow on the surface. The experimental project will undertake investigation of this novel anti-fouling strategy through the quantification of microbial colonization on micro-fabricated structures under various externally imposed hydrodynamical conditions.

Mission Relevance

Fundamental understanding of microbial systems is relevant to the DOE mission of scientific discovery and innovation. The proposed work is expected to benefit energy loss in systems with bio-fouling, and thus the project is also relevant to the DOE mission of energy security. The proposed investigation is also expected to appeal to the Department of Energy Office of Biological and Environmental Research (DOE-BER).

Results and Accomplishments

During FY 2012, progress was made in the study of biomimetic anti-fouling surfaces. Numerical simulations were initially performed using Comsol Multiphysics® to evaluate the effect of mesoscale surface topographies on hydrodynamics. These fluid mechanical simulations were carried out in the laminar flow regime, and the effect of various design parameters on the flow of fluid was evaluated. The simulations are aiding fundamental understanding of the effect of meso-scale topographies and also provided initial design parameters. Microfabrication-enabled platforms were constructed for investigating the effect of surface topography on microbial adhesion dynamics. Various microfabrication-related processes such as photo-lithography and etching processes were employed to construct microfluidic devices. These microfluidic devices are currently serving as a test bed to investigate the effect of mesoscopic topographies on microbial adhesion. Initial experiments have been performed with both particles and microbes, and currently the microbial adhesion in these devices is being evaluated.

06637

High-Performance Computer Simulation Study of the Mechanism of Nerve Agent Degradation by an Enzymatic Bioscavenger

J.M. Parks, J.C. Smith, P. Langan, T.W. Wymore

Project Description

Nerve agent bioscavengers are enzymes that can degrade highly toxic organophosphorus nerve agents. However, their activity toward these substrates must be improved through protein engineering to be sufficiently useful in real world applications. In this work, enzymatic bioscavengers will be studied using high-performance computer simulations to determine their biochemical reaction mechanisms in atomic detail. Wild-type and mutant diisopropyl fluorophosphatase (DFPase) will be studied using pure quantum mechanical and hybrid quantum mechanical/molecular mechanical (QM/MM) free energy simulations. Density functional theory (DFT), ab initio, and semiempirical quantum chemical methods will be used. Protein structures and sequences will also be analyzed using various bioinformatics techniques to suggest mutations that may improve enzymatic activity toward specific nerve agent substrates.

Mission Relevance

Our work is relevant to DOE missions in biological sciences, global security, and high-performance computing, The work is also aligned with the missions of other federal agencies, including, for example, the Department of Defense (DoD) and the Department of Homeland Security (DHS). Indeed, a recent BAA from DoD (BAA 13-1, October 2012) requests proposals seeking to develop “catalytic and/or stoichiometric chemical warfare agent scavengers from biological molecules (e.g., antibodies and enzymes) which provide protection against nerve agent incapacitation and lethality for extended periods following their administration.” We intend to pursue funding through this call once sufficient preliminary data have been obtained.

Results and Accomplishments

We recently hired Troy Wymore, previously at the Pittsburgh Supercomputer Center, to work on this project. He began work on October 1, 2012. His areas of expertise are in QM/MM simulations of enzyme mechanisms, structural bioinformatics, and high-performance computing. He is currently working with the PI to perform simulations of wild-type DFPase with the DFP and sarin substrates to obtain key insight into the catalytic mechanism of the enzyme.

CENTER FOR COMPUTATIONAL SCIENCES

06566

Thermonuclear Supernova Simulation: Towards Increased Physical Fidelity to Calibrate the Dark Energy Standard Candle

O.E. Bronson Messer and W.R. Hix

Project Description

Thermonuclear supernovae (Type Ia SNe) are believed to result from the complete disruption of a massive white dwarf via explosive thermonuclear burning. Their use in cosmology as distance indicators, as well as comprehension of their role in galactic chemical evolution, ultimately depends on a reliable and robust understanding of the explosion mechanism. We have undertaken a study of turbulent thermonuclear combustion in these events, with particular attention paid to the effects of increased physical fidelity in simulations—through increased resolution, increased dimensionality, and more realistic nuclear kinetics—for white dwarf densities believed to be important for deflagration-to-detonation transitions (i.e., transitions from subsonic to supersonic burning) in these events. The resulting models will ultimately be used in full-star simulations of Type Ia SNe, providing previously unattainable realism and providing significantly better simulation data with which to confront observations. We have targeted improvements to physical implementations via new network methods and enhancements to simulation software via exploitation of previously untapped parallelism via node-level threading and the use of graphics processing units (GPUs) to achieve this increased fidelity.

Mission Relevance

This work effectively joins two primary strengths of the Laboratory – leadership-class computing and expertise in nuclear astrophysics and nucleosynthesis – in a single project that directly supports at least two of the near-term priority facilities for the Office of Science, namely, the Facility for Rare Isotope Beams and the Joint Dark Energy Mission. Especially because of their utility in making cosmological distance measurements, the Office of Science High-Energy Physics Program has shown a strong interest in Type Ia SNe science. The National Science Foundations (NSF) and the National Aeronautics and Space Administration (NASA) also support Type Ia SNe investigations.

Results and Accomplishments

We have partially completed a series of detonation simulations at low white dwarf (WD) densities that we will use for baseline metrics against which subsequent simulations can be measured. These simulations have also allowed us to investigate the effects of explicitly suppressing nuclear burning inside numerical shocks (this is the current standard practice in astrophysical simulations of this type), and we are preparing a publication on this issue.

Our quasi-statistical equilibrium (QSE) solver was upgraded in format to be compatible with the multi-solver version of the flexible reaction network XNET, which is the basis of the generalized nuclear burning module we have designed for FLASH. This QSE-enabled XNET module has been installed in FLASH 2.5, and testing and validation are ongoing. The QSE code was also adapted to allow weak reactions to be considered. This modification is not immediately important for our studies at low density, but it ensures that we will be able to use the same network technology for all densities of interest in full-star simulations. Work has also been done to give the QSE-network the ability to select from four choices for the size and the number of QSE groups based on the temperature and density conditions.

We have also completed several initial implementations of a hybrid OpenMP-GPU XNET solver. By experimenting with multiple API's for Jacobian generation (e.g., CUDA Fortran, OpenACC, HMPP directives) and multiple accelerated linear algebra libraries (e.g., CULA, MAGMA, Cray LibSci), we have effectively mapped out the available state of the art for this port.

Information Shared

S.T. Parete-Koon, O.E.B. Messer, C. Smith, W.R. Hix, and M.W. Guidry, "Ash-Detonation Interactions in Multi-Dimensional Simulation of Type Ia Supernovae," *Journal of Physics Conference Series*, accepted for publication, 2012.

CENTER FOR NANOPHASE MATERIALS SCIENCES

05963

Addressable Nanopore Array: Multiscale Fluidic Interface to Cell Culture

C.P. Collier, S.T. Retterer, T.E. McKnight

Project Description

Developing a real-time spatiotemporal map of molecular events that unfold during cell-cell and cell-matrix interactions is critical to understanding the biochemical drivers and consequences of phenotypic changes in individual cells and tissues. However, decoding these complex signaling cascades within a living organism can be extremely cumbersome. Relevant in vitro tissue models and cell culture provide tractable and informative alternatives. The focus of this proposal is to develop and validate a fluid interface to facilitate control and sampling of the local micro-environment surrounding cultured cells. The interface will be comprised of an addressable nanopore array (ANA) etched into an ensemble of surface micromachined fluid channels, which will enable the local delivery of dosing molecules to cultured cells and facilitate the capture of dilute response biomarkers secreted from cell culture into discrete water-in-oil droplets.

Mission Relevance

Successful completion of the work proposed here will result in a technological platform for probing tissue samples in cell culture and for drug screening, disease detection, tissue engineering, and directed differentiation of cells, with improved sensitivity and specificity compared to conventional methods. Results may thus be directly applicable to targeted DOE Office of Biological and Environmental Research (BER) initiatives such as systems biology. In addition, practical technological advances, such as in sensors and detection technology, resulting from this research may be exploited for cross-cutting programs such as environmental quality and national security.

Results and Accomplishments

This year, we have successfully completed Task 2, a demonstration of controlled dosing via steady-state and pulsed concentration gradients from “dosing” pore openings, and Task 3, capture of fluorescent molecules leaked from the main channel into water-in-oil plugs through “sampling” pore openings. For Task 2, dosing involved applying positive pressure to both ends of a surface micromachined dosing channel loaded with an aqueous fluorescent solution, forcing material through the pore into the main channel where cell culture will be located. For Task 3, we detected fluorescent molecules captured from highly dilute aqueous solution from the cell culture area in the main channel, and entrained in ultrasmall water-in-oil droplets in the surface micromachined channel developed in Task 1.

05965

Thermopower at the Atomic Scale

P. Maksymovych

Project Description

This proposal seeks to develop a nanoscale measurement of thermopower, a critically important variable in thermoelectric energy conversion. The past decade has witnessed numerous theoretical and experimental proposals aiming at significant improvement of thermoelectric figure of merit through nanoscale modifications. However, today there exists a tremendous gap between our ability to implement such modifications and to evaluate thermoelectric performance at the commensurate length scale. In this project, we will develop a unique approach for measuring thermopower down to the atomic scale based on scanning probe microscopy. We will be able to measure electronic and thermoelectronic properties simultaneously, and correlate thermoelectric effects on well-defined semiconductor surfaces with the respective behavior in the bulk.

Mission Relevance

Thermoelectrics convert waste heat to useful power and enable electronic cooling, potentially generating tremendous energy savings in each case. New proposals to enhance thermoelectric performance involve non-trivial modifications of the electronic structure (beyond conventional doping), nanostructuring, and surface modification – most of which are not directly accessible by the presently dominant bulk characterization methodologies. This project will develop a method specifically designed to provide the spatial resolution that matches the nearly atomic-scale heterogeneity of nanostructured materials and the energy resolution that enables combined measurement of the electronic structure and the energy-dependent elastic scattering (responsible for thermopower). The methodology will be broadly applicable to electronic conductors, paving the way not only to understanding of thermoelectrics on a local scale but also a novel, atomic-scale imaging of complex electronic properties and phase transitions in solid state electrolytes and correlated electron materials.

Scientific/Technical Accomplishments

The key accomplishment of the project at present is a systematic analysis of the thermoelectric effect in a tunable tunnel junction. The Seebeck coefficient is typically measured with a probe lead (or wire) in mechanical contact with the studied object. Unfortunately, in this case the accessible energy scale is limited only to the immediate vicinity of the Fermi level, while the spatial resolution is > 10 nm in the best cases. We have therefore turned to tunneling contacts, where an atomic-scale vacuum gap separates the lead from the surface. We have successfully implemented tunneling thermovoltage measurements in all-metal tunnel junctions, combining ~20 μV energy resolution at the Fermi level, <1 nm spatial resolution, and an ability to probe occupied and empty electronic states in a large (several eV) window around the Fermi level. The challenge of the tunneling contact, however, is to decouple the contributions of the tunneling transport from the elastic scattering within the material to the net measured thermovoltage. We have proven that (1) it is possible to decouple tunneling and surface-specific thermoelectronic response in a tunable tunnel junction, where the width of the tunneling gap is systematically varied while measuring thermovoltage; (2) the tunneling contribution is directly related to the changes of the effective local work function, thereby directly verifying the Stovneng-Lipavsky model that is often used to interpret tunneling thermovoltage experiments; (3) optimizing the the gap width can significantly enhance thermovoltage contrast, increasing the spatial resolution of thermoelectronic imaging; (4) ignoring the tunneling contribution (as in a number of prior papers) may lead to wrong conclusions on the magnitude of thermopower and type of carriers in the surface; (5) thermovoltage in a tunable tunneling contact can potentially be used to evaluate a thermal gradient between the contact leads without explicit temperature calibration, which is presently not achievable by any experimental technique. Preliminary measurements on the surface of bismuth telluride – a canonical thermoelectric – are currently in progress, together with a more advanced theoretical analysis of tunneling thermovoltage beyond the assumptions of the Stovneng-Lipavsky model.

Information Shared

P. Maksymovych, “Electronic Thermometry in Tunable Tunnel Junction,” Provisional patent application no. 61/697,455, July 2012.

P. Maksymovych, “Single Contact Tunneling Thermometry,” Provisional patent application no. 61/666,322, September 2012.

05968

Probing Oxygen Reduction/Evolution Reactions on the Nanoscale: Towards Viable Lithium-Air Batteries

S. Jesse and S.V. Kalinin

Project Description

Lithium-air battery (LAB) systems are the leading contenders for high-density energy storage, exceeding by more than tenfold the capacities of classical intercalation chemistries and approaching that of hydrocarbon fuels. The broad deployment of Li-air systems is limited by an extremely large charge-discharge hysteresis leading to 30–40 percent energy loss during operation and slow kinetics of the oxygen reduction reaction (ORR). The guided search for effective electrocatalysts is limited by a dearth of experimental information on the factors controlling electrochemical activity. Here, we aim to establish the capability for probing kinetics and thermodynamics of the oxygen reduction and evolution reactions (OER) on the level of single microstructural, morphological, and compositional elements, and rapid screening of local factors affecting electrocatalysis on a single nanoparticle level. The specific aims of the project are (a) development of dynamic electrochemical strain microscopy (DESM) as an enabling instrumentation for probing ion diffusion and ORR/OER on the nanoscale, (b) validation on model system lithium-ion conductors, and (c) investigation of lithium-ion conductors with surfaces treated with catalyst particles. The establishment of this approach will lead to the development of a capability that will propel ORNL to the forefront of competition for applied and basic science DOE funding initiatives in energy areas, establish the infrastructure for cutting-edge energy research, and contribute to resolving one of the longest-standing problems in the electrochemical community – understanding oxygen reduction and evolution on the single-defect and catalyst particle level.

Mission Relevance

The broad implementation of electrical and hybrid vehicle technology, development of distributed energy sources, and optimization of mobile electronic devices requires a significant increase of the stored energy density, ideally approaching that of hydrocarbon fuels. The use of atmospheric oxygen as an active component of the cathode in Li-air batteries and fuel cells directly addresses this challenge by utilizing the oxidizer present in ambient. The rapidly growing effort to develop metal–air batteries is a strong indicator of future trends in the field. However, the progress is stymied by the lack of nanoscale information on the mechanisms underpinning Li-air battery operation, precluding development of the predictive models and optimization of these devices (reducing charge-discharge hysteresis, increasing number of operation cycles, etc). The success of this proposal will open multiple opportunities in (a) basic science of energy storage and conversion systems, (b) future instrumentation development, and (c) Li-air battery development and applications, and will enable a unique characterization tool for probing ORR and OER on the nanoscale with high throughput and applicable to realistic materials systems in realistic environments. The development of local electrochemical characterization on the single-nanoparticle level and its future integration with microRaman, focused x-ray, and other nanoscale structural and chemical probes offer a tremendous potential for future instrumental development.

Results and Accomplishments

The initial studies have demonstrated the feasibility of local formation of Li particles on the surface of Li-ion conductive glass-ceramics (LICGC) with subsequent irreversible oxidation. To mitigate this problem, we have developed a glove-box set-up that precluded particle oxidation, and allowed partially reversible formation of Li nanoparticle, effectively forming world smallest battery. We have further developed SPM based detection based on tip displacement and Faradaic current incorporated in the feedback loop to achieve high-resolution mapping of irreversible electrochemical reactivity on LICGC, and differentiate the reactivity of AlPO4 phase and glass phase. Enhanced reactivity on the interfaces between the two was observed, suggesting an important role that the interfaces can play in the macroscopic ionic conductance of the material. We further extended this approach towards kinetic studies using frequency down-sweep method, and observed switching between two dissimilar regimes attributed to nuclei with 0 and 1 effective atoms size. We explored the role of the second half reaction and demonstrated that quantitative electrochemical studies are possible with an SPM tip, extending the concept of ultramicroelectrode to the nanoscale level. Finally, we demonstrated the formation of devices emulating Li anode in Li-air battery, and hence demonstrated feasibility of studying both cathodic and anodic processes in Li-air battery.

Information Shared

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06260

Towards Atomic-Level Understanding and Control of the Giant Magnetocaloric Effect: Revolutionary Materials for Efficient and Clean Refrigeration

Z. Gai, T.Z. Ward, P. Snijders, M. Stocks

Project Description

The recent discovery of the giant magnetocaloric effect (GMCE) has generated great excitement due to the possibility of developing revolutionary solid-state refrigeration technologies. Compared to current technologies, GMCE refrigeration is environmentally benign and remarkably more efficient. Despite the promise of these materials, a major scientific challenge remains. This challenge originates from the fact that the magnetic-field-induced magnetic phase transition that yields the large entropy change central to GMCE is generally strongly coupled to a structural phase transition, resulting in large thermal hysteresis losses that significantly reduce cooling efficiency. To overcome this major scientific challenge, we propose the novel approach of using epitaxial strain to suppress the structural transition and thus reduce the thermal hysteresis loss. Specifically, we will grow epitaxial GMCE thin films, thereby locking the crystallographic structures to that of the substrates. Moreover, separating the magnetic and structural phase transitions will allow a definitive study of the GMCE mechanism. We bring to bear experimental and theoretical fluency in nonequilibrium growth and magnetic materials to address fundamental science issues of direct energy relevance.

Mission Relevance

If successful, delivery of this proposal opens a whole new perspective for cooling applications, and the field will grow into a much broader program with an impact on advanced energy technologies, and we expect to create intellectual property with great economic potential. The future program could be supported by BES, DARPA, EERE, ARPA-E, NASA, and many industrial R&D programs. This research is aligned with the main DOE mission of BES: fundamental research to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels in order to provide the foundations for new energy technologies and to support DOE missions in energy, environment, and national security. On the more applied side, DARPA's Defense Sciences Office (DSO) programs and Strategic Technology Office (STO) would have interests in this proposal, as our understanding and precise control of the MCE will bridge the gap from fundamental science to applications by identifying and pursuing the most promising ideas within the science and engineering research communities and transforming these ideas into new DoD capabilities.

Results and Accomplishments

In this project, $LaFe_2Si_2$ thin films are successfully grown on Si(111) substrate in a single-crystal format. While the bulk material is nonmagnetic and no MCE, unique to the films, the magnetic property are tuned from Pauli paramagnetic to ferromagnetic, and MCE are observed around 50K. The ferromagnetic transition is a first-order transition, and the magnetic entropy $\Delta S \approx$-8.5 J/Kg K is obtained under a magnetic field of 7 T. The magnetocaloric effect is characterized by a 14 K hysteresis in the field cooling and field warming process. Our temperature-dependent X-ray measurements exclude the correlation between the striking MCE of the thin film and structural transition. Density functional theory (DFT) calculations indicate that the strain-induced distance variations of Si-Fe bonds control the magnitude of the magnetic moment and MCE.

This project provided support to a postdoc (Guixin Cao) for 1 year. Related result will be presented orally at the upcoming APS March meeting in Baltimore. A manuscript is in the preparation process for submitting to a top scientific journal.

Information Shared

Guixin Cao, German Samolyuk, Siwei Tang, Liang Qiao, Wenbin Wang, Jieyu Yi, T.Z. Ward, Michael Biegalski, Wolter Siemons, David Mandrus, Malcolm Stocks, Zheng Gai, "Strain induced ferromagnetism and magnetocaloric effect in LaFe2Si2 thin film," APS March Meeting, Baltimore, MD, 2013.

CHEMICAL AND ENGINEERING MATERIALS DIVISION

06632

In Situ Study of Magnetoelastic Coupling in Magnetic Shape Memory Alloys

X.-L. Wang, A. Pramanick, A.D Stoica, Z. Gai, M. Stocks

Project Description

The goal of this project is to demonstrate the possibility for and benefits of developing atomistic level understanding of magnetoelastic coupling in ferromagnetic martensitic structures, for the future design and development of Magnetic Shape Memory (MSM) alloys. Smart materials that provide rapid responses to mechanical and magnetic stimuli hold the promise for future generations of sensors and actuators. MSM alloys that exhibit such responses can transform a wide spectrum of transducer technologies in diversified fields such as aerospace, automotive, underwater navigation, biomedical, surveillance, and consumer electronics. Compositional and microstructural design of MSM alloys with desired magneto-mechanical responses hinges on a fundamental understanding of the physical mechanisms of strong magnetoelastic coupling. A concerted study involving neutron scattering, spin-polarized scanning electron microscopy, and first-principles calculations is proposed to demonstrate our ability to characterize the coupling between the structural and magnetic order parameters under the simultaneous application of stress and magnetic field. We expect this project to launch a new field at ORNL, attracting future research programs that exploit the coupling between physical properties and mechanical behaviors in the design of new multifunctional materials.

Mission Relevance

The proposed study is of both fundamental and practical interest. DOE BES is interested in exploring the fundamental aspect of the coupling between physical and mechanical behaviors, with the goal to exploit this phenomenon to “control the mechanical properties of materials,” as mentioned in 2010 BES Budget Request for Mechanical Behavior and Radiation Effects. Because of their unique properties, MSM alloys have great potentials for use in sensor and actuator technologies in wide variety of industries, notably the defense industry. In addition to DOE, this project is also of relevance to interests from other federal agencies. The Navy Research Laboratory expressed specific interest in receiving proposals “for research and development of new microsensors and microsystems to measure physical phenomena such as magnetic and electric fields.” The Air Force Office of Scientific Research called for proposals “to establish the fundamental understanding required to design and manufacture new aerospace materials and microsystems for multi-functional structures and to predict their performance and integrity based on mechanics principles.” Other potential funding agencies include the National Institutes of Health (NIH), where MSM alloys are being developed in bio-medical applications as, for example, bone replacement.

Results and Accomplishments

Our in situ neutron diffraction measurements on Ni-Mn-Ga MSM single-crystal samples under quasi-static compressive mechanical stress proved that the pseudo-plastic macroscopic strain arises from microscopic twin variant reorientation [*Scripta Materialia*, **65**, 540–543 (2011)]. We have also demonstrated the capability for in situ study of the magnetization rotation and crystallographic reorientation of twins under magnetic field using neutron scattering. A highlight of our accomplishments is the use of polarized neutron beams to characterize the evolution of magnetic moments in Ni-Mn-Ga single crystals under applied magnetic fields. This was the first time that polarized neutron diffraction was successfully demonstrated on a time-of-flight instrument at a spallation neutron source. The high flux of the neutron beam at the instrument and high polarization efficiency enabled such measurements to be taken within short time frames, thereby facilitating in situ characterization of the material state during application of external magnetic fields. This current methodology enables characterization of the different electronic and structural phenomena that contribute to the overall magnetization of a material, as we have outlined in our recent article in the *Journal of Applied Crystallography*. In addition to neutron scattering measurements, we have measured the magnetic susceptibilities of the Ni-Mn-Ga single crystals at various temperatures from room temperature to 230 K using SQUID. Our measurements show that the process of magnetic-field-induced twin reorientation in Ni-Mn-Ga single crystals is highly temperature sensitive. While at room temperature twin reorientation occurs instantaneously at 0.5 T, cooling to 253 K causes twin reorientation to occur more gradually in multiple increments from 0.5–1 T. We have scheduled beam times for in situ diffraction experiments with neutrons and synchrotron X-ray to understand this phenomenon, which possibly arises due to complex interactions between magnetic moment and crystal lattice. Complementary real-space characterization with spin-polarized electron microscopy and ab initio first-principle calculations are also in progress to supplement our experimental achievements so far.

Information Shared

A. Pramanick, V. Lauter, X.-L. Wang, A. Ke, H. A. Ambaye, R. J. Goyette Jr, J. Yi, Z. Gai, and A. D. Stoica, “Polarized neutron diffraction at a spallation source for magnetic studies,” *Journal of Applied Crystallography* **45**, 1024–1029 (2012).

A. Pramanick and X.-L. Wang, “Characterization of magnetoelastic coupling in ferromagnetic shape memory alloys (FSMA) using neutron diffraction,” invited Review Article, *JOM*, Special Topic: Diffraction across Length Scales, in press, DOI:10.1007/s11837-012-0497-8.

A. Pramanick, X.-L. Wang, K. An, A. D. Stoica, X. P. Wang, J. Yi, Z. Gai, and C. Hoffmann, “Characterization of spin lattice coupling in ferromagnetic shape memory alloys using in situ neutron diffraction,” presented at 2012 MRS Fall meeting at Boston, MA.

A. Pramanick, X.-L. Wang, K. An, A. D. Stoica, X. P. Wang, J. Yi, Z. Gai, and C. Hoffmann, “Characterization of spin-lattice coupling in ferromagnetic shape memory alloys using unpolarized and polarized neutron diffraction,” presented to American Conference on Neutron Scattering, Washington D.C., 2012.

CHEMICAL SCIENCES DIVISION

05964

Microwave Activation for Advanced Catalytic Conversion of Biomass to Hydrocarbon Fuels and Chemical Feedstocks

W.L. Griffith and L.A. Berry

Project Description

We propose to develop proof of principle for a revolutionary new technology for selective microwave activation of catalysts for production of hydrocarbon fuels and chemical feedstocks. This process could convert a number of low-valued by-product biomaterials – lignin monomers, cutin waxes, and fatty acids – to high-valued hydrocarbons and aromatics. Microwave-activated catalysis meets national needs for renewable fuels and greenhouse gas reductions. Process advantages may include (1) reduced temperature operation (150°C less than conventional processes), (2) no added solvents, (3) no hydrogen requirement, (4) high concentrations of a limited number of key target products, and (5) production of aromatics and cyclics needed in “drop-in” fuels. Successful proof of principle could meet the needs of the Department of Energy (DOE), the Department of Defense (DoD), and industry for directly usable, infrastructure-compatible petrochemicals and fuel replacements from biomass. Tasks to demonstrate proof of principle include catalysis, microwave application, and analytical studies to demonstrate the potential utility of advanced microwave-assisted catalytic conversion. Computer models of the system that could serve as a basis for the “full commercial system” extrapolations and estimates needed in downstream technology development proposals are also planned.

Mission Relevance

Successful completion of this project will enable new R&D activities in these DOE Office of Energy Efficiency and Renewable Energy (EERE) areas: (1) Office of the Advanced Materials Program (AM, formerly ITP) orenergy-efficient production of solvents and feedstocks for industrial chemicals from biomaterials – and (2) Biomass Program (BP) – lignin and cutin-based coproducts, infrastructure-compatible fuels. Timing of this Seed Money research is expected to permit targeting of the early stages of these developing efforts: sustainable manufacturing and infrastructure-compatible fuels. In these agencies (Multiagency Biofuels DoD-Navy, DOE, USDA), successful proof-of-principle results could provide the capability to generate required aromatics and naphthenics for military fuels that cannot now be derived from biomass. These DoD components currently fund biofuels programs: (1) Navy (with USDA), (2) Defense Advanced Research Projects Agency (DARPA), 100% bioderived JP-8 fuel, (3) Air Force (green jet fuel), and Marines (emerging, primarily diesel). Mass and energy balance data are critical to completing formalized energy and feasibility assessments in proposals.

Results and Accomplishments

Data that provides a basis for estimating feasibility, energy, and emissions of industrial-scale processes are required in proposals of targetted funders and will be developed. In order to accomplish this, we have completed, evaluated, and verified improvements to an existing small-sample microwave system which provides separate control of microwave application and sample temperature. These accomplishments include (1) added solid-state, low-voltage, variable-frequency microwave amplifier system; (2) added computer controlled, solid-state, high-speed switching to pulse power; (3) added fast response system to monitor power at sample chamber; (4) added computer fine-tuning of the microwave system to minimize reflected power as a function of temperature; (5) integrated these improvements into a LabView control and data acquisition system; and (6) acquired access to a Comsol multiphysics simulation system to support interpretation of the data and estimate scale-up. These improvements establish a testing platform to provide the data required to both establish proof-of-principle and to estimate feasibility and energy for industrial-scale processes as required in proposals of targetted funders. The larger sample size (5 ml) possible with this system will greatly improve our ability to evaluate products and mass balances for samples. In the next year, the improved microwave system will be used to develop proof of principle for microwave-activated catalytic conversion of C8-C25 fatty acids, C18-C25 alcohols, lignin model compounds, and lignins to corresponding hydrocarbons and aromatics.

06246

Synthesis of ^{50}Ti Pentamethylcyclopentadienyl Trimethyltitanium from Isotopically Enriched Titanium Dioxide for Super Heavy Element Synthesis

G.M. Brown, D.A. Hillesheim

Project Description

The synthesis of super heavy elements (SHE) is an important collaborative effort between Oak Ridge National Laboratory (ORNL) and Flerov Laboratory of Nuclear Reactions (FLNR) of Joint Institute for Nuclear Research (JINR), (principal investigator at FLNR – Yuri Oganessian). In order to support the next phases of this partnership, namely, the synthesis of elements 119 and 120, a ^{50}Ti ion beam is required for the “hot” fusion reaction with various isotopes of berkelium and californium. The compound pentamethylcyclopentadienyl trimethyltitanium (Cp*TiMe$_3$) has been demonstrated to produce a stable ion current within an Electron Cyclotron Resonance (ECR) source where the Cp*TiMe$_3$ is introduced to the ECR plasma via the Metal Ions from Volatile Organic Compounds (MIVOC) technique. The objective of this project is to develop and demonstrate a synthetic method that allows efficient and high-yield synthesis of Cp*TiMe$_3$ beginning with ^{50}Ti-enriched TiO_2. This technique will enable the development of titanium beams for future SHE experiments, strengthening ORNL’s visibility in this high-profile research and creating opportunities for increased funding in this area.

Mission Relevance

Fundamental research in the synthesis of SHE is part of the mission of the Office of Science of DOE. The discoveries and advancements in SHE synthesis are of great interest to nuclear physics as a method to empirically test the competing theories of nuclear structure. One theory suggests that an “island of stability” exists in an element with 120 protons and 184 neutrons. This work would provide a pathway to approach this island by the fusion of ^{50}Ti with neutron-rich isotopes of berkelium to produce element 119 and californium to produce element 120. Beyond the physics of the nuclei of SHE's, the chemistry of these elements is of great interest in hopes that observations of relatively stable nuclei will answer questions about the chemical properties of these elements. While theories exist to predict the electronic and chemical behaviors of elements with hundreds of electrons and some experiments have been performed, more experimental evidence is needed to differentiate among competing theories and further the current state of nuclear physics. In order to produce heavier nuclei and approach the "island of stability," one would need to increase the proton count of the target material as well as the proton count of the ion beam element. Since the half-life of elements heavier than californium is unrealistically short for the required 6 months irradiation time of the target by the ion beam, the solution is increasing the Z of the ion beam element. Titanium-50 is a particularly stable, neutron-magic nucleus, with a 5% natural abundance, and it is possible to isotopically enrich a titanium sample to such a degree as to be useful for SHE synthesis. Scientists at FLNR (JINR) have worked extensively with MIVOC techniques for ECR ion sources, and they have identified Cp^*TiMe_3 as a good candidate compound able to meet the required beam intensity and stability characteristics needed for sustained target bombardment in the pursuit of SHE synthesis.

Results and Accomplishments

The specific aims of this project were to (1) develop a high-yield synthetic pathway for Cp^*TiMe_3 based on established organometallic techniques that would allow the valuable, isotopically enriched ^{50}Ti to be recovered from unconverted material and recycled and (2) deliver a sample of normal isotopic Cp^*TiMe_3 (spectroscopically characterized) to our collaborators for beam development and optimization processes. We accomplished these goals and more. Our collaborators at FLNR-JINR provided us a sample of enriched $^{50}TiO_2$ which we were able to nearly quantitatively convert to Cp^*TiMe_3.

We utilized a three-step reaction sequence to demonstrate the quantitative conversion of titanium dioxide to pentamethylcyclopentadienyl trimethyltitanium(IV). In the first step, solid TiO_2 reacts with CCl_4 at 500°C in a specially design, sealed vessel to form $TiCl_4$. In this reaction CO_2 is the only by-product, and the reaction is quantitative (100% yield). Excess unreacted CCl_4 does not impede next step and is carried over. In the second step, titanium tetrachloride is converted to pentamethylcyclopentadienyl trichlorotitanium(IV) by reaction with pentamethylcyclopentadienyltrimethylsilane. The reaction is easily monitored because it is accompanied by a dramatic color change (clear to red). Removal of the solvent leads to crystallization of the Cp^*TiCl_3, which is obtained in 93% yield. For the third step of the process, we took advantage of the fact that Cp^*TiCl_3 reacts quantitatively with organolithium compounds by reacting it with methyllithium. The product is left in solution and transferred to a suitable containment vessel. Extreme care must be taken with this material: it is reactive with water and oxygen and decomposes when exposed to light. The desired product was obtained in this step with a yield of 95%. Using this route, gram quantities of material have been prepared. A proof-of-concept demonstration of titanium recovery from spent material was carried out on the waste generated from converting a non-enriched sample of TiO_2.

$$TiO_2 + CCl_4 \rightarrow TiCl_4 + CO_2$$

$$TiCl_4 + (CH_3)_5C_5Si(CH_3)_3 \rightarrow Cp^*TiCl_3 + SiCl(CH_3)_3$$

$$Cp^*TiCl_3 + 3\ CH_3Li \rightarrow Cp^*TiMe_3 + 3LiCl$$

Following our recognition that Cp^*TiMe_3 was such a sensitive compound, we briefly collaborated with Fred Meyer to investigate other titanium compounds with good volatility as possible sources for a titanium ion beam. Tetrakis(dimethylamino)titanium(IV) and tetra(isopropoxy)titanium have both been used for the chemical vapor deposition of titanium-containing materials. In both cases, Meyer was unable to detect the Ti^{+} ion via ECR or electron impact ionization mass spectrometry. Thus Cp^*TiMe_3 remains as the preferred source for a titanium ion beam.

06248

Polar Perovskite Oxides with Local-Bond Frustration

C. Bridges

Project Description

The goal of this project is to provide experimental confirmation for a novel concept in which chemical disorder can be manipulated to produce enhanced polar behavior in the perovskite structure, and to thereby provide a new, rational approach to the design of polar materials with giant dielectric responses. If successful, it will be possible to predict strategies and even specific compositions for bulk polar oxides with unprecedented properties such as high polarization and giant piezoelectricity. Therefore, this proposal aims to demonstrate an important paradigm in condensed matter sciences: *a rational approach to materials discovery in which compounds with exceptional properties will be discovered and synthesized on the basis of first-principles calculations.* The focus will be the effect on dielectric properties of bismuth substitution into the high dielectric permittivity material $Sr(Zn_{1/3}Nb_{2/3})O_3$, based upon the results of recent computational studies that suggest a large enhancement in dielectric response with doping.

Mission Relevance

The ability to create materials by design has been highlighted as a Grand Challenge in the NRC report *Frontiers in Crystalline Matter*, and the control over and understanding of emergent phenomena is one of the five Grand Challenges of Basic Energy Sciences in the *Directing Matter and Energy* report. A close relationship between theory and experiment is critical to meeting these challenges, as this will enable the optimization of the materials design process by limiting the parameter space for predictive calculations. This project will address these challenges by demonstrating directly that first-principles calculations can be used to provide new materials with enhanced dielectric properties. Furthermore, the development of ferroelectric and piezoelectric polar materials is of interest to the Department of Defense for piezoelectric energy generation, sensors, and fuel injectors.

Results and Accomplishments

(x) $Bi(Zn_{2/3}Nb_{1/3})O_3$ – (1-x) $Sr(Zn_{1/3}Nb_{2/3})O_3$ system

The high dielectric permittivity parent compound $Sr(Zn_{1/3}Nb_{2/3})O_3$ has been prepared and confirmed to be phase pure. Initial attempts to form the x=0.5 sample predicted by Density Functional Theory (DFT) were unsuccessful. Therefore, reactions for the x = 0.05, 0.1, and 0.2 compositions were carried out. X-ray diffraction data show that higher temperature re-firing of the x=0.2 composition did not completely remove impurity peaks. Repeated re-firing even of the x=0.05 sample did not remove impurities. The impurity level was observed to vary as a function of doping level. From the diffraction pattern it can be determined that a polar perovskite oxide is present, but that this is likely to be the x=0 end member $Sr(Zn_{1/3}Nb_{2/3})O_3$. These results suggest that at ambient pressure it is not possible to form the predicted compositions (x) $Bi(Zn_{2/3}Nb_{1/3})O_3$ – (1-x) $Sr(Zn_{1/3}Nb_{2/3})O_3$, where $x \neq 0$. Therefore, initial investigations on two other systems predicted in the literature by DFT to show enhanced dielectric responses have shown promise for the presence of pure compositions, and suggest that with further investigation they may provide a useful experimental confirmation of the materials by design approach.

06266

A Dereplication Strategy for Natural Products Discovery

G.B. Hurst, D.A. Pelletier, M.B. Shah, T.-Y.S. Lu, K.G. Asano

Project Description

Natural products (NPs) have proven beneficial for human health, agriculture, and industry. Many NPs originate from secondary metabolites produced by microbial organisms in order to enhance their survival in competitive native habitats. The ORNL Plant-Microbe Interfaces (PMI) Scientific Focus Area has developed a unique collection of over 1000 microbial strains isolated from the root tissues and surrounding soils of mature *Populus deltoides* trees. Currently, the PMI collection is not being evaluated for production of novel beneficial NPs. We propose a strategy for surveying this collection for nonribosomal peptides, a class of secondary metabolites that has yielded antibiotics (bacitracin), immunosuppressives (cyclosporine), and antitumor agents (actinomycin). To avoid rediscovery of previously known compounds (“dereplication”), we propose mass spectrometric profiling of microbial culture extracts, grouping similar mass spectra via spectral matching, and distinguishing spectral groups for “known” compounds from groups representing potentially novel compounds. The latter groups will be further tested for bioactivity.

Mission Relevance

Nonribosomal peptides (NRP) mediate microbial interactions with their environments. In soil microbial communities, flow and sequestration of nutrients, interactions with other microbes and with plant hosts, and other important phenomena affecting production of biomass and fixation of carbon may be affected by the production of nonribosomal peptides. Tools for studying NRP, such as that proposed here, could benefit future studies relevant to DOE missions in energy and the environment.

Nonribosomal peptides (NRP) are the basis for many compounds investigated as potential drugs by the pharmaceutical industry. New methods to discover novel NRP would benefit institutes within the National Institutes of Health (NIH) such as the National Institute of General Medical Sciences (NIGMS), the National Cancer Institute (NCI), and the National Institute of Allergy and Infectious Diseases (NIAID). We plan to submit a proposal to the NIH for funding to extend these studies to a larger subset of the PMI bacterial isolate collection.

Results and Accomplishments

We performed research in five areas: development of a method for detecting NRP, extracting NRP from bacterial culture supernatants, initiating a spectral library for NRP, informatics for matching spectral signatures of NRP, and characterization of NRP produced by selected PMI bacterial isolates.

We chose tandem mass spectrometry for generating spectral signatures of NRP, because of our existing infrastructure for proteomics studies. We modified existing proteomics protocols for analysis of NRP, using a platform based on liquid chromatographic separation interfaced with tandem mass spectrometric measurement (LC-MS-MS).

We successfully demonstrated both liquid-liquid extraction into ethyl acetate, and solid-phase extraction (SPE) for enriching NRP from bacterial culture supernatants.

We compiled an initial library of spectral signatures for 17 commercially available NRP. These compounds generally provided rich signatures, which should form a reliable basis for spectral matching.

We evaluated computational matching of spectral signatures of known NRP in a library with newly obtained spectral signatures. Initial results suggest that we can potentially determine rapidly whether NRP produced from a bacterial strain correspond to previously discovered compounds, thus reducing time and expense for further characterization.

We applied these approaches to a standard bacterial strain (*Bacillus subtilis* ATCC 6051) that produces the NRP surfactin, successfully identifying the compound. We obtained initial data for five PMI bacterial strains, and are finalizing analysis of these results for evidence of NRP production.

Information Shared

G.B. Hurst, D.A. Pelletier, M.B. Shah, K.G. Asano, and T.-Y. S. Lu, “A Dereplication Strategy for Natural Products Discovery,” poster presented at the Seventh Annual LDRD Poster Session, ORNL, September 10–12, 2012.

06624

High-Rate High-Capacity Reversible Multielectron Cathodes

C. Bridges, M.P. Paranthaman, G. Veith

Project Description

The goal of this project is to examine whether nitride modification can be used to provide a new approach to the design of high-capacity, high-rate capability cathodes for reversible batteries. If successful it will be possible to overcome traditional problems with irreversibility and poor conductivity of state-of-the-art multielectron cathodes. This proposal aims to demonstrate that *the key to a breakthrough for high-rate capability and reversible capacity is to dramatically improve the conductivity of a high-capacity conversion electrode material*. Our goal is to demonstrate an electrode with a high specific capacity at $30^{o}C$ and at high currents, and to develop an understanding of how nitride anion modification can be used to dramatically enhance conversion cathode performance at high rates. The focus is on the use of surface and bulk modification of metal fluoride cathodes, and the formation of nanostructured composites for enhanced electrochemical performance.

Mission Relevance

There is an urgent need for new electrochemical cell chemistries to achieve increased electrical energy storage capacity and rate capability for future energy storage needs, yet few viable new cathode materials have emerged. A highly attractive approach highlighted in the BES report on *Basic Research Needs for Electrical Energy Storage* is to utilize a redox couple involving multiple oxidation states of the electrode material, as has been demonstrated in metal fluoride conversion cathodes. This work will address a key challenge in energy storage, provide a pathway for increasing energy density, and is of interest for the Office of Basic Energy Sciences, the Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technology program, and Industrial Technology Program (ITP).

Results and Accomplishments

Nitride modified powders have been prepared, both with surface and bulk modification. The surface modification has thus far failed to demonstrate a notable improvement in electrochemical performance, though work is ongoing to improve upon this result. The bulk modification has demonstrated a notable enhancement in rate capability and cyclability in cycling tests with CR2032 coin cells. We have examined the impact of voltage range and cycle rate on capacity, and are expanding this to consider the influence of temperature and particle morphology.

06630

Inexpensive Efficient Hybrid Neutron Sensor

J. Xu, Z.W. Bell, D.L. Pickel

Project Description

To detect neutrons emitted from special nuclear materials (SNM), sensitive and inexpensive solid-state neutron sensors are needed. Our ultimate goal is to develop a low-cost three-dimensional (3D) interdigitated hybrid material with increased neutron detection efficiencies of 30–40%. The proposed hybrid micro-structure consists of n-type ZnO microcones and a p-type polymer/boron containing blend filling in the space between the microcones. The *novelty* of this structure includes (1) a unique electric field created by microcones that allows efficient collection of radiation-generated charges and (2) the inexpensive polymer that serves to convert neutrons to alpha particles and conduct hole carriers. Intrinsic neutron detection efficiency for proposed hybrid microstructure is expected to be ~40%. This efficiency is many folds higher than the efficiency provided by current neutron detectors using coated planar diodes. *The proof of principle* of this SEED project is, in basic, to demonstrate diode characteristics of the proposed hybrid materials and, in aggressive, to deliver a preliminary neutron detection efficiency of 5–10%. This project is planned into two phases. In the first phase (9 months), a functional planar n-ZnO/p-type polymer/boron containing blend hybrid will be demonstrated by measuring its diode properties. In second phase (3 months), a prototype microcone-based hybrid neutron sensor will be demonstrated with a preliminary efficiency of 5–10%. Achievement of this preliminary result can potentially obtain funding from the Department of Energy Defense Nuclear Nonproliferation Research and Development (DOE NA22), The Department of Defense Defense Threat Reduction Agency (DoD DTRA), and the Department of Homeland Security Domestic Nuclear Detection Office (DHS DNDO).

Mission Relevance

DOE NA22 has repeatedly called for proposals to develop solid-state neutron detectors, to replace ^{3}He gas tubes. This is expected to continue because of the national shortage of ^{3}He and the urgent demand for preventing nuclear proliferation. In this project, we would demonstrate the proof-of-principle for inexpensive efficient boron-containing hybrid materials as micro-structure neutron sensors. The microstructure is expected to have the potential of achieving ~40% neutron detection efficiency at low cost because such a structure is capable of tolerating defects and will be made of inexpensive materials.

Results and Accomplishments

ZnO nanowires with the desired morphology were grown on an aluminum zinc oxide (AZO) buffer layer substrate using a thermal chemical vapor deposition process that we developed to provide vertical alignment of the nanocones. Achieving vertical alignment requires the deposition of a 200-nm-thick AZO film as a buffer layer prior to cone growth. The ZnO nanocones, with an approximate length of 1 μm, covered the entire substrate with a cone density of ≈ 14 cones μm^{-2}. The next step was to develop a polymer film for containing the boron (B) precursor. Phosphonic ester functionalized poly(3-hexylthiophene), P3HTs, to surface coat the ZnO nanowires, were prepared by Grignard Metathesis Polymerization, followed by post-polymerization functionalization. Characterization of the phosphonic ester functionalized P3HT by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) showed the presence of the desired end-functionalized polymer in about 40% yield, but it is expected that this can be increased upon further optimization of the reaction conditions. Solutions of the phosphonic ester functionalized P3HT in chloroform were prepared for preliminary studies. Initially, the polymer will be drop cast onto model substrates, such as flat films of ZnO. If this fails to lead to uniform films, then we will experiment with spin coating the polymer films. The initial objective of these coating studies were to confirm that the phosphonic ester functionalized P3HT would coordinate with the ZnO surface providing intimate contact between the polymer and ZnO. The extent of surface coverage on flat ZnO will be assessed by ellipsometry and atomic force microscopy (AFM). Once it has been shown that good surface coverage is possible on flat surfaces, extension to the ZnO nanowires should easily follow. The next steps will be to identify a proper B precursor molecule for incorporation into the film, an appropriate solvent to use for dispersing it into the polymer, and finding a way to functionalize the P3HT so that it will interact with and mix thoroughly with the B precursor molecule.

COMPUTATIONAL SCIENCES AND ENGINEERING DIVISION

05884

Drag Reduction with Superhydrophobic Surfaces

C. Barbier and B. D'Urso

Project Description

Superhydrophobic surfaces such as leaves of a lotus plant consist of a hydrophobic surface combined with microstructures or protrusions. These surfaces are extremely difficult to wet, and recently they have been shown to reduce drag in water flow. However, their drag reduction has been investigated mainly in the laminar region (small objects, small velocity), and few data are available in the turbulent regime (larger objects, larger velocity), where most practical applications are.

We will fabricate a new generation of superhydrophobic material that will combine both microscale and macroscale features for optimizing drag reduction in the turbulent regime. These materials will be tested in the Center for Nanophase Materials Sciences (CNMS) with a cone-plate rheometer. In parallel, numerical tools will be developed and validated on these measurements. They will be then used to demonstrate the capabilities of these materials for practical applications such as pipelines or seafaring vessels.

Mission Relevance

The scope of this work is consistent with DOE's commitment to nanotechnology research and development as well as to advanced computational methods. This research will expand the application of superhydrophobic surfaces for drag reduction in pipelines, on ships, and in many other contexts. In so doing, it creates the potential for substantial energy savings in the wide range of applications where drag creates energy losses. Thus, it is well aligned with DOE objectives.

An efficient drag reduction technology will be particularly useful to the Department of Defense or Office of Naval Research for their vessels, and the Department of Agriculture for irrigation applications.

Results and Accomplishments

The slip boundary condition was implemented in OpenFOAM and was validated with theory. A series of calculations was run for two different slip lengths (25 and 50 μm) for a cone-and-plate geometry and a range of rotational speeds varying from 25 to 1,000 rpm. Convergence of the calculations was improved by writing an application that maps the fields from one case to another by multiplying the pressure and velocity fields with an appropriate factor. The simulations were mainly used to determine the slip length in the turbulent regime.

The superhydrophobic samples began with annealed 99.9995% pure aluminum discs, which were cut flat by single-point diamond turning. For grooved samples, a series of concentric grooves (or riblets) were cut into the sample with a 90 degree dead sharp diamond tool. The surface structures were formed on the surface by a series of anodizing steps in citric acid with alternating etching steps in 2% tetra methyl ammonium hydroxide. The anodizing steps created aluminum oxide pores that grow into the aluminum substrate, while the etching widens the pore at each step. The combined effect was to create flared aluminum oxide pores which intersect each other, leaving a pattern of sharp surface features. Finally, the samples were spin coated with a sub-micron-thick layer of Hyflon AD60, a hydrophobic polymer, which leaves the surface superhydrophobic.

Samples with 10, 100, and 1,000 micron deep grooves were tested at CNMS with a commercial rheometer (AR 2000, TA Instruments) with an angular velocity between 2 and 150 rad/s. A stainless steel cone 60 mm in diameter, 2^{o} in cone angle, and 51 μm in truncation was used. A sample holder was built in order to test the samples at rotational speed above 80 rad/s. At low Reynolds number, drag reduction varying from 10 to 30% is observed. As the rotational speed increased, the drag reductions decreased but remain above 10% for the surfaces with 100 and 1,000 micron grooves. Based on the simulations, the slip length of the grooved superhydrophobic surfaces was on the order of 100 microns, which is two times larger than the slip length found in the literature in the turbulent regime. The sample with the 100 micron deep groove performed especially well over the whole flow conditions investigated with a drag reduction ranging from 10 to 15%.

Information Shared

C. Barbier, B. D'Urso, E. Jenner, "Drag Reduction with Superhydrophobic Riblets," ASME 2012 International Mechanical Engineering Congress & Exposition, Houston, TX, Nov. 9–15, 2012.

06254

Event Enemeration for Security Analysis of Embedded Systems (EESAES)

N. Paul, J. Poore, T. Swain, L. Lin, C. Nolan, G. Lamb

The authors recognize Jesse Poore's contribution, who is now deceased. His work and encouragement on this effort helped ensure itssuccess.

Project Description

We developed a proof-of-concept system for discovering security vulnerabilities in embedded systems (e.g., a Smart Grid AMI meter). We adapted the sequence-based specification theory, originally developed to refine requirements and produce precise specifications, to find security vulnerabilities in embedded systems. Our original hypothesis was that we could adapt the research and tools of sequence-based specification to systematically and mathematically find security vulnerabilities through event enumeration.

Software is developed and released without benefit of exhaustive analysis of its behavior in all possible sequences of events. Consequently, it is released with inconsistency and incompleteness in behavior that become security vulnerabilities. Beginning from a well-defined system state such as power-on or reset, we can enumerate the complete set of events that allows for systematic system state analysis. This produces a mathematical model of the "as-built" behavior, based on user guides and experimentation, that we can analyze from a security perspective. We found several challenges that we were able to overcome in this approach, and the resulting research direction and tool prototype are now *attackability metrics* – a comprehensive tool that allows one to assess the relative security of a given system.

Mission Relevance

This research directly supports DOE Strategic Theme 1 (energy security) and DOE Strategic Theme 3 (US economic competiveness and U.S. scientific discovery). Rather than relying on human intuition and expertise, by using an automated rigorous mathematical process to find security vulnerabilities, we can increase the probability that we find security vulnerabilities in software. By applying this approach to Smart Grid software, we can strengthen US energy security, and, through its application to other software, this will ultimately give the US a competitive advantage. (Software will contain less security vulnerabilities after undergoing this event enumeration security analysis.) Detecting security vulnerabilities in software is a problem throughout the federal government. Within the Department of Homeland Security (DHS), the Science and Technology Directorate has recently been reorganized to promote cyber security at the top level. Safeguarding and Securing Cyberspace was one of the five core missions of DHS identified in the DHS Quadrennial Review, with an objective to invest in innovative technologies to secure cyberspace.

Results and Accomplishments

We evaluated our hypothesis of systematically finding vulnerabilities and did the following.

- Found that our original hypothesis was not feasible given our approach to the our initial abstraction level

- Changed our initial approach to a successful methodology where we identified a way to measure relative security through attackability metrics. This approach used event enumeration, but it did so through first building a slightly modified model of the system.

- Successfully shared our initial work with the Department of Defense (DoD) SPIDERS program and was given the task to apply our work to the SPIDERS’ tasks

- Received additional funding to apply this work to the evaluation of medical device systems. As a member of the leadership board of the National Health Information Sharing and Analysis Center (NH-ISAC), we are now using our work to further the mission of DHS to protect our national critical health infrastructure.

06622

Experimental Validation of Revised Electrodynamics

L.M. Hively, P.G. Evans, D.L. Fugate, M.W. McCarthy, J.K. Munro

Project Description

Classical electromagnetism needs a “gauge condition” to solve Maxwell’s equations. A revised theory avoids a gauge by adding scalar-wave energy ($\xi^2/2$) to the classical Lagrangian. ξ is a dynamical quantity, $\xi = -\nabla \bullet \boldsymbol{A} - \varepsilon\mu\, \partial\Phi/\partial t$, rather than zero as in the Lorenz gauge. $\boldsymbol{A}$ and Φ are the vector and scalar potentials, respectively. ε and μ are the permeability and permittivity, respectively (not necessarily vacuum values).

This theory predicts an energy-carrying scalar wave, and a longitudinal-electric wave (LEW) that carries energy and momentum. The goals are (1) a clear, testable prediction and (2) use of the prediction from (1) to design of a simple, directly falsifiable experiment to distinguish the waves from background and systematic noise.

Mission Relevance

This work addresses basic physics at the most fundamental level in support of the U.S. Department of Energy's Office of Science mission, "Science for Discovery," which seeks to unravel nature's deepest mysteries. The Office of Naval Research (Division of Ocean Sensing and Systems Applications) is developing communication systems that operate in the ELF/VLF bands (100 Hz–10 kHz), as a trade-off between bit rate and send-receive distance. The US Navy needs higher speed, which could potentially be realized by the new waves.

Results and Accomplishments

The revised theory predicts an electro-scalar wave that involves joint propagation of the longitudinal-electric and scalar waves for a gradient-driven current (no current loops). No detection of the electroscalar wave would falsify the revised theory. Detection at >5 standard deviations would falsify the Lorenz gauge (ξ=0) and support the revised theory.

We attempted two experiments. One test launched a TM11 mode at 10 GHz from a rectangular waveguide, and measured the on-axis longitudinal electric wave (LEW) versus distance from the radiating open end. The LEW power decreased over one wavelength, and then oscillated with a period of 3 cm, due to re-radiation from the electric-dipole detector. (Reflections and scattering have a period of 1.5 cm.) Any detector will have this problem, implying that this approach is not a good test of the theory. Moreover, this experiment did not guarantee no curl-free currents (e.g., with a longitudinal, non-conductive gap). The reciprocity theorem states that a charged cylinder can also be a receiver of electro-scalar wave from the sun. However, no voltage fluctuations occur in a fully charged super-capacitor, because a closed loop exists. Another experiment is planned for the next phase of this work. Specifically, charge will be moved from one charge storage device to another (e.g., conducting, spherical shell) by a voltage source. After removal of the voltage source, current will be allowed to flow between the charge-storage devices. Classical theory predicts that the current flow will generate a magnetic field; the revised theory predicts no magnetic field.

Information Shared

L.M. Hively and G.C. Giakos, "Toward a more complete electrodynamic theory," *Int'l. J. Signals and Imaging Syst. Engr*. **5**, 3–10 (2012).

COMPUTER SCIENCE AND MATHEMATICS DIVISION

05905
Asynchronous Algorithms for Exascale Computations

R. Deiterding and J. Barhen

Project Description

Harnessing the compute power of the upcoming generation of exascale super computers is a daunting task. Exascale machines will consist of millions of parallel computing elements, thereby mandating changes in the present computational algorithms. One of the most promising paths forward builds upon the concept of concurrently asynchronous algorithms. This involves a methodology that implements concurrent tasks in a parallel solver, built on a fixpoint iteration scheme, without explicit waiting at synchronization points. While the theoretical conditions for convergence of numerous asynchronous iterative methods are well established, almost no practical results are available for the current generation of distributed memory high-performance computing systems. The objective of this proposal is to quantify the benefit of asynchronous iteration for prototypical, yet representative, parallel linear algebra solvers. In order to obtain results of general practical interest, we are concentrating on the two most important classes of iterative methods for sparse linear problems: multigrid algorithms and Krylov subspace methods. In particular, we are investigating the benefit of asynchronous communication in the smoothing iterations of a grid-based geometric multiplicative multigrid implementation as it often occurs in simulation codes based on partial differential equations and in the solving iterations of a conjugate gradient method for signal processing.

Mission Relevance

Linear iterative methods are among the most crucial components for obtaining good scale-up of simulation software on exascale systems. Numerous application codes, for instance, in fusion or combustion simulation, engineering or astrophysics, require implicit discretizations on computational meshes, thereby leading to large sparse linear problems. The Department of Energy Office of Advanced Computing Research has a fundamental interest in exploring new classes of linear iterative algorithms for sparse problems that can effectively use exascale systems. The effective utilization of exascale systems is also of great interest to numerous other federal agencies, including the Department of Defense, the National Aeronautics and Space Administration, and the Missile Defense Agency, which carry out large-scale simulations of (partial) differential equations using linear iterative methods.

Results and Accomplishments

Concentrating on exascale architectures, we have implemented a large number of prototypical iterative grid-based smoothers for the Poisson equation that are parallelized with domain decomposition using message passing (MPI) and employ multi-threading on graphic processing units (GPU) to perform local smoothing iterations quickly. After first tests with entirely chaotic communication, we are focusing on applying asynchronous iteration for communication reduction and increasing local workload. In general, the speed-up from GPU-accelerated execution is of critical importance to compensate for the reduced convergence rate in asynchronous methods. Our prototype implementations with hybrid MPI-CUDA parallelization exhibit significant runtime improvements for simple iterations methods with $O(N^2)$ algorithmic complexity (N denoting the number of unknowns). Some improvements could also be found for parallel smoothers in a full geometric multigrid algorithm, the most effective iterative method with O(N) complexity. For MPI-only and hybrid MPI-OpenMP implementations, the inevitable convergence rate reduction results generally in reduced performance, underscoring why asynchronous iteration has hardly been employed on existing petascale machines.

Further on, we have implemented a novel Central Processing Unit/GPU-parallel conjugate gradient method for inverting a noise covariance matrix from sensor analysis. The approach employs a tailored preconditioning and performs matrix-vector multiplications without explicit synchronization. Within the context of CUDA streams, the execution of concurrent GPU compute kernels is overlapped with data transfers and host computations, which allows a major reduction of idle times and exploits the hundreds of cores on the GPU device. The combination of all these measures results in a runtime reduction by a factor 50 and larger.

Information Shared

B. Cuff and R. Deiterding, *Hybrid parallelization of iterative methods*, ORNL/TM-2012/493, Oak Ridge National Laboratory, Oak Ridge, Tenn. (2012).

E.Ponce, E., N. Imam, and J. Barhen, “Conjugate gradients implementation on a Tesla GPU: a tool for fast hyperspectral sensor signal optimization,” Proceedings of Third International Conference on Engineering Optimization, Rio de Janeiro, Brazil (2012).

C. Kotas, E. Ponce, H. Williams, and J. Barhen. “Coherent spatio-temporal sensor fusion on a hybrid multicore processors system,” Proceedings, 15th International Conference on Information Fusion, Singapore, 2012.

06255

Scalable Algorithms for Structure Identification on Tree-like Complex Networks

B.D. Sullivan, M. Mahoney, A. Adcock, C. Kotas

Project Description

Large-scale, complex networks naturally represent relationships in a variety of settings, for example, social relationships, computer/communication networks, and genomic sequences. Efficient analysis of these networks is an outstanding issue important to numerous sponsors, including Department of Energy (DOE) / Advanced Scientific Computing Research (ASCR), as analysis can reveal important details about social hierarchy, computational bottlenecks, etc. We propose to advance the state of the art in complex network analysis by investigating and characterizing relationships between two notions of "tree-like-ness" for large-scale complex networks.

Although there is a large body of work suggesting that such networks have tree-like properties, existing algorithmic/statistical tools for identifying tree-like structure were developed for more structured applications, limiting their usefulness. The two notions we focus on are hyperbolicity, a geometric notion describing the maximum deviation of shortest path distance from a tree metric, and tree-width, a combinatorial quantity from structural graph theory measuring the scale of the subgraphs which must be collapsed in order to see an underlying tree. To date, there is little research elucidating and exploiting the relationships between them. Establishing theoretical connections, bounds, and heuristics will have implications for algorithms in areas including compact routing, sparse spanners, and community detection. This work will establish the proof-of-principle evidence connecting hyperbolicity and tree-width needed for future proposals to pre-identified sponsors.

Mission Relevance

The proposal supports the DOE mission by laying the groundwork for new methodologies for understanding petascale data and complex networks, both areas where we have strong indications of future calls and investment through the ASCR Applied Mathematics program. Specifically, our methods will help elucidate the "intermediate structure" of complex networks – salient characteristics and structural properties which are not captured by local metrics (e.g., clustering coefficient) or global ones (e.g., degree distribution). This intermediate structure plays a critical role in the dynamic evolution of the network and the behavior of diffusion processes on it, two problems identified as critical in DOE workshops.

Results and Accomplishments

Technical accomplishments include the design and implementation of OpenMP codes for computing Gromov hyperbolicity, k-core decompositions, and new visualization techniques. These codes enabled computation of exact hyperbolicity distributions for the largest networks ever to be analyzed. The team has also formulated a new conjecture relating hyperbolicity to tree-width in terms of isometric cycle lengths.

This project led to the award of funding to the PI under the Defense Advanced Research Projects Agency (DARPA) Graph-theoretic Research in Algorithms and the PHenomenology of Social networks (GRAPHS) program. The new project, SPARTN: Sparse Projections Achieving Randomization in Tree-like Networks, is a joint effort with Stanford University.

The PI (Blair Sullivan) has been asked to speak at several invitation-only workshops, including "Large Graphs: Modeling, Algorithms, and Applications" at the Institute for Mathematics and its Application, "Geometry of Large Networks" at American Institute of Mathematics, and the Institute for Computing in Science Workshop "Graph and Hypergraph Problems in Computational Science." She has also given invited talks on work originally stemming from this project at Emory University, the University of North Carolina at Chapel Hill, Georgia Institute of Technology, Duke University, and the Workshop on Massive Modern Data Sets.

Finally, two Oak Ridge High School Math Thesis students, Megan Kelly and Neall Caughman were named Siemens Semifinalists for their work on sparse data dimensionality reduction related to this SEED project mentored by the PI.

06618

I/O Coordination to Improve Application Performance Stability on Exa-scale Platforms

X. Ma, R. Gunasekaran, S. Vazhkudai

Project Description

High Input/Output (I/O) performance variability has become a severe problem, which hampers the productivity of extreme-scale applications on leadership computing facilities. This is fundamentally due to the shared nature of supercomputers and further deteriorates as the machines continue to scale. However, existing job scheduling algorithms and execution environments do not take into consideration the interference between co-executing jobs. In this project, we are exploring a new approach to mitigating I/O performance variability to analyze the contention behavior on shared storage systems, and enable I/O-aware job scheduling. Such contention-aware handling has not been previously studied for parallel job scheduling, and our project will bring paradigm changes to how parallel jobs are scheduled on shared supercomputing platforms. In this Seed project, we are focused on examining the feasibility and potential gain of capturing applications' I/O patterns for the purpose of I/O aware job scheduling and reducing intra-application interference by moderating the usage of storage resources for jobs running concurrently.

Mission Relevance

The project will take an initial step towards a revolutionary advancement in parallel I/O handling and batch job scheduling. We will be able to improve both individual applications' performance stability and resource utilization at leadership-class computing facilities. We are collecting data from the Oak Ridge National Laboratory (ORNL) leadership compute platform –Titan – and working to improve widely used scheduling algorithms, which increases the chances of proposal acceptance. With preliminary results showing the promise of I/O-aware scheduling, there will be a substantial amount of research to solve challenging problems, meriting 3–5 years of further investigation. I/O and storage system scalability and performance management have been explicitly listed in research priorities and proposal solicitations by multiple institutes such as the Department of Energy (DOE) and the National Science Foundation (NSF). This project especially fits the DOE Exa-scale programs and the NSF Computing and Communication Foundations Program.

Results and Accomplishments

In this project, we are developing a novel approach to characterize data-intensive applications' I/O behavior from noisy, zero-overhead server-side I/O traces collected without interfering with the scientific applications' compute and I/O cycles. We are specifically targeting I/O-intensive applications running on Titan, the primary peta-sale compute platform at ORNL. The server-side I/O traces are collected from Spider storage system, which primarily serves the Titan supercomputer plus several smaller clusters. The server-side trace is simply the read/write throughput measured from each of the 96 RAID controllers at a moderate time granularity, once every two seconds. Such server-side traces contain no information regarding individual applications' I/O workloads. However, each instance of a target application's execution will result in a segment of server-side I/O throughput trace, which we call a trace sample. We use the scheduler's log to identify the time period during which a specific application of interest ran, and collect the I/O trace sample for that time period. By collecting multiple such trace samples and correlating them together, we filter out the "background noises" and identify the target application's native I/O traffic.

We have accomplished two major milestones in this project. First, we have proven and established the viability of using zero-overhead server-side I/O measurements and schedulers log to profile applications without interfering with the applications compute cycle in real time. Second, we have developed a wavelet-transformation-based approach towards identifying an applications signature from noisy I/O measurements. We first tested our approach by generating well-defined workloads using the standard IOR tool and extracted the workload signature from the server side trace. We are currently evaluating our approach of extracting the I/O signature from real-application runs that ran on Jaguar (prior to the upgrade to Titan) and the Spider storage system.

06623

Joining Neutron Scattering and Simulations towards Improved Lipid Models Ring

X. Cheng, J. Katsaras, J.C. Smith, R.F. Standaert

Project Description

Understanding the structures and properties of membranes is critical to many biological processes and technologies. Unfortunately, atomic-resolution structures are not obtainable for hydrated membrane lipids because of their fluid-like characteristics. Critically, neutron scattering offers substantial contrast between the lipid molecules and D_2O, thus providing vital information required for the determination of membrane structures. However, the neutron scattering data require simulation models for interpretation. While molecular dynamics (MD) simulation has become a standard tool for interpretation of membrane neutron data, there remain hurdles to the full exploitation of the unique advantage of high-performance MD simulation in neutron membrane research. The biggest challenge is the lack of accurate lipid models (that describe how atoms interact with each other in the system) specifically optimized to reproduce the overall structures of membrane bilayers. Here, we propose to improve atomistic force field models of biologically relevant lipid molecules through critical comparison of neutron scattering and simulation data. The success of the project will open new opportunities for neutron scattering studies of biomembranes and their interactions with cationic peptides, anesthetics, and membrane proteins, thus developing a leading-edge biomembrane neutron and simulation platform that should help bring ORNL to the forefront of biomembrane research.

Mission Relevance

The methodology developed here in refining the analysis of scattering experiments by MD simulation will benefit the neutron user program and in-house R&D by creating a vastly improved membrane modeling capability, which could be incorporated into larger proposals to DOE programs funded through several offices including the Biological and Environmental Research (BER) Genomic Science Program, Bioenergy and Structural Biology Program, and the Basic Energy Sciences (BES) user facilities, and Physical Bioscience, Biomolecular Materials, and Chemical Physics programs. The platform may also be expanded to study efflux pumps (counteract microbe toxicity), which are thought to be central to large-scale biofuel production. Therefore, this work will also be highly relevant to the DOE BER Advanced Biofuels Program.

Results and Accomplishments

We have aimed to combine high-performance molecular dynamics simulations with X-ray and neutron scattering experiments to elucidate the structure of a few biologically relevant lipid molecules, including 1,2-di-O-hexadecyl-sn-glycero-3-phosphocholine (DHPC), 1-stearoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (SOPE), 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-L-serine (POPS), n-dodecyl-β-D-maltoside (DDM), and cardiolipin. We have completed parameterization and validation of the force fields for DHPC. Specifically, a scattering density profile for the ether lipid bilayer was developed from MD simulations, which was then used to simultaneously fit the experimental scattering data, yielding the various bilayer structural parameters. Constrained surface area MD simulations were performed to reproduce the experimental data. This iterative approach resulted in good agreement between the experimental and simulated form factors. Detailed molecular interactions taking place between cholesterol and ether lipids were then determined from the validated MD simulations. The insights gained into cholesterol's molecular organization within ether lipid bilayers and its interactions with ether lipid molecules lend a general understanding to the molecular mechanism of ether lipid–mediated cholesterol trafficking, and the roles that the different lipid species have in determining the structural and dynamical properties of membrane-associated molecules. Systematic improvement and validation of the force fields for the other four lipid molecules are currently in progress.

06625

Multigrid Algorithm for K-Version Finite-Element Method

R.S. Sampath and S. Allu

Project Description

The finite-element method (FEM) is the most widely used numerical technique for solving partial differential equations (PDEs), which are used to model various processes in almost all branches of science. The k-version FEM, which was developed recently, is a more efficient framework for solving PDEs compared to standard FEM because it generates smaller systems of equations for the same accuracy in the solution. However, the size of the problems that can be solved today using the k-version FEM is critically limited by the solvers available. Over the past three decades, some very powerful methods have been developed to solve the systems of equations resulting from FEM. The most notable of these is the multigrid algorithm. However, multigrid is not a general-purpose algorithm; its implementation depends both on the problem being solved and the numerical methods used to solve it. Multigrid algorithms have traditionally focused on standard FEM; the objective of this proposal is to extend multigrid to the k-version FEM, test it on a model problem, and quantify the benefits of the approach.

Mission Relevance

The Applied Mathematics program of the Department of Energy (DOE) Office of Advanced Scientific Computing Research (ASCR) within the office of science has a fundamental interest in developing highly accurate and efficient methods to solve PDEs; the proposed work will be directly relevant to this program. The method developed in this proposal could also support the DOE initiatives on Uncertainty Quantification (UQ) and Exascale Computing by helping to reduce modeling/discretization errors and effectively utilizing the available computing resources to deliver more accurate results.

The proposed work is also aligned with the interests of the Computational Mathematics program of the Air Force Office of Scientific Research (AFOSR) and the Mathematical Sciences research program of the Army Research Office (ARO), both of which support fundamental research on fast and higher-order accurate numerical techniques.

Results and Accomplishments

We developed a code to generate the k-version shape (FE basis) functions in one, two, and three dimensions and for ‘k’ = 0, 1, 2..., 10. We used these shape functions to discretize the Poisson equation on a uniform mesh and formed an equivalent system of linear equations. We used a conjugate gradient (CG) solver preconditioned using an algebraic multigrid (AMG) algorithm to solve this system of equations; we used the CG and AMG implementations provided in the Trilinos package for this purpose. We also developed a parallel (MPI-based) geometric multigrid algorithm (GMG) to solve this system of equations; we used the PETSc package to handle the basic matrix and vector operations, LU factorization, and standard iterative schemes like Jacobi, Gauss-Seidel, and CG. The restriction and prolongation operators used in our GMG are different from those used in the standard GMG for h-version FEM discretizations because they must account for the fact that that the entries in the discrete representation of a function for the k-version FEM not only correspond to the nodal values of that function (as in the h-version case) but also the higher order derivatives of that function. We used standard iterative relaxation schemes like Jacobi and Gauss-Seidel as smoothers for both AMG and GMG. We tested the performance of AMG and GMG in one, two, and three dimensions, for different values of ‘k’, and for different mesh sizes. We observed that both AMG and GMG converged to the solution at a rate that is independent of the mesh size. However, the setup cost for GMG was much lower than that of AMG. If we fixed the number of smoothing iterations at each level of the multigrid V-cycle, the convergence rates (for both AMG and GMG) deteriorated with increasing ‘k’. Currently, we are designing a new smoother that would resolve this issue. The code being developed as part of this project is available at http://code.google.com/p/kfemg/source/checkout.

06666

Ultrafast Structural Dynamics Probed by Photoionization and Microwave Rayleigh Scattering from Laser-Induced Plasma

F. Rudakov

Project Description

Resonance Enhanced Multi-Photon Ionization (REMPI) coupled with photoelectron spectroscopy and mass spectrometry has been widely used for studying ultrafast photoinduced chemical reactions. Both photoelectron spectroscopy and mass spectrometry perform extraction of charged particles from the ionization region and therefore require high vacuum, yet the rates and quantum efficiencies of chemical reactions may be greatly affected by the environment. Moreover, molecular collisions may result in chemical reactions, which cannot occur in a molecular beam.

We propose implementing a recently developed technique, Radar-REMPI, which allows for detection of photoionization process at a broad range of pressures, for studying ultrafast photoinduced reactions under chemically realistic conditions. In the proposed design the molecules under investigation are ionized. Photoionization results in a small-volume plasma, which is detected via microwave Rayleigh scattering. Within the Rayleigh scattering limit the amplitude of the scattered microwaves is proportional to the number of electrons in the plasma. Measuring the intensity of the scattered microwaves as a function of the time delay between pump and probe pulses reveals information on the lifetimes of the electronic states involved in photoinduced chemical reaction.

Mission Relevance

The Department of Energy has several programs in the field of ultrafast studies. The proposed technique is scientifically novel and allows molecular structure changes under chemically realistic conditions to be observed. Rydberg electron binding energy spectra are insensitive to molecular vibrational motion. Therefore, the technique can also be utilized for nonintrusive and in situ detection of combustion intermediates, and since the complexity of the Rydberg spectra does not scale with the size of the molecule, the technique can be potentially applied for characterization of biomolecules, large organic molecules, and clusters. The proposed design may also find applications in nuclear cycle monitoring and nonproliferation control.

Results and Accomplishments

Using our experimental setup consisting of Nd:YAG pumped OPO coupled with a microwave homodyne transceiver detection system, we demonstrated capability of Rydberg spectra for distinguishing between chemicals with very close structures. Even a subtle change in molecular structure is reflected in Rydberg electron binding energy. In our design we performed photoionization using 266 nm photons and photons in the range of 460–2400 nm. The laser-induced plasma was probed with 11 GHz microwave radiation. We observed that at resonance conditions between the 3s state and higher lying Rydberg states, the ionization efficiency drops (which is opposite to what is usually observed). We performed time-resolved measurements aimed to explain the dips in the ionization efficiencies at resonance conditions.

The experimental data obtained as a result of this work was utilized in the following three proposals, two of which were submitted to the National Science Foundation (NSF) and one to the Army Research Office (ARO).

- Peter Weber and Fedor Rudakov (Co-PI), “Ultrafast Structural Dynamics in Highly Energetic Molecular Systems Probed by Photoionization and Microwave Rayleigh Scattering,” white paper was submitted to ARO and invited for full proposal submission. The proposal is under review.

- Fedor Rudakov (PI), “Ultrafast Structural Dynamics in Highly Strained Hydrocarbons Probed by Photoionization,” submitted to NSF. The proposal is under review.

- Fedor Rudakov (PI), “A new Spectroscopic Tool: Standoff Trace Chemical Sensing Using Two-Dimensional Ion-Dip Spectroscopy,” submitted to NSF. The proposal is under review.

ENERGY AND TRANSPORTATION SCIENCE DIVISION

05962

$CuInS_2$/ZnS Core/Shell Nanocrystals—A Designer Red Emitter to Revolutionize Solid-State Lighting Technology

M. Hu, Q. Dai, I. Ivanov, C. Duty

Project Description

This project has investigated a unique integrated surface/defect engineering approach (via nanocrystal surface shell growth, molecular ligand passivation, plus pulsed thermal annealing) to achieving high photoluminescence (PL) efficiency and stability in a novel $CuInS_2$/ZnS nanomaterial for use as a designer red emitter in solid-state white lighting technologies. An environmentally benign, non-injection chemical synthesis process has been studied. Such a designer material has high potential to replace the currently used red emitters in industry that face issues in efficiency and toxicity as well as criticality of supply. We have verified and evaluated the proposed approach regarding individual/combined effectiveness in reducing the defect level and thus enhancing the quantum efficiency of red emission. This effort attracts collaboration and sponsorship from industrial and government sponsors, and development of such emitters could provide the means by which DOE's need for safe, efficient light sources could be met.

Mission Relevance

This project is directly relevant to the mission in energy efficiency and clean energy. We expect relevant upcoming opportunities for advanced material/process development and application in energy technologies with the Solid-State Lighting program of the Office of Energy Efficiency and Renewable Energy (EERE) Building Technologies Program, the Advanced Manufacturing Office, and the Solar Energy Technologies Program. It could also benefit the Department of Defense Defense Advanced Research Projects Agency (DOD/DARPA) and the National Institutes of Health (NIH).

Results and Accomplishments

The project has focused on demonstrating an integrated surface/defect engineering approach to achieving high efficiency and stability in the proposed nontoxic nanomaterials. A reproducible and potentially scalable green chemistry process for surface shell and ligand engineering, followed by thermal annealling, is used to synthesize the nanomaterials. We expect the resulting designer red emitter to have a significant impact on solid-state lighting applications. We have collected essential data on emission efficiency, stability, reproducibility, and process scalability.

This project has established the chemical synthesis procedures and completed time-course kinetic studies for both nanocrystal $CuInS_2$ core and ZnS shell. We have verified the reproducibility of the core/shell nanocrystal synthesis. We have achieved demonstration of nearly two-orders-of-magnitude enhancement of PL emission intensity in the desirable red emission range. This proves that the low lattice mismatch (2–3%) between $CuInS_2$ and ZnS helps the low-defect growth of shells to enhance the PL emission efficiency. Repeated stability data were also collected, indicating that shell protection significantly improved the stability. FY 2012 effort has further refined the core-shell synthesis strategy, identified proof-of-principle results for pulsed thermal annealing reduction of defect levels in processing thin films, and demonstrated applicability of the microwave-assisted process.

Information Shared

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Andrew J. Haring, Amanda Morris, and Michael Z. Hu, "Controlling Morphological Parameters of Anodized Titania Nanotubes for Optimized Solar Energy Applications," *Materials* 5 (September 2012).

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Michael Z. Hu, "Engineering of NanoMaterials for Clean Energy Applications," invited talk, 2011 International Conference on Small Sciences (ICSS2011), August 15–18, 2011, Sydney, Australia.

Steven M. Klase and Michael Z. Hu, SULI poster presentation, "Chemical Synthesis of $CuInS_2$ Quantum Dots Nanocrystals for Clean Energy Applications," ORNL, August 12, 2011.

05967

Transition-Metal Carbides as Ingredients for Active and Stable Bio-Oil Upgrading Catalysts

J.-S. Choi, V. Schwartz, S.A. Lewis

Project Description

This project addresses a critical technical challenge in developing pyrolysis-based processes to produce infrastructure-compatible hydrocarbon fuels from lignocellulosic biomass: to design active and stable catalysts for pyrolysis oil (bio-oil) upgrading with minimal use of precious metals. We will demonstrate a novel class of catalysts by incorporating molybdenum carbides as substitutes for platinum-group metals, a key component of the best-known catalysts in bio-oil upgrading. The precious-metal-like surface reactivity as well as refractory character of carbides could lead to active and stable catalysts in the upgrading of water-, oxygen-, and acid-rich bio-oils. To achieve desired catalytic performance, surface properties of molybdenum carbides such as hydrogen activation and hydrophilicity-hydrophobicity balance will be controlled with nano-synthesis and micro-scale characterization capabilities. Catalytic performance will be evaluated in laboratory reactors using model compounds representing different fractions of bio-oils to broadly assess the upgrading potential of carbide-based catalysts. The study of the catalyst durability aspect will be particularly emphasized.

Mission Relevance

With DOE's move away from biomass conversion technologies for producing ethanol to those for producing drop-in biofuels, thermochemical technologies are receiving much greater emphasis. Pyrolysis is a particularly promising technology. However, bio-oils produced from pyrolysis are not suitable for direct application in internal combustion engines without further upgrading. To enable pyrolysis-based processes, effective catalyst technologies need to be developed. Conventional catalysts developed for the petroleum industry have proven inadequate for bio-oils. This project aims to address this challenge by developing novel catalysts that can strengthen DOE biofuel programs (Biomass Program, Vehicle Technologies Program). Catalytic technologies enabling biofuels production should benefit the US Department of Agriculture (USDA) and the Department of Defense (DoD) as well, which are increasingly promoting production of advanced biofuels from renewable sources. In particular, the USDA supports research projects to accelerate the development of a commercial advanced biofuels industry based on non-food, non-feed biomass crops.

Results and Accomplishments

Significant progress has been made in the synthesis, characterization, and evaluation of catalytic performance and hydrothermal stability of molybdenum carbides. The results confirmed the potential of transition-metal carbides as active and stable bio-oil upgrading catalysts. A series of bulk molybdenum carbides were prepared and characterized with x-ray diffraction, BET, x-ray photoelectron spectroscopy, microscopy, and CO chemisorption to determine structural changes as a function of synthesis parameters and hydrothermal aging conditions. Using a laboratory batch reactor, carbides were evaluated in the hydrodeoxygenation of guaiacol and acetic acid as well as real bio-oils. Carbides were active and, under certain conditions, outperformed a commercial carbon-supported ruthenium catalyst. Furthermore, carbides showed unique product selectivity and good hydrothermal stability in the harsh upgrading conditions employed in this study. Our results were shared with the DOE Office of Energy Efficiency and Renewable Energy (EERE) Biomass Program, which has decided to support this work, beginning in FY 2013 as a directed research project, to develop carbide-based catalysts tailored to bio-oil upgrading processes.

Information Shared

J.-S. Choi, V. Schwartz, E. Santillán-Jiménez, M. Crocker, S.A. Lewis Sr., H. M. Meyer III, K.L. More, "Catalytic Performance of Molybdenum Carbides in Aqueous-Phase Hydrotreating of Acetic Acid," to be presented at the ACS National Meeting, New Orleans, LA, April 7–11, 2013.

06351

Improving the Efficiency of Small-Volume Engines Using Thermally Insulating Cylinder Materials

M.D. Kass and B.C. Kaul

Project Description

The proposed effort seeks to improve the efficiency of miniature reciprocating engines (<10 cc cylinder volume) to enable the feasibility of hydrocarbon fuels for propulsion and small electrical power generator applications by incorporating a ceramic liner to reduce both fuel and thermal losses during combustion. Hydrocarbon fuels have over 45 times more energy density than the best lithium batteries; however, because the efficiencies of these engines are less than 5%, they are not feasible sources for power or propulsion (in many cases). The small cylinder volume causes high loss in efficiency for two reasons: (1) the increased surface area-to-volume ratio translates to high heat loss via conduction through the cylinder liner and (2) the piston-wall gap clearance relative to the cylinder volume is large enough to allow a significant fraction of the compressed fuel (and reactants) to escape from the combustion chamber. One consequence of these two effects is that mini-engines must be operated at excessively high speeds (typically greater than 2000 rpm) in order to maintain stable combustion, which unfortunately translates directly into high frictional losses and also limits combustion optimization. Replacing the standard steel liner with a silicon nitride material having lower thermal conductivity and thermal expansion will reduce both thermal and mass losses, resulting in significantly increased efficiency.

Mission Relevance

The goal of the proposal is to gain insight into the combustion process and thermodynamic balance of small-volume reciprocating engines. Information gained from this effort will be used to guide the development of more efficient engine designs by understanding the impact of ceramic materials as cylinder liners. The engine research programs within Department of Energy's Office of Energy Efficiency and Renewable Energy will benefit from the knowledge gained from this study. Likewise, this information is expected to advance the development of small unmanned air vehicle (UAV) engines and portable power generation for the US Department of Defense.

Results and Accomplishments

A 4-stroke OS FS-30S engine was used in the evaluation because the cylinder volume was small (~5 cc), and the cylinder geometry did not include any inherent stress risors. The original cylinder liner was composed of low-carbon steel, and additional liners composed of silicon nitride were manufactured by Ceradyne for use in this study. The engine was mounted to a 20HP motoring dynamometer and was operated at speeds of 2000, 3000, 4000, and 5000 RPM. For each speed, the throttle was placed in a high lean position and then adjusted and set to a point where stable combustion occurred. For each condition, the fuel consumption was measured. These runs were performed with both the original and ceramic liners. The results showed that the fuel consumption was lowered by 25 to 30 percent for each speed when the ceramic liner was used in place of the standard steel one. Additionally, the exhaust temperatures were significantly higher when running with the ceramic liner (compared to the steel one). Unfortunately, the engine torque was too low to separate out from the background noise. Therefore, precise determination of the brake specific fuel efficiency could not be made. However, the reduction of fuel consumption does indicate that the engine was either operating more efficiently, and/or stable combustion occurred under leaner conditions. Either effect is a significant benefit for small engine operation.

In order to better assess fuel efficiency, the engine was operated under static test conditions using a propeller. Although measurement of the load cannot be made with this method, engine load is concurrent with engine speed, and therefore, a true fuel efficiency comparison can be made under constant speed and load for both cylinder liner materials. The engine was operated at 6000 rpm, and the fuel flow was measured under lean operation. When equipped with the ceramic liner, the engine exhibited an approximate 5% improvement in fuel efficiency and a nearly 250% increase in flow exergy (or thermal availability) of the exhaust. This demonstration of improved efficiency and thermal availability should lead to an expansion of small-volume research and points to pathways for using small-volume engines as sources of portable electrical power generation and propulsion.

06638

Blue-Energy Harvesting by ORNL Mesoporous Carbon Electrodes

C. Tsouris and J. Gabitto

Project Description

This project employs ORNL mesoporous carbon (MC) electrodes to seek improved recovery efficiency of the free energy change in electrical double-layer capacitors that are charged in seawater and discharged in freshwater. Due to its high electrical conductivity, accessible pore size, and desirable hierarchical structure, the ORNL MC has been found to be superior to other carbon materials in electrosorption applications, such as deionization of brackish water and energy storage, and can enable a breakthrough in the development of a capacitive blue-energy technology. This small Seed Money project is focused on obtaining high electrosorption capacity for seawater and demonstrating that mesoporous carbon electrodes can be used to reach high energy-recovery efficiencies. In the first year of the project, an experimental assembly has been set up, and preliminary data of seawater electrosorption have been obtained. A theoretical model based on the electrical double-layer theory has also been developed to provide a better understanding of the sorption phenomena occurring during charging and discharging of the electrodes.

Mission Relevance

The energy obtained by salinity gradients, referred to as blue energy, has long been considered a promising renewable energy source for the future. In delta areas, where rivers with low-salinity water flow into seawater, there is potential for substantial energy recovery. Mixing of a high-concentration saline solution with freshwater to produce a brackish solution dissipates more than 2.2 MJ of free energy per cubic meter of freshwater treated. This value is equivalent to the potential energy released by water falling from a height of 220 m. It has been estimated that the combined power from all large estuaries in the world could reach 2 TW, approximately 20% of today’s worldwide energy demand or close to present-day electricity use. A capacitive blue-energy technology can also be combined with renewable energy, such as wind or solar, to make renewable energy more attractive. The results of this work could lead to an improved energy recovery of blue energy using electrical double-layer capacitors with MC electrodes.

Results and Accomplishments

Experimental work is carried out using a flow cell with a pair of ORNL MC electrodes for capacitive energy extraction and the required electrical circuit. The setup is similar to capacitive deionization systems. Two tanks with freshwater and seawater are connected to a feeding pump. Each experiment consists of four steps: (1) charging (2) switching step I, (3) discharging, and (4) switching step II. Preliminary experiments have been conducted, and the parameters for each of the above steps have been optimized. The charge stored is calculated by integration of the current versus time curve for the charging and discharging steps. The potential values between the two electrodes are continuously monitored during each experiment. The amount of electrical work produced is obtained by the area generated in a plot of potential versus charge stored of a complete four-step cycle. Results on the energy-recovery efficiency will be provided upon the completion of the project.

06665

Acoustic Signature Reconstruction in Heavy Foliage

M.D. Kass, B.W. Van Hoy, C.E.A. Finney, S. Daw, S. Lewis

Project Description

The proposed effort seeks to demonstrate the detection and reconstruction of acoustic signals in heavy foliage in order to facilitate and enable the detection of illicit activities, which are currently shielded in heavy forested regions. Foliage texture and complexity effectively attenuate source signals via spectral broadening and reverberation, making it difficult, if not impossible, to identify and locate sound sources. Past studies have shown that sound direction could not be accurately determined by the human ear alone.

This effort seeks to measure the attenuation of narrow-band and broad acoustic spectrums to assess attenuation factors as a function of foliage complexity. Foliage metrics will be measured using an existing software-based method used to calculate landscape metrics. Establishing a correlation between foliage metrics, density, and distance will enable source ranging and reconstruction of the original acoustic signal.

Mission Relevance

Detection, identification, and localization of acoustic signals are of interest to various government agencies tasked with border security, counterterrorism, and drug interdiction. The Department of Homeland Security (DHS) and the US Army are activity pursing technologies to improve sound detection in heavy foliated environments. Additionally, the DOE Office of National Nuclear Security Administration is also interested in maintain border security to ensure that nuclear materials are not brought in illegally. The objective of this study is to correlate acoustic degradation with foliage parameters for improved detection and identification. Since degradation is expected to be characteristic of distance and foliage type, then ranging may also be achievable.

Results and Accomplishments

The ORNL team evaluated two sites on the Oak Ridge Reservation for their potential impact on sound signal degradation. Site #1 consisted of a sweet gum plantation (and therefore had a small level of complexity), while Site 2 was composed of heavy mixed foliage (having high complexity). A speaker was used to emit narrow bands of 50Hz, 100Hz, 500Hz, 1000Hz, 5000Hz, and 10,000Hz. In addition, a portable gasoline generator was also used as a source. For each foliage site, the acoustic spectrum was measured at 0 m, 36 m, 67 m, and 118 m. For each distance, four microphones (including one enclosed in a parabolic reflector) measured the sound spectrum. The foliage at each site was noted, and the complexity is being determined using photographic methods. Preliminary results show that at 67 m in the sweet gum forest stand, the low and high frequencies (and the generator) could not be heard using the human ear. On the other hand, at 67m (in the mixed foliage), the generator could be audibly detected. This result was not expected and is likely due to acoustic channeling caused by the nearby road.

Analysis of the frequency attenuation has revealed that the 1000 Hz emission did not experience spectral broadening as a function of distance in the foliated environments. This result was not expected and shows that certain frequencies will not structurally degrade in heavy foliage. Another interesting observation is that the sound spectrum emitted by the generator underwent a phase shift with distance. This feature can be used to range such sources and may be valuable in signal reconstruction.

06669

Printed Engines to Enable Characterization of Combustion Processes of Small-Scale Internal Combustion Engines

M.D. Kass, M. Noakes, R. Dehoff, L. Love

Project Description

The proposed project seeks to demonstrate the application of additive manufacturing (AM) technology for printing reciprocating engine systems. This new manufacturing process will enable measurement of parameters not currently possible, providing novel insight into small-volume combustion. Specifically, this proposal seeks to evaluate additive manufacturing methods for the fabrication of components or systems that are subjected to the extremes in pressure, temperature, and chemistry characteristic of reciprocating internal combustion engines. Successful demonstration will lead to increased manufacturing versatility while reducing manufacturing costs for small engines. The combustion processes for small-scale engines have never been adequately characterized or understood; therefore, it is difficult to design for maximum efficiencies. This effort will seek to integrate small-scale sensors into the cylinder head to achieve combustion characterization. Success will lead to the development of micro-engine technology for small-scale compact power sources for portable applications and provide the first example of a printed internal combustion engine.

Mission Relevance

Advances in engine development will require novel and sophisticated measurement of combustion parameters. Improved engine efficiency is a hallmark of the US Department of Energy's Vehicle Transportation program. In situ, precise measurements of pressure and temperatures are needed to optimize engine performance. The geometries of engines are becoming more complex, and sensor insertion is becoming more problematic. Additive manufacturing offers the potential to precisely locate and embed sensors without altering the geometry significantly. Small-volume engines are extremely inefficient, and elucidation of their combustion parameters will enable more efficient designs, leading to new uses of hydrocarbon fuels for portable power and small vehicle propulsion. Both of these topics are of great interest to the US Department of Defense.

Results and Accomplishments

This effort was initiated in late September for a total FY 2012 allocation of $5K. During this time, representative engines were procured and other resources were lined up for the subsequent FY 2013 effort.

ENVIRONMENTAL SCIENCES DIVISION

05898

Air Stable and Low-Cost Iron Carbon Nanocomposite for Environmental Remediation

J. Gao, W. Wang, L. Liang, A.J. Rondinone, F. He

Project Description

Removal of chlorinated hydrocarbons in groundwater and soils represents a challenging environmental issue. Nanoscale zerovalent iron (NZVI) is a promising material for remediation of these contaminated sites. However, with more than a decade of development, current NZVI technology still suffers from high material cost, instant aggregation in water, and inability to target hydrophobic contaminants [i.e., dense non-aqueous phase liquids (DNAPLs)] in source zones. We tackled these problems by developing a novel and inexpensive iron-carbon (Fe-C) nanocomposite through ball milling of micro-scale iron with activated carbon powder. Through physical characterization, trichloroethene (TCE) degradation tests, and organic phase partitioning tests, we established the proof of principle that this novel, low-cost material cannot only efficiently degrade chlorinated contaminants but also can attack DNAPL phase.

Mission Relevance

Chlorinated solvents are among the most widely detected contaminants in soil and groundwater at thousands of Department of Energy (DOE) and Department of Defense (DoD) contaminated sites. We aim to develop and demonstrate this novel material for application in rapid and in situ remediation of source zone in contaminated federal (including DOE), industrial, and private sites. This project has direct relevance to ongoing site remediation efforts of DOE and other federal agencies (e.g., DOD and USEPA) including the DOE EM-30 (Office of Engineering and Technology), DoD Strategic Environmental Restoration and Development Program (SERDP), Environmental Security Technology Certification Program (ESTCP), and National Institute of Environmental Health Sciences (NIEHS) Superfund Research Program.

Results and Accomplishments

Our ultimate goal is to develop a novel, low-cost Fe-C nanocomposite material and utilize it for effective degradation of chlorinated hydrocarbon contaminants. During the project, our efforts focused on three primary tasks.

Task 1– Synthesis and characterization of the Fe-C nanocomposite. We synthesized the Fe-C nanocomposite by ball milling micro-scale iron and activated carbon powder using propylene glycol as a lubricant. The resultant products were characterized using BET Surface Area Analyzer, Dynamic Light Scattering (DLS), Scanning Electron Microscopy – Energy-dispersive X-ray Spectroscopy (SEM-EDX), Transmission Electron Microscopy – Electron Energy Loss Spectroscopy (TEM-EELS). The TEM and

SEM results showed that Fe and C particles were incorporated into each other. Further, the XRD results suggested that a new phase, iron carbide, was formed during the milling process. The Fe-C composite also has a large surface area, mostly from carbon.

Task 2 –Testing the bare NZVI and Fe-C nanocomposite for dechlorination. We have conducted the dechlorination experiment on a model contaminant, trichloethene (TCE), using the prepared Fe-C nanocomposite and bare NZVI. The results showed that Fe-C nanocomposite material instantaneously removed more than 90% of trichloroethene (TCE) from contaminated solution mostly through sorption. The monitoring of reaction products further showed that TCE was continuously degraded after the rapid sorption period. This indicates that the electrons from Fe(0) core can be conducted to the TCE sorption site through the graphene layers in the carbon.

Task 3 – Dispersing Fe-C nanocomposite in water: Stability, mobility, and partitioning characteristics. We have successfully dispersed the nanomaterial in water using carboxymethyl cellulose (CMC) as a stabilizer. However, with propylene glycol as the lubricant (high viscosity, due to safety reason), the obtained Fe-C composite particles were not small enough to move through a sand column. The partitioning properties of the Fe-C composites were tested by introducing an organic solvent (i.e., hexane) to a stable Fe-C aqueous suspension. We observed that when in contact with hexane, the composite material quickly partitioned into the organic phase due to the hydrophobicity of the carbon structure, suggesting that this composite can attack the DNAPL phase in future field application.

Information Shared

F. He, J. Gao, W. Wang, L. Liang, "Air stable Fe-C nanocomposite for degradation of chlorinated solvents," US patent (ORNL patent Ref. 2453), in application.

05961

Boosting Organic Solar Cell Efficiency Using Mangnetism and Ferroelectricity

X. Xu, T.Z. Ward, D. Sun, M. Yoon

Project Description

Organic solar cells are highly attractive for energy production due to their low cost, light weight, mechanical flexibility, and environmental benignity. However, they are currently limited by low efficiency. Here, we propose a novel approach that combines both magnetism and ferroelectricity to significantly improve the power conversion efficiency (PCE) of organic solar cells. This unprecedented approach aims at simultaneously improving the diffusion of excitons and charge collection, two critical factors governing the PCE of organic solar cells. Specifically, we will merge the following two steps into one solar cell system: (1) chemically attaching molecular magnets in organic conjugated photovoltaic (PV) polymers, and (2) introducing a ferroelectric dipolar interface to enhance PV response. In step one, the locally spin-polarized transport induced by molecular magnets increases the population of longer life-time triplet excitons, effectively improving the efficiency of exciton diffusion. In step two, the built-in electric field added by the permanent dipolar (ferroelectrics) interface enhances the net driving force inside PV materials, improving the charge collection efficiency. Combining these two approaches, we expect a dramatic enhancement of organic solar cells' PCE. This initiative is conceptually sound and holds great promise to advance the development of organic solar cells as the next generation in low-cost, environmentally friendly solar devices. With this initiative, ORNL will be placed in a strong position to attract follow-on funds to develop organic solar cells with high PCE.

Mission Relevance

In this SEED project, we propose to improve the PV performance of organic solar cells via the singlet-to-triplet exciton conversion using locally spin-polarized transport and charge collection with ferroelectric interfaces. Theoretical research will be pursued to precisely describe molecular interactions and to identify structural properties of the materials using state-of-the-art techniques. Additionally, we will theoretically explore the formation mechanism of excitons and their transport processes including the effect of electron-phonon interactions.

Results and Accomplishments

Initial theoretical work showed that the experimental approach should find success in future applications. While multiple devices were fabricated, interfacial issues slowed progress. Several funding packages were submitted for external funding in the form of National Science Foundation (NSF) and Department of Energy (DOE) funding grants, but none were accepted. The PI left ORNL in 2012.

06650

Sensor-Fusion Technology for Improving Accuracy of Cable Deployed Acoustic Doppler Velocimeter Measurements Subject to Flow-Induced Motions

V. Neary and B. Gunawan

Project Description

Instantaneous velocity measurements (***u***) are needed to calculate hydrodynamic forces and power acting on marine and hydrokinetic (MHK) technologies and to derive projections of annual energy production, baseline cost of energy, machine performance, and survivability. However, accurate measurement of ***u*** is challenging due to flow-induced motions (FIM) of cable-deployed acoustic Doppler velocimeters (ADV), the most suitable instrument to measure turbulence at field scale. Deploying stationary ADVs to offset FIM is generally cost prohibitive because it requires permitting and towers designed to withstand large loads. The present study tests the efficacy of a sensor fusion technology designed to combine measurements from an inertial measurement unit (IMU) with ***u*** from the ADV to correct FIM errors when cable deployed. A cabled ADV and IMU attached to a 200 lb USGS sounding weight is deployed in an open channel flume to quantify FIM errors and collect coordinated motion and instantaneous velocity measurements to test an FIM error correction algorithm.

Mission Relevance

MHK energy technologies convert kinetic energy of waves and water currents to generate electricity. Accurate measurements of approaching velocity and turbulence profiles along the planned locations of MHK machines, particularly their energy extraction planes (EEP), are essential for estimating key metrics for resource assessment, site selection, and monitoring, including annual energy production, baseline cost of energy, available power to determine machine performance, and hydrodynamic loads to design for machine survivability. The most practical instrument for obtaining these measurements in the field is the acoustic Doppler velocimeter (e.g., the Nortek Vector), but deployment of the ADV in the field to collect these profiles accurately and economically presents a technical challenge that we propose to address with a novel sensor-fusion technology. If successful, this technology would improve the accuracy and lower the cost of assessing these metrics and would significantly advance ORNL's position in advanced velocity and turbulence measurements for a growing global energy industry, including significant measurement needs for energy project siting and environmental monitoring.

Results and Accomplishments

An IMU and a Vectrino ADV were installed in a 200 lb USGS sounding weight and cable deployed in a 2.75 m wide and 1.8 m deep laboratory channel at three different flow rates: 2.8, 2.6, and 2.4 m^3/s, to produce bulk velocities of 1, 0.95, and 0.55 m/s. The water depths were set at 1, 1, and 1.6 m, respectively. Measurement points were set at 0.5 m above the bed for all cases. Instantaneous velocity measurements ($\boldsymbol{u}$) were collected with a stationary (ST) ADV at the same measurement point as the cable-deployed (CD) ADV to obtain measurements virtually free of FIM errors that could be used to quantify FIM errors. Our study demonstrated that FIM errors are significant at water currents similar to those that will be observed at hydrokinetic energy sites. Measurements of three important parameters for MHK machine design, streamwise velocity, streamwise turbulence intensity and lateral velocity were biased by up to 7%, 9%, and an order of magnitude, respectively. We attempted to correct FIM errors in the CD measurements using the recorded IMU data. However, we were unable to test the FIM error correction algorithm because the ADV and IMU measurements were not synchronized. The experiments will have to be repeated to obtain synchronized ADV and IMU measurements to evaluate the performance of this algorithm. We have ordered a Vector ADV with a factory-synchronized IMU using DOE funding from another project. However, additional funding is needed to repeat the experiments. We hope to find additional funding through the technology transfer program.

GLOBAL NUCLEAR SECURITY AND TECHNOLOGY DIVISION

05969

Authenticated Radio Frequency Identification

B.J. Stinson, M.J. Kuhn, N.C. Rowe

Project Description

Analysis, simulation, and laboratory experiments are being conducted to verify the validity of a novel wireless authentication method suitable for radio frequency identification (RFID) tags. The work will verify that short pulse [i.e., ultra-wideband (UWB)] radio systems and time-of-flight (ToF) measurements can be used to implement a location and device authentication protocol in practical RFID applications. This protocol simultaneously provides device authentication and location authentication, both of which are critical for implementing RFID in high-security tagging, tracking, and secure wireless data transmission applications.

This research has direct application in the use of RFID for high-value asset tracking, tagging, locating, and tamper indicating, specifically in the nuclear safeguards industry. The DOE National Nuclear Security Administration (NNSA) and the International Atomic Energy Agency (IAEA) often desire to use RFID for standoff verification of an item's location or seal status. These applications are long-term deployments with inventory and monitoring subsystems that rely (often intrinsically) on the ability to trust the data and location of the transmitting RFID tag. However, tags are not commercially available which provide this level of trust; namely, tags are not available that provide device and location authentication. Opportunities therefore clearly exist to further develop this technology beyond the research and proof-of-principle stages.

Mission Relevance

Radio Frequency Identification (RFID) provides clear advantages in many applications ranging from commercial "everyday" products such as contactless credit cards to high-value asset tracking and monitoring. NNSA, the IAEA, the Department of Defense (DoD), and other agencies have the desire to use RFID for tagging/tracking applications. However, all of the agencies have a need for *authenticated* RFID that provides assurance that the tag and reader system are trusted entities and have not been spoofed. In a radio frequency (RF) system, spoofing can occur in two ways: either the tag can be replicated and/or the tag can be physically removed and replaced with a repeater system. To mitigate the former requires that the device use an authentication method such that it is exceedingly difficult to replicate the tag. The latter requires that the device's *location* be authenticated.

The lack of both device and location authentication in commercial (and known research) systems is a crippling inadequacy which continues to keep RFID from being a viable solution in high-security environments. In general, the commercial RFID industry is focused on tracking low-cost commodities and has directed product research and development to meet those needs. In addition, we anticipate that the future will continue to bring RFID to more secure sectors of the commercial market, including contactless credit cards, passports, medical data, and more. Government agencies will continue to have needs for tracking valuable or sensitive assets with considerably different priorities from commercial entities.

The research efforts proposed will provide validity to the conceptual design of an active RFID system based on UWB radios. The researchers believe that two-way active UWB communication is the most robust and complete technology on which to build a location authentication framework. If successful, this system will combine both device and location authentication by performing a challenge-response authentication protocol simultaneously with ToF measurements. The ToF measurements provide the ability to bound the known location of the tag to within a small region. Success of this concept in the proof-of-principle stage will lead to the development of valuable IP, with a high potential for government and commercial customers and licensees.

Results and Accomplishments

Based on simulations and modeling from last year, microwave circuits were designed and built to test the feasibility of the ToF measurement methodology. The novel aspects of the developed transceiver are that it is both deterministic and fast. That is, the time required to respond to a query from another radio is both a fixed value and a very small value. Hardware testing was successful, and we demonstrated the first known fully deterministic UWB transceiver with a fixed response time of only 22.5 ns. The transceiver uses a noncoherent latched comparator which converts UWB pulses into digital signals.

Original project goals were a fixed response time of 10 ns. This was based on a desire to limit the tag location uncertainty to within 3 meters. While the demonstrated results were slower (at 22.5 ns), they still show a proof-of-principle for location tracking/authentication with an uncertainty of about 6.5 meters. We consider this a success. With further efforts the response time may be decreased.

At this point, the work is completed, and the original goal of showing proof-of-principle for a deterministic UWB transceiver was achieved. The modeled designs and developed hardware is well positioned to be used as leverage for follow-on funding proposals. Additional funding will allow development towards a complete design which provides device authentication and location authentication in a reader/tag scenario.

06567

High Spatial and Temporal Resolution Particle Detectors

J.S. Neal, J.T. Mihalczo, L.A. Boatner

Project Description

In radiation imaging systems, particle detectors are often used to not only detect the presence of particles incident on the face of the detector but also to identify the spatial position on the detector face where the interaction occurred. This spatial information can then be used as part of the image reconstruction process. In Associated Particle Imaging (API) applications, for instance, an alpha particle detector is used to “tag” an alpha particle with an associated neutron in both space and time. To increase the efficiency and accuracy with which associated neutrons are tagged, faster alpha particle detectors with higher spatial and temporal resolution are desired. In this project, we propose to fabricate and test innovative high-resolution fiber-optic scintillation detectors where one or more scintillation activator dopants (e.g., Ce^{3+}) are optimally incorporated into one end of the fibers at a predetermined sensitization depth.

Mission Relevance

The relevance of this project to the Department of Energy (DOE) national security missions is to provide significantly improved (in terms of position and timing resolution) charged particle detectors that can be used for the detection and identification of highly enriched uranium (HEU – shielded and un-shielded) and plutonium as well as for NA-24 safeguards applications (i.e., the detection of undeclared nuclear material and activities as well as the characterization and verification of declared nuclear material).

Results and Accomplishments

Un-doped yttrium aluminum perovskite (YAP) crystals were obtained from Scientific Materials Corporation (Bozeman, MT) after a long search for un-doped material that was not sensitized in the bulk through the addition of Ce^{3+}. While obtaining the YAP crystals, our team attempted to establish a collaboration with researchers at the University of Pisa, Italy, but was ultimately unsuccessful. After additional searching, we were able to establish a collaboration with Dr. James Harrington of Rutgers University Laboratory for the Development of Specialty Fiber Optics. Dr. Harrington is an expert at drawing single-crystal fibers using the laser-heated pedestal-growth technique. This technique will be especially beneficial to our efforts as it is a crucible-less method for forming single-crystal fibers and thus should minimize the potential for contamination of the fibers. The YAP crystals from Materials Corporation were cut and polished at Oak Ridge National Laboratory (ORNL) to the specifications provided by Dr. Harrington. Efforts are now under way to draw the starting material into single-crystal fibers. Additionally, we have worked with Schott Glass America to define the process to fabricate a fiber-optic faceplate using single-crystal fibers. Conventional, silica-based fiber-optic faceplates use a well-established drawing method for forming faceplates, but it is unlikely that this method will apply to the formation of a faceplate comprised of YAP single-crystal fibers. Discussions with Schott Glass America are currently ongoing. Fiscal Year 2013 work will focus on characterizing fibers fabricated by Dr. Harrington, studying methods for the controlled doping of fiber ends with cerium via ion implantation, thermal diffusion, etc., and characterizing the doped fibers as scintillators.

Information Shared

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MATERIALS SCIENCE AND TECHNOLOGY DIVISION

05872

Can Neutrons Do It: Probing Performance of Li-Ion Batteries In Situ

Z. Feng, L. Cai, X.-L. Wang, K. An, S.E. Nagler, W. Zhang, C. Daniel, N. Dudney

Project Description

High-power Li-ion batteries need a cycle life of over 6,000 and calendar life of 15 years or longer in order to achieve the economic viability in battery-powered vehicles and in future electricity infrastructure. This is about one order of magnitude higher than current technology provides and is a tremendous challenge because its capacity fades due to internal degradation. Factors contributing to the performance of Li-ion batteries are very complex and vary significantly with the electrode materials, battery manufacturing processes, as well as charging/discharging rates, temperature, and other operating conditions. There is a paramount need to directly probe *inside* a "real-world" battery cell as it operates, to understand the fundamental processes and mechanisms of lithiation and de-lithiation, lithium transport, and the buildup of internal stress and temperature that contribute to the performance of battery. Addressing this need, the project aims to develop an innovative in situ neutron diffraction experiment approach to probe the Li-ion battery performance and degradation. Specifically, we will map the three-dimensional distribution of internal temperature, stress, the lithium intercalation processes, and the state-of-charge (SOC) conditions of representative batteries used in the electric vehicles – the capability of comprehensive nondestructive diagnostics of "real" battery/battery package performance under realistic operation conditions. It will establish a capability for battery performance and battery materials R&D, a critically important subject in electrical energy storage.

Mission Relevance

The in situ neutron diffraction capability developed in this project will support DOE's major initiatives on high-power batteries for automotive applications and electric storage infrastructure. Specifically, it offers the unique capability to "see" *inside* a large format prismatic battery cell in a nondestructive way to understand and quantify the chemical, thermal, and mechanical processes and how these might affect the overall cell durability and performance to degradation resistant electrode materials and manufacturing/packaging technologies. The research will benefit the Energy Storage Technologies of the DOE Office of Energy Efficiency and Renewable Energy Vehicle Technologies Program. It will also benefit the DOE Office of Electricity Delivery and Energy Reliability, as well as the Wind and Solar Energy Programs.

Results and Accomplishments

We have successful completed more experiments on three different types of large format batteries from different battery OEMs and suppliers, on the VULCAN beamline of the Spallation Neutron Source (SNS). The batteries had different chemistries, and tested at different charging and discharging rates. We were able to determine the local SOC inside the battery by means of our novel neutron diffraction approach developed in this research. This novel approach also reduced the data collection time to about 2–3 minutes, which is sufficiently fast for in-situ measurement of the transient behavior of batteries during charging-discharging cycles. Very rich information about the SOC of batteries was obtained and analyzed. For example, the experimental results show that during a rapid charge cycle (1 C, full charge in an hour), the graphite anode undergoes a disorder-to-order transition as Li ions are incorporated between the graphene layers, forming $Li_{12}C$ and Li_6C intercalation phases at fully charged condition. In contrast, the discharge follows the staging sequence of $Li_6C \rightarrow Li_{12}C \rightarrow Li_{24}C$, before the anode returns to the graphite phase. A lattice dilation as large as 4% was observed during a charge-discharge cycle. Most importantly, the degradation process in the large format prismatic battery cell was clearly observed for the first time, and the process of such degradation was revealed. Our work demonstrates the potential of in situ neutron diffraction measurements for study of the dynamic chemical and structural changes in "real-world batteries" under rapid, realistic cycling conditions and for providing insights on degradation and other outstanding issues in energy storage materials.

Information Shared

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05902

Design of Coaxial TiO_2 Nanotube Arrays for Solar Energy Utilization

M. Chi, X. Qiu, M. Yoon, Z. Bi, I. Ivanov, M.P. Paranthaman

Project Description

The goal of this proposal is to introduce a new concept for combining band structural and morphological-engineering towards a novel design of co-axial p-n junction nanotubes for solar energy utilizations. TiO_2 nanotubes will be used as a model system for the proof-of-principle purpose. This co-axial nanostructured TiO_2 could lead to a significant improvement of the cost-efficiency in current solar energy utilization techniques, such as photovoltaics, photocatalysis (solar fuel production), carbon capture, etc. The research is motivated by the fact that high-conversion-efficiency solar energy utilization can be realized by using nanostructured semiconductors arranged in unique configurations. This is accomplished by means of altering and enhancing the absorptive and carrier-generating properties of semiconductors in dramatic and specific ways. The proposed design incorporates a radial *p-n* junction inside TiO_2 nanotubes through a cost-efficient nitrogen doping approach. TiO_2 nanotubes with such a unique architecture are expected to have significantly enhanced light-capture efficiency, the capability of covering a wide range of the solar spectrum, and improved carrier collection efficiency. With this proposal we seek to verify this design both theoretically and experimentally. The proposed concept can eventually not only enable cost-effective scalable solar energy utilization approaches but also provide a new nanoscale test bed for future designs of novel nano-structured materials for photoinduced nanoelectronic devices and diverse nano-systems.

Mission Relevance

Federal funding agencies such as the DOE Office Basic Energy Science (BES) and Officed of Energy Efficiency and Renewable Energy (EERE) are focused on discovering novel materials and advancing fundamental understanding of the physical mechanisms associated with the conversion of solar energy into electricity. For example, DOE's Solar Energy Technologies Program (SETP) has various activities and funding opportunities for research programs directed towards cost-effective, long-lasting, highly efficient solar energy conversion and utilization. The work undertaken here has the opportunity for world leadership in nanomaterials for low-cost, high-efficiency PV applications. Furthermore, other federal agencies such as the Defense Advanced Research Projects Agency (DARPA) and the Industrial Technology Program (ITP) are increasing their support of solar energy technologies, as evidenced by numerous specific initiatives and ongoing calls for research related to solar energy use.

Results and Accomplishments

Guided by our initial theoretical calculations, we have successfully realized the control of site-selective doping of nitrogen inside TiO_2 (anatase) nanotubes; that is, nitrogen enters inner wall of the nanotubes preferentially, which results in radiantly doping along axial direction inside the nanotubes. Highly ordered TiO_2 nanotube arrays, having varying nanotube diameters, lengths, and inter-pore distances, were prepared by modifying experimental variables, for example, voltage, electrolyte concentration, and temperature. Controlled N-doping was performed by carefully controlling ammonia gas atmospheres and temperatures. It was observed that the nanotubes, which were prepared at 40 V and post-annealed in ammonia at 550°C for 45 min, gave the best N-substitutional concentration and selective distribution. This sample also showed the best absorption at visible light region as expected. Electron energy loss spectrometry (EELS) was performed to differentiate the interstitial and substitutional doping locally. Our microscopy experiments confirmed the selective N-doping inside single nanotubes. More excitingly, theoretical calculations have elucidated the origin of such interesting preferential doping behavior – the different surface atomic structures between the inner and outer wall of nanotubes as intrinsic charcteristics of anodized nanotubes. Such atomic structure variation was further proved by high-resolution electron microscopy. In summary, we successfully achieved a novel design of TiO_2 nanotubes with a built-in *p-n* junction structure through simple nitrogen doping. Such architecture is expected to possess significantly enhanced light absorption over a wider solar spectrum range. Furthermore, the fundamental understanding of the preferential doping mechanism, developed within this project, can provide valuable guidance of designing nanomaterials with novel coaxial structures in a much broader range of material systems.

Information Shared

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05944

Turning Chalcopyrites into Dilute Magnetic Topological Insulators (DMTI) via Magnetic Doping

D. Xiao, W. Zhu, G.M. Stocks

Project Description

The recent discovery of topological insulators has generated widespread research activity in the condensed matter and materials science communities. These materials are expected to display a variety of unconventional spintronics effects and could lead to entirely new device paradigms critical to basic energy research. A prerequisite for these practical applications is that ferromagnetism must be introduced alongside topological orders in these materials. We propose to theoretically investigate the possibility of establishing robust bulk ferromagnetism in topological insulators via magnetic doping or strong correlation effect, and their consequent effects on the topological properties of the host material. Successful execution of the proposed research will lay the fundamental basis for developing energy-efficient spintronic devices based on the unique properties of topological insulators. This work will provide a foundation to open a new direction in current ORNL Office of Basic Energy Sciences (BES) work on low-dimensional materials and grow funding opportunities.

Mission Relevance

As part of the energy strategy for the future, there is a basic research need for understanding the emergent topological phenomena in complex materials. The interplay between magnetism and the unusual metallic surfaces of these insulators may result in new spintronic or magnetoelectric devices, which are critically important in basic energy research because of their potential in energy-efficient applications. Our proposed work also addresses some of challenges identified in the 2007 report from the BESAC – “to discover how remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and to control these properties.”

Successful execution of the proposed research will lay the fundamental basis towards developing energy-efficient spintronic devices based on the unique properties of topological insulators. It will place ORNL in an excellent position to propose new work in response to anticipated calls from the Defense Advanced Research Projects Agency (DARPA), spin transport electronics – both as originators as well as partners with other institutions who will need our expertise in theoretical understanding of magnetism in topological insulators.

Results and Accomplishments

The objective of this SEED project is to theoretically investigate the possibility of realizing various topological states and phenomena in realistic materials. Note that after our SEED funding was approved and before the project officially started, one of the team members, Dr. Zhenyu Zhang, left ORNL unexpectedly. To ensure there are enough personnel committed to this project, we have used the funding to support an exchange graduate student, Mr. Wanxiang Feng, at the University of Tennessee. The following is a brief description of this project.

During the first phase of this project, we have developed a highly efficient method to describe the band topology of crystalline solids within the density functional theory. Part of the result was published in *Computer Physics Communications* **183**, 1849 (2012). It is so far the only method that can be applied to study crystals with arbitrary symmetry. Next we applied our method to investigate a number of different material systems.

(a) We predicted that bilayers of perovskite-type transition-metal oxides grown along the [111] crystallographic axis are potential candidates for two-dimensional topological insulators. The topological band structure of these materials can be fine-tuned by changing dopant ions, substrates, and external gate voltages. Our results may open new directions focusing on topological phenomena in the rapidly growing field of oxide electronics. This work is published in *Nat. Commun.* **2**, 596 (2011).

(b) We theoretically explored the possibility of tuning the topological order of cubic diamond/zinc-blende semiconductors with external strain. We showed that lattice expansion can induce a topological phase transition of small band-gap cubic semiconductors via a band inversion, and further breaking of the cubic symmetry leads to a topological insulating phase. Our result provides a generic guiding principle for tuning the topological order of the cubic semiconductors and offers an opportunity for experimentally exploring the properties of the topological surface states on such technologically relevant materials for practical applications. This work is published in *Phys. Rev. B* **85**, 195114 (2012).

(c) We showed that inversion symmetry breaking together with spin-orbit coupling leads to coupled spin and valley physics in monolayers of MoS2 and other group-VI dichalcogenides, making possible controls of spin and valley in these 2D materials. Our result provides a route towards the integration of valleytronics and spintronics in multi-valley materials with strong spin-orbit coupling and inversion symmetry breaking. This work is published in *Phys. Rev. Lett.* **108**, 196802 (2012), and *Phys. Rev. B* **86**, 165108 (2012).

Results from this SEED project represent a major step in our understanding of topological phenomena in realistic materials, and also helped us to secure Office of Basic Energy Sciences (BES) funding for ERKCS92.

Information Shared

Computer Physics Communications **183**, 1849 (2012)
Nat. Commun. **2**, 596 (2011)
Phys. Rev. B **85**, 195114 (2012)
Phys. Rev. Lett. **108**, 196802 (2012)
Phys. Rev. B **86**, 165108 (2012)

05957

Separation of Carbon Dioxide from Flue Gases

B.L. Bischoff and C.K. Narula

Project Description

The goal of this project is to demonstrate the feasibility of supported liquid membranes for the separation of CO_2 from flue gas. At present, the state-of-the-art method relies on selective absorption of CO_2 in aqueous amines at source and release at collection point to separate CO_2 from emissions. The inherent inefficiencies due to low chemical efficiency of the process, energy needs, and evaporation and decomposition of aqueous amines make this process energetically and economically expensive. Our proposed liquid-membrane-based CO_2 separation process overcomes the problems associated with traditional aqueous amine process because it operates at a constant temperature, which decreases energy penalties, evaporative losses, and decomposition of the amine solution.

The proof-of-principle experiments will demonstrate that our thin inorganic-based liquid amine membranes can produce a high-purity CO_2 stream on a continuous basis with high flux. We estimate the footprint of the CO_2 separation plant, based on our liquid membrane process, to be 1/10 the size of aqueous amine process. The successful completion of the project will place ORNL in a competitive position to respond to anticipated calls from DOE Offices of Fossil Energy (FE) and Energy Efficiency and Renewable Energy (EERE) for follow-on funding.

Mission Relevance

DOE Secretary Chu, in his letter to Science, stated that "overwhelming scientific evidence shows that CO_2 emissions from fossil fuels have caused the climate to change and that a dramatic reduction of these emissions is essential to reduce the risk of future devastating effects." Cleary, DOE is placing high priority to CO_2 separation, capture, and sequestration. In the United States, the majority of current emissions come from the production of electricity, primarily from coal-fired power plants. Existing coal-fired power plants account for over 30% of the CO_2 emissions in the United States. As such DOE has set a post-combustion CO_2 capture targets of 90% CO_2 capture at less than 20% increase in the cost of energy.

Results and Accomplishments

A series of nanoporous membranes, to be used as supports for the liquid amine membranes, was fabricated. The membranes were made by first forming tubular supports from 316L stainless steel and applying a thin (less than 5 µm thick) aluminum oxide separative layer to the inside surface. The supports have a pore size of approximately 4 µm. The average pore-sizes of the aluminum oxide layer ranged from less than 5 nm up to 8 nm. A membrane with an average pore size of 4.7 nm was impregnated with a solution of 50% monoethanolamine (MEA) in water. A test system, capable of operating at temperatures up to 300°C, was set up to evaluate the membranes. The permeance of both nitrogen and carbon dioxide was determined by monitoring the rise in pressure of a known volume on the product side of the membrane. Results of this first membrane showed no detectable flow of either nitrogen or carbon dioxide at room temperature. Tests at 90°C showed an initial selectivity of 5.3 that increased to over 10 after an hour of operation. Tests showed good stability of the membranes. There was no evidence of a major loss of amines after a week of tests at temperatures ranging from room temperature to 90°C.

A second membrane, with an average pore size of 4.6 nm, was impregnated with a 50% aqueous solution of triethanolamine (TEA). Triethanolamine was selected because it has a very high boiling point, low vapor pressure, and is soluble in water. As with the MEA membrane, this membrane showed no detectable flow of either nitrogen or carbon dioxide at room temperature. As the temperature was increased, the permeance, which is the flux per unit membrane area per unit pressure, increased for carbon dioxide, while there was no little or no detectable flow for nitrogen. The ideal selectivity, the ratio of carbon dioxide permeance to nitrogen permeance, was calculated at temperatures where there was a detectable nitrogen permeance. During many of the tests, there was no detectable flow of nitrogen which would indicate an infinite selectivity. The permeance at 90°C was determined to be $6.5 \times 10\text{-}11$ moles$\cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ with an ideal selectivity of almost 30. The ideal selectivity at 50°C was slightly lower at 25, but the permeance was a factor of 3 lower. A selectivity of 30 would result in a product where the carbon dioxide has a purity of 84% when the feed concentration is 15%. When the temperature was increased to 105°C, the apparent flux of carbon dioxide increased dramatically. When the temperature was lowered back to room temperature, it was evident that a leak formed during the excursion to 105°C. A subsequent treatment with the aqueous amine solution was successful in returning the membrane back to the initial state. After retreatment of the membrane with fresh amine solution, the membrane was operated for over 3 weeks at temperatures ranging from room temperature to 90°C. The properties of the membrane were stable over this testing period.

In summary, high selectivities for carbon dioxide were obtained at temperatures ranging from 50 to 90°C. This range is consistent with the temperature of flue gas exiting the cleanup stages. Difficulties in measuring very low flows for nitrogen resulted in no detectable flow for many of the tests. This made calculation of an ideal selectivity not possible for a large fraction of the data. Improvements to the test system are needed to allow measurement of lower flow rates. Triethanolamine showed higher selectivity of carbon dioxide over nitrogen and showed good stability at temperatures up to 90°C. Future work would include the influence of pore size along with long-term tests to determine stability of amine layer. The membrane showed loss of amine when operated at 105°C. It is believed these leaks were due to loss of water as it has a higher vapor pressure than the TEA. By lowering the amount of water in the amine solution, the amine may be able to be operated at higher temperatures without evaporative losses. Because flue gases can contain close to 10% water vapor, it may be possible to utilize almost pure TEA to facilitate the separation. Future work would look at amine concentration in relation to membrane operating temperature and membrane stability. If the membrane can be operated at higher temperatures, the trend predicts that both the permeance would increase and the selectivity would increase.

Information Shared

Brian Bischoff and Lawrence Powell, "Selective Separation of Carbon Dioxide from Flue Gases," AIChE Annual Meeting, 2012.

05959

Direct Imaging of Energy Generation and Collection in Photovoltaic Nano-Materials: EBIC in the STEM

B.S. Guiton, A. Mouti, S.J. Pennycook

Project Description

Electron-beam-induced current (EBIC) measurements are being implemented in the aberration-corrected scanning transmission electron microscope (STEM). Electron-hole pairs formed by the beam – which acts analogously to a tiny ray of light – are collected and used to form an image, essentially mapping the energy conversion efficiency of the photovoltaic material in question. This will enable us to identify recombination centers and structures conducive to successful charge carrier collection. The highly intense and focused electron beam of the aberration-corrected microscope allows signal collection from much smaller regions than previously possible, permitting the characterization of cutting-edge photovoltaic materials on the scale of a single active nanostructure. This proof-of-principle study comprises a systematic test of a range of single axial p-n junction-containing nanowire devices with varying radii. Future research is anticipated on several cutting-edge inorganic nano-material photovoltaic systems, including radial-junction nanowires, hybrid structures, and nano-ink thin films. This represents the first viable method to directly image successful light-harvesting structures for nano-photovoltaics.

Mission Relevance

We anticipate that proof of this technique – the necessary characterization step to engineer nanostructured photvoltaics of useful efficiency – will be of mounting importance as US energy security comes to rely increasingly on renewable energy sources. This research is highly applicable to the Basic Energy Sciences

(BES) Division of Materials Sciences and Engineering and Division of Chemical Sciences. It is also highly supportive of the mission of the Office of Energy Efficiency and Renewable Energy's Solar Energy Technologies program. This project is highly applicable to several programs of the National Science Foundation, including the programs in Ceramics, Solid State and Materials Chemistry, Condensed Matter Physics, and Electronic and Photonic Materials, to the Solar Energy Initiative, and to the Energy for Sustainability program. In addition, energy research – and in particular solar energy technology development – is a key priority for the Department of Defense, and for the missions of the National Aeronautics and Space Administration.

Results and Accomplishments

Significant progress has been made towards the goal of collecting EBIC data from single-nanowire devices, using two different microscopy set-ups. We have prepared single-nanowire devices from both Si and ZnO p-n junction nanowires (grown by us at the University of Kentucky), characterized the electronic and structural properties of these prototype devices, and are currently undertaking EBIC measurements of such a device. We have attempted a number of device fabrication methods, including (1) using micromanipulation in the focused ion beam (FIB) instrument in which connections to the feed-through bonding pads are made using ion-beam-induced deposition and (2) by drop-casting as-grown wires onto the device substrate followed by lead fabrication using electron-beam lithography. The e-beam lithography method proved to be the more successful, due to challenges with FIB micromanipulation. I-V curves have been collected from these devices ex situ, allowing us to identify wires which contain p-n junctions (those which show rectifying as opposed to ohmic behavior). Initial EBIC measurements attempted with prototype devices have allowed us to identify and troubleshoot several sources of noise. Taking measurements using the JEOL 2200FS we identified noise sources which are prohibitively high for the low EBIC signals we are attempting to collect, due to shielding methods used in the commercial Protochips holder. For this reason we are now building a custom detection system on a dedicated STEM (VG Microscopes HB601), in parallel with a complementary cathodoluminescence system. Here, noise levels can be controlled, and initial measurements are promising.

05960

Tuning the Chemical Reactivity of Metal Nanoparticle Aggregates by Actively Controlling Their Electronic Coupling

G.M. Veith, D.E. Jiang, A.R. Lupini, M.C. Troporevsky

Project Description

A fundamental challenge in the field of nanotechnology is tuning the properties of nanoparticles, in particular, the chemical reactivity and catalytic properties of metal nanoparticle aggregates. We propose adjusting the electronic coupling between nanoparticles to tune the chemical reactivity of metal nanoparticle aggregates. We believe this can be achieved by applying an electric field to the system, thus providing a novel way of actively controlling a chemical reaction. Recent theoretical studies on the electronic coupling between metal nanoparticles support our hypothesis. Utilizing the electronic coupling as a new tuning variable offers the paramount advantage of being able to tune the catalytic activity of metal nanoparticles in real time during the course of a reaction.

Mission Relevance

This project intends to establish a strong ORNL presence in the rapidly expanding field of tunable nanoparticles for clean energy production, nano-manufacturing, storage, and utilization. The importance of catalysis for energy production and utilization is extensively covered in the 2008 DOE report *Basic Research Needs: Catalysis for Energy*, which highlights DOE's financial support for research in catalysis. The results of this study will be very relevant to DOE's catalysis programs in the Office of Science and Energy Efficiency and Renewable Energy (EERE), both of which focus on investigating more efficient energy production from several domestic sources.

The ability to tune the binding energies of molecular species could be used to control the capture and release of molecules such as CO_2. The demonstration of our concept will have an important impact to agencies such as Advanced Research Projects Agency – Energy (ARPA-E) or DOE Fossil Energy programs to pursue sequestration of CO_2.

Results and Accomplishments

To tune the coupling of metal-metal nanoparticles, many silver nanoparticles were prepared with different types and lengths of capping ligands with nitrogen head groups. These particles were characterized for the CO absorption and inter-particle spacing using surface area and electron microscopy, respectively. In parallel, first-principles density functional theory calculations of the binding of the CO on the silver particles were completed, providing theoretical guidance for the separation required to develop electronic coupling between the silver particles. These studies showed that variations in CO binding energies can be achieved by either changing the inter-particle spacing or applying an electric field. To understand the role of nitrogen on the head groups' influence on CO absorption, reference samples of metal nitrides were made with pure nitrogen, that is, no hydrocarbon chains. This work lead to the discovery of the new precious metal nanoparticles $PtN_{6.7}$ and $PdN_{5.7}$. These 1–2 nm particles were grown on flat substrates and high-surface-area powders. The nanoparticles were completely catalytically inactive. This inactivity confirms the experimentally validated stoichiometry; since there is so much nitrogen on the nanoparticles, they block all the metal active sites. The chemistry has been expanded to include nitrides of gold, iridium, and iron. Films of these materials were almost as conductive as pure metal films, possibly providing a method to reduce precious metal consumption in consumer electronics.

Information Shared

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A. Villa, D. Wang, G. M. Veith, L. Prati, "Bismuth as a modifier of Au–Pd catalyst: Enhancing selectivity in alcohol oxidation by suppressing parallel reaction," *Journal of Catalysis,* 292(1), 73–80 (2012).

06257

Zeolite Membranes for the Capture of Krypton and Recovery of Xenon from Voloxidation and Dissolver Off-Gas

R.R Bhave, W. Koros, G. (Bill) DelCul, R. Jubin

Project Description

The proposed concept focuses on fabrication of engineered zeolite membranes to demonstrate an innovative and potentially breakthrough process for the capture of krypton (Kr) and recovery of highly pure xenon (Xe) from standard and advanced voloxidation and dissolver off-gas generated from nuclear fuel cycles. Advanced fuel cycles create complex gas mixtures that pose formidable challenges to perform selective separations for the purpose of recovery and/or capture of gaseous components. Zeolite adsorbents have been proposed and evaluated for the separation of Xe and Kr from the head-end off-gas. However, these have not been evaluated for recovery and/or capture in pure form, which is highly desirable. The capture of Kr and recovery of pure Xe (valued at $30/liter) with zeolite membranes would be a major advancement over the current state-of-the-art options for off-gas treatment that include molecular sieve adsorbents and cryogenic distillation.

The development of optimized small-pore silico-alumino phosphate, alumino-silicate, and titano-silicate inorganic molecular sieve membranes for highly selective separations is novel and involves significant risks. However, successful demonstration of proof of concept would strongly position ORNL to address the objectives outlined by the DOE Office of Nuclear Energy for the Modified Open Fuel Cycle (MOC) research and development. Our focus will be to fabricate engineered zeolite membranes to demonstrate the capture of Kr and recovery of highly pure Xe.

Mission Relevance

Separations are one of the key focus areas of Fuel Cycle Research and Development. Our novel research initiative to develop highly selective zeolite membranes can play an important role to achieve DOE mission of near-complete spent nuclear fuel recycle and waste minimization. This is a critical national need for long-term energy security.

Results and Accomplishments

Hydrothermal synthesis of MFI and LTA has been carried out in order to prepare seed crystals for fabricating zeolite membrane. Synthesis parameters such as reaction time, temperature, and compositions were varied systematically to control the microstructure of zeolite as well as their crystal size and shape. We have shown that crystal size of MFI can be finely tuned from 50 nm to 300 nm while different crystal morphologies (hexagonal, cubic, and coffin) were observed. The diversity in shape originated from the three-dimensional microstructure of MFI as well as its sensitivity to synthesis conditions. Due to dimensional identity of LTA microstructure, cubic morphology was only made with controllable crystal size from 100 nm to several microns. Both zeolites were monodispersed and colloidally stable so that suspensions of these crystals can be used for zeolite crystal deposition on porous supports by wet coating methods.

We used a seed growth technique for making thin LTA membrane on stainless steel support. In the technique, a formation of a thin seed layer plays an important role to determine quality of resulting zeolite membrane. First, in order to decrease roughness and pore size of stainless steel tubes for nanocrystal deposition, porous alumina layer was deposited on the tube. A continuous alumina layer was observed. It was found that a dip-coating method using zeolite nanocrystal sol was sufficient to generate uniform and defect-free coverage on porous stainless steel with a porous alumina intermediate layer. The dip-coating method has strong benefits because it is simple and practical and can be used for various geometries of porous supports such as tube, plate, and hollow fiber. LTA nanocrystals were evenly dispersed and deposited on the tubular alumina layer. Coating parameters such as the immersion duration (10–600 seconds), the pulling rate, and concentration of suspension (1–5 wt %) did not have significant effects on resulting seed layers. After optimization of seed layer deposition conditions, hydrothermal syntheses were carried out on the LTA layers using either conversional heating as well as microwave irradiation. Continuous LTA membranes were obtained from both hydrothermal approaches, and surface morphologies of synthesized LTA films from both the methods appeared to be similar. Using wide-angle x-ray diffraction, it was shown that pure LTA membrane was obtained without micro-structural impurities such as FAU and SOD. Gas permeation studies will be performed on LTA membranes prepared from both hydrothermal syntheses procedures.

Information Shared

An invention disclosure was filed describing the use of zeolite membranes for the capture of krypton and recovery of pure xenon from voloxidation and dissolver off-gas (IDSA 2012-02787).

06259

Determination of Coating Mechanical Properties Using In Situ High-Temperature Digital Holographic Imaging

S. Dryepondt and C. Mann

Project Description

The goal of this project is to determine the in situ properties of industrial and model coatings at high temperature by the novel application of digital holographic imaging. Real-time observation during high-temperature exposure of aluminum-containing coatings deposited on different substrates will allow for the characterization of a number of life-limiting coating properties such as ductility, toughness, creep resistance, microstructure evolution, and phase transformation with time and temperature. The demonstration of such a unique experimental capability, along with the Laboratory's well-established capabilities for materials and image science, will enable ORNL to compete for funding opportunities to establish realistic models of coating degradation and thus improve the lifetime of, and predictive capability for, coated gas turbine and power plant components as well as those used in other applications where coatings are needed. The capability for real-time, high-temperature, nondestructive evaluation also has great potential for projects related to quality control and/or cost reduction in manufacturing processes.

Mission Relevance

Coatings such as iron or nickel aluminides have demonstrated their ability to protect nickel- and iron-based alloys from corrosion attack. The development of a unique case of digital holography imaging, which allows for the real-time imaging of materials exposed to high temperatures, would greatly improve the understanding of coating degradation mechanisms and will be of great interest for turbine manufacturers, not only for materials development but also as a means of prognosis or condition-based servicing. The ability to assess coating brittleness would moreover represent a priceless asset regarding future research on aluminum coatings for automotive and fossil energy applications.

The recent interest expressed by ITP for manufacturing processes improvement also represents a remarkable funding opportunity for real-time high-temperature nondestructive evaluation. Such a capability could potentially be integrated in a line manufacturing process to readily assess component surface quality.

Results and Accomplishments

A high-temperature (up to 1500ºC) stage was purchased and inserted in the digital holographic imaging system. NiPtAl coatings were deposited by chemical vapor deposition on single-crystal superalloy coupons. The coated coupons were then machined to fit the 5 mm × 5 mm hot stage chamber and carefully polished with sandpapers and 0.3µm alumina powder. First heating trials revealed that digital holographic imaging of the coating surface was successful up to ~1000ºC, but at higher temperature, oxidation of the coating surface started to degrade the signal significantly. The setup will be upgraded to flow an inert gas through the hot stage during heating to limit oxidation.

The system was instead used to characterize the martensitic transformation of NiAl and NiPtAl alloys of composition similar to the coatings, because the transformation occurs at a temperature low enough to avoid surface oxidation, and this transformation can generate high stresses in the coating. The steps formation during heating at the specimen surface due to the transformation from martensite to austenite was monitored, and post-processing of the images yielded 3D movies showing a step height increasing from ~100 nm to a maximum of ~1 µm. The transformation temperature was highly dependent on the alloy composition, from ~75ºC to 625ºC, and the back transformation during cooling, from austenite to martensite, was never complete. Similar experiments will be conducted on coated specimens during the second year.

06262

Electrochemical Energy Storage in Solutions of Renewable Organic Quinonoid Species for Energy Dense Flow Batteries

W.E. Tenhaeff

Project Description

Redox flow batteries with high energy densities and low costs hold the promise for transformative electrical energy storage (EES) systems. In this project, a novel “half flow” battery concept is described consisting of protected lithium metal anodes and energy dense catholyte solutions of naturally occurring, renewable, organic charge storage materials. The overall objective of this project is to perform proof-of-principle experiments demonstrating that highly concentrated solutions of these materials can be electrochemically cycled reversibly, which is required for practical flow battery operation. Interfacial and intermolecular charge transfer processes and competing chemical and physical processes will be characterized to understand the limitations of these solutions in flow battery applications. The synthetic organic chemistry expertise at ORNL will also be exploited to elucidate paths to even greater energy densities. Success will establish ORNL’s leadership in understanding the fundamental aspects of multi-electron charge transfer processes in concentrated quinonoid solutions.

Mission Relevance

This project seeks to develop an electrochemical energy storage technology that utilizes abundant, renewable organic materials to store electrical charge. Unlike many cathode materials for conventional lithium ion batteries based on scarce transition metal elements that are imported from foreign countries, these organic species can be produced domestically. This will result in greater energy independence. The technology is relevant to grid level and transportation energy storage applications. If the technology performs as anticipated it could displace costly alternative technologies, such as vanadium redox flow batteries and conventional lithium ion batteries. The study is relevant to problems currently funded by DOE’s Office of Science, Office of Energy Efficiency and Renewable Energy, and Office of Electricity.

Results and Accomplishments

The proposed objective of the project is to demonstrate reversible energy storage in concentrated quinonoid catholyte solutions and the operation of “half-flow” batteries using these solutions and protected lithium anodes. To achieve these goals, the project was divided into three tasks.

1. Systematically characterize redox reversibility in concentrated solutions
2. Chemical functionalizations to increase energy densities
3. Incorporation of catholytes in model “Half-Flow” cells

Commercial sources of several functionalized quinones with appreciable aqueous solubilities were discovered. The electrochemical behavior of 1,2,4-benzenetriol (HQ-OH) was characterized. In 1 mM solutions, it was shown that the two electron transfers of HQ-OH are electrochemically reversible. At higher concentrations, the electron transfers became electrochemically irreversible, which was preliminarily linked to irreversible adsorption of HQ-OH to the electrode surface. Potential techniques to prevent this adsorption have been identified. It was shown that the maximum solubility of HQ-OH is greater than 3 M, yielding a theoretical energy density greater than 560 Wh L^{-1}. This is 7.5× greater than the theoretical energy density of conventional vanadium-based catholytes. Further chemical modifications of the quinone species to increase energy densities are not required, but other functionalizations may be investigated to inhibit adsorption to electrodes.

For the last task, FY 2012 efforts focused on developing protected lithium anodes. Protected lithium anodes are required for the flow battery concept to be successful. The design, fabrication, and evaluation of the various anode components have been completed. Hermetically sealed lithium anodes have been successfully developed. The next task is to characterize their electrochemical performance.

06263

Creating Tunable Self-Organized Photonic Devices within Complex Oxides

T.Z. Ward, X. Xu, I. Ivanov

Project Description

Light-based circuitry is a transformational technology that promises to replace existing electron-driven machines with faster, more secure computing and communications devices based on the flow of photons. One of the primary obstacles limiting this technology is in the materials used to control the photons. Standard devices must be engineered into photonic structures that provide only narrow tunability and relatively low switching speeds in the gigahertz range. In this proposal, we submit a novel method of creating highly tunable devices with orders higher switching speeds based on the inherent electronic phase separation in single crystal manganites. In these materials, it is possible to control the formation and geometry of competing electronic states having vastly different optical properties. These emergent electronic phases have been shown to exhibit transition times (switching speeds) in the terahertz range and are highly sensitive to multiple field types which should allow a never-before-attainable level of on-the-fly tunability. The primary goal of this study is to demonstrate the suitability of electronically phase separated materials for a new generation of optoelectronic devices.

Mission Relevance

State-of-the-art photonic devices have wide ranging applications that span many fields and industries: telecommunications, information processing, lighting, metrology, spectroscopy, holography, and medicine, with ever more emerging. Improvements in these devices coming from this proposal fit well with DOE's mission in the form of (1)lower energy consumption than current devices (energy solutions) and (2) success, which will generate immediate intellectual property (economic development).

Results and Accomplishments

Single-crystal manganite and vanadate thin films have been grown and investigated for basic resistive and magnetic properties. We have identified La[1-x]Sr[x]MnO[3] and VO[2] as the most easily accessible systems for temperature-dependent optical measurements. In these systems, electronic-phase separation is present near room temperature and each has shown a strong sensitivity to strain and electric fields which we are using to tune the orientation and transition dynamics of the inherent competing dielectric phases.

The most notable accomplishment to date is in our successful development of a new technique that allows for noninvasive, on-the-fly domain characterization. We have found that it is possible to utilize laser speckle patterns reflected off of a phase separated material's surface to observe transition temperatures for domain formation and give statistic information on average domain size through the nucleation and growth processes. As an example, VO[2] is well known to have large-scale phase separation near its metal-insulator transition temperature. Previous studies required laborious scanning probe or local optical observations which only allowed direct observation on the order of 100's nm – 1's microns, which were then used to draw conclusion on the macroscopic domain mosaic. Our newly developed method allows observation of macroscopic optical information on the millimeter scale which gives information on long-range domain dynamics and domain sizes. These results are in preparation for journal submission and are planned to be presented at next year's fall Materials Research Society (MRS) meeting. This work will be used as the basis for Department of Defense (DoD) and National Institutes of Health (NIH) funding proposals to be started next spring.

06265

A Novel High-Resolution Scintillator for Gamma-Ray Detection: $CaI_2:Eu^{2+}$

L.A. Boatner and J.S. Neal

Project Description

The "rediscovery" of $SrI_2:Eu^{2+}$ in 2008 and the achievement of outstanding performance through the application of significantly improved purification and crystal growth techniques have led to an explosion in new research efforts and funding for the development of new high-resolution scintillators. One such potential member of this family, CaI_2:Eu, was also initially investigated by Hofstadter, and this material received a cursory more recent and unsuccessful attempt at single-crystal growth and characterization in 2009. In principle, CaI_2:Eu has the potential to exceed the excellent scintillation performance of $SrI_2:Eu^{2+}$ due to theoretically higher light yield. Our team has participated in the fabrication and characterization of both single-crystal (R&D-100 Award in 2010) and ceramic $SrI_2:Eu^{2+}$ scintillators over the past 3 years, and we are well aware of the fabrication challenges presented by $CaI_2:Eu^{2+}$ scintillators. Recently, we have produced near-optically transparent CaI_2 ceramic samples with significantly less effort than that required for $SrI_2:Eu^{2+}$ scintillators. This research project investigates the application of advanced single-crystal growth techniques and spark plasma sintering and pressure-assisted sintering (hot isostatic pressing) to the formation of transparent ceramic $CaI_2:Eu^{2+}$ scintillators in both single-crystal and ceramic forms in order to develop a practical high-resolution scintillator with superior performance.

Mission Relevance

The project is directed toward the development of improved, easily deployable gamma-ray detectors that can be used in DOE National Nuclear Security Administration (NNSA) applications for the detection and identification of highly enriched uranium (HEU – both shielded and un-shielded) and plutonium as well as for NA-24 safeguards applications (i.e., the detection of undeclared nuclear material and activities, as well as the characterization and verification of declared nuclear material). The improved scintillators, whose development is one of the ultimate main objectives of this research effort, can be applied to monitoring the movement or diversion of nuclear material, the processing of nuclear material, handheld devices for on-site and other inspection activities, and intermediate-size portable neutron detection systems. New funding has not been obtained at this point.

Results and Accomplishments

Molten (or solid) calcium iodide does not adhere to modern glassy carbon Bridgman crucibles, and accordingly, we have now successfully applied vitreous carbon crucibles to the Bridgman growth of large (1.4 in. diameter) single crystals of $CaI2:Eu2^{+}$. These large single crystals were uncracked, and they exhibited minimal to no cleavage associated with the mica-like nature of the crystal structure. Accordingly, our initial concept and premise have proven to be correct, and it is, in fact, possible to apply modern crucible materials and techniques to the growth of large single crystals of this material. We have successfully grown $CaI_2:Eu^{2+}$ single crystals with a range of Eu^{2+} activator concentrations (4 to 10%). X-ray-excited luminescence spectra were obtained and the peak of the emission as found to occur at 472 nm. Pulse height spectra have been obtained and utilized to obtain the scintillation light yields for this material using various gamma ray sources – including 662 keV excitation from ^{137}Cs. A light yield of 75,500 photons/MeV was obtained for the case of $CaI_2:Eu^{2+}$ with a Eu concentration of 6%. Our carbon-free hot pressing system was used to carry out compaction studies of CaI_2 doped with europium. This represents the initial step that we have found to be necessary for the formation of transparent polycrystalline ceramics of halide materials of this type. Subsequent to the initial hot pressing step, the compacted bodies were hot isostatically pressed at pressures up to 35,000 psi. The expected improvement in optical transparency following this compaction treatment was, however, not observed.

06345

Rare-Earth-Free Magnets: Compute, Create, Characterize

D.S. Parker, M.P. Brady, A. Payzant

Project Description

The goal of this effort is to discover rare-earth free magnetic materials with high Curie temperature and energy product which may, upon further development, be suitable for applications such as permanent magnet motors in hybrid electric vehicles and generators in wind turbines. Rare-earth magnets, such as the Nd-B-Fe material, are currently used in these applications – major components of a national energy strategy. However, the supply of these rare-earth materials is very uncertain, creating a great need for rare-earth-free magnetic materials. We address this need via first-principles calculations to guide the synthesis and study of rare-earth-free magnetic materials, employing ORNL’s outstanding experimental expertise. Materials will contain substantial fractions of *3d* magnetic elements such as Fe or Co in combination with *5d* elements such as W, Ta, or Re, and *2p* elements such as N, C, or B. The premise is that the *2p* element covalent bonding may, via *3d-5d* hybridization, induce a magnetic moment on the *5d* elements.

This effort is intended to produce candidate materials and would substantially improve our scientific knowledge of rare-earth-free magnetism, strategically placing ORNL to lead development efforts for these magnets, with accompanying DOE funding opportunities.

Mission Relevance

This project is highly relevant to the DOE mission to "address [US] energy, environmental and nuclear challenges through transformative science and technology solutions." The fundamental US energy challenge is to ensure an adequate supply of energy and help attain energy independence. The easiest and most cost-effective way to do this is to reduce petroleum energy consumption, using such technologies as hybrid and battery-electric vehicles, and wind turbines – all of which require powerful magnets only at present possible with the rare earth materials whose supply is highly uncertain. We aim to find other magnetic materials with performance similar to these rare earth magnets but without the rare earth elements. DOE offices, such as Basic Energy Sciences, as well as Energy Efficiency and Renewable Energy, will benefit substantially from this research.

Results and Accomplishments

We have identified numerous magnetic compositions that are likely to have favorable magnetic properties if our synthesis efforts succeed. In particular, we have found theoretically that several prospective magnetic materials, such as antiperovskite Co_3WN and tetragonal Co_6W_2NC, show significant ferromagnetic ordering energies (nearly 100 meV per Co), indicating a potential for a substantial Curie temperature, and in addition a large magnetic moment on the tungsten site (between 0.6 and 0.75 Bohr magnetons for these materials). Such a moment is a finding of great importance given that the coercivity, and ultimately energy product, is determined largely by the magnetocrystalline anisotropy energy (MAE), which originates in the spin-orbit coupling of the heavy tungsten element. We additionally found theoretically that a material previously reported as Mn_2TaO_3 would be ferromagnetic and would show a T=0 magnetocrystalline anisotropy energy nearly four times as large as that of the commonly used Nd-Fe-B magnets and thus could be a high-performance magnetic material, if it could be synthesized in a stable form. A third major finding is that if sufficient proportions of iron are used in combination with 5*d* elements (typically the ratio is about 8:1 on an atomic basis), the resulting structure nearly universally exhibits a substantial moment (0.5 Bohr magnetons or greater) on the 5*d* site, implying a substantial MAE if an appropriately anisotropic crystal structure can be synthesized.

Additional results from this research effort have included two publications on magnetic properties of rare-earth free magnets (listed below), including one in *Physical Review Letters*. Results from this research effort were sufficiently promising that the Materials Science and Technology Division (MSTD) Advanced Materials Group participated in the Critical Materials Hub proposal (we currently await the response to this proposal), which if accepted will bring a funding level of 1 FTE per year for 5 years to the group.

Information Shared

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06350

Integral Vacuum Pump for Flywheel System

J.G.R. Hansen

Project Description

The project was to develop a conceptual design for and analytically demonstrate proof of principle of a flywheel vacuum system that cannot overheat due to probable commonly occurring vacuum failures, for example, roughing pump malfunction, seal degradation, joint leakage, etc. The vacuum system design incorporated a two-stage molecular pump that takes advantage of the spinning rotor surface and rotor shaft to extract gas molecules from a vacuum cavity.

Material characteristics of importance include low outgassing rates and energy absorption in the event of touchdown of a loose rotor. The path to material improvements to significantly improve vacuum system performance and safety was identified.

Use of a two-stage molecular pump to generate flywheel vacuum is innovative in that no known patent or flywheel developer uses this approach.

Mission Relevance

DOE has programs that can benefit from use of flywheels for high-power energy storage.

DOE Office of Energy Efficiency and Renewable Energy (EERE) – Flywheels are especially well suited to hybrid vehicle powertrains. Flywheels absorb high power produced by regenerative braking and then provide high power for subsequent vehicle acceleration. Safety concerns due to possible flywheel burst have caused US vehicle manufacturers to reject flywheels for hybrid vehicle applications. The project addresses safety issues caused by loss of vacuum. Loss of vacuum can cause overheating of a flywheel rotor, leading to its burst.

DOE/Office of Electricity Delivery and Energy Reliability (OE) – Flywheel-based energy storage technology can assist grid-based distribution by providing stabilization of distributed generation systems, frequency response reserve, angular instability control, and reactive power support. Fast ramp-rate flywheel energy storage systems can level out the peaks and valleys that renewables (wind and solar photovoltaics) create. The project addresses reliability issues caused by loss of vacuum for a stationary flywheel application.

Results and Accomplishments

A conceptual design was produced using Mathcad for a two-stage molecular pump designed so that spiral grooved surfaces are incorporated both in the vacuum vessel inner surface just outboard of the outer diameter of the rotor and in a cylinder just outboard of the flywheel rotor shaft. The flywheel geometry used in the conceptual design was that of the PowerBeam flywheel.

Monte Carlo–based conductance models were developed to simulate the vacuum developed by rotation of the flywheel rotor in its vacuum enclosure. The Monte Carlo simulation was a molecular flow simulation of molecules through the pump. It was a three-dimensional simulation taking into account the spiral groove geometry of the pump grooves and the moving rotor surface. Windage drag on the rotor was estimated for a range of pressures. Simulation covered flow regimes from molecular flow to viscous laminar and turbulent flow. Variables in the design analysis included both rotor and shaft gaps and rotor speed. Pump speeds (L/s) and compression ratios were calculated and examined in the design evaluation process. Data on vacuum level, rotor drag, and rotor temperature versus rotor speed were delivered in other detailed reports to document vacuum system performance.

Outgassing of the rotor composite material provided the vacuum system load. Bearings were selected so that the calculated bearing drag did not overwhelm the windage drag. Heat transfer analyses showed that the rotor only needed to be 10°F hotter than the casing for radiant heat transfer to effectively cool the rotor to a reasonable operating temperature.

The study concluded that the molecular pump showed great promise.

Information Shared

J.M. Starbuck and J.G.R. Hansen, *Safety Assessment of PowerBeam Flywheel Technology*, ORNL/TM-2009/251 (October 2009).

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06628

Development of Lignin-Based Activated Carbon Fibers for Methane Adsorption Applications

N.C. Gallego, C.I. Contescu, T.D. Burchell

Project Description

The goal of this small SEED project is to obtain a few experimental data points to demonstrate the potential of lignin-based activated carbon fibers (ACF) to store methane at moderate pressures (≤ 500 psi) and near-ambient temperature. The experimental data points are needed to make a stronger case when responding to the recently released Advanced Research Projects Agency – Energy (ARPA-E) FOA DE-FOA 0000672, “Methane Opportunities for Vehicular Energy (MOVE)”.

In this project we will use available lignin fibers produced in our laboratory under the Low-Cost Carbon Fiber project. We will process them into carbon fibers (via stabilization and carbonization steps) and will activate the obtained carbon fibers using physical method with CO_2 to two different burn-off levels. The surface properties (surface area and pore size distribution) of the obtained ACF will be characterized using standard methods, and the room-temperature, methane adsorption capacity of the two sets of ACF will be measured at pressures ≤ 500 psi.

Mission Relevance

The successful demonstration of the potential of lignin-based carbon fiber, as a low-cost adsorbent for methane storage, will position ORNL to respond to the ARPA-E FOA “Methane Opportunities for Vehicular Energy (MOVE).” It is expected that approximately $30 million will be available for new awards (approximately seven to nine awards) under this ARPA-E FOA. ORNL is in an excellent position to respond to this solicitation and to carry out the required research to develop sorbent materials that meet the targets. This small SEED project will help us obtain a few experimental data points on the methane adsorption capacity of novel lignin-based activated carbon fibers, and provide updated support information when responding to the ARPA-E call.

Results and Accomplishments

We processed two sets of readily available lignin fiber into carbon fibers (stabilization and carbonization steps) following previously determined conditions. The obtained carbon fibers were activated using physical method with CO_2 at 850°C. The obtained burn-off levels were 21% and 52%. The surface properties (surface area and pore size distribution) of the obtained ACF were characterized using nitrogen adsorption measurements at 77 K. It was found that the surface areas of the two sets of ACF were 1120 and 1750 m^2/g and the total pore volumes were 0.40 and 0.57 cm^3/g, respectively. The room-temperature, methane adsorption capacity of the two sets of ACF was measured, and their capacities at 20 bar (2 MPa) were 7.1 and 8.2 wt %, respectively. These results demonstrate that lignin-derived carbon fibers can be activated using CO_2 as physical activation agent. Although the results are promising, more work needs to be done in order to optimize the activation procedure and to increase the methane adsorption capacity.

The data obtained in this project were included in a multi-organizational proposal (ORNL, 3M, and GrafTech International) and submitted to DOE ARPA-E in response to the MOVE broad agency announcement. The object of this proposal was to develop low-cost engineered sorbent materials from a bioregenerable feedstock (lignin) for low-pressure methane storage and vehicular applications.

06631

Towards High-Performance, Earth-Abundant, Thin Film Cu_2O-Based Solar Cells

S.H. Wee, A. Goyal, J.-K. Lee

Project Description

Cu_2O is regarded as a very suitable material available for photovoltaic application because it has a direct-band gap with E_g ~ 1.9–2.1 eV, providing a high absorption coefficient in the visual region, sufficient mobility, and a relatively large minority carrier diffusion length. Thin film Cu_2O solar cells also satisfy the economical and environmental requirement necessary for the terawatt-scale deployment because they are made of an abundant, low-cost, and nontoxic material. However, high-performance, thin film Cu_2O-based solar cells have yet to be demonstrated. All previous reports use a highly defective, polycrystalline Cu_2O layer, which among other factors significantly limits performance. In our group at ORNL, we have developed expertise in fabrication of single-crystal-like metallic substrates in long lengths and widths. This opens up the possibility for a single-crystal-like Cu_2O-based solar cells. In keeping with this long-range vision, the primary goal of this project is to determine the degree of improvement possible in high-quality, single-crystal-like Cu_2O films in terms of relevant photovoltaic properties. Demonstration of appreciable improvement will allow for significant possibilities for follow-on funding, including demonstration of cell stacks on single-crystal-like copper substrates as well as finding more suitable *n*-type layers for such Cu_2O-based solar cells.

Mission Relevance

The mission of the US Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy (EERE), Solar Energy Technology Program (SETP) is to accelerate the development and large-scale deployment of solar technologies in the United States and to ensure that solar power is a viable and economic source for the nation’s power needs. DOE estimates that $1/W and lower photovoltaic (PV) solar system costs would make solar energy technologies cost competitive with other forms of energy production technologies. High-performance earth-abundant oxide solar cells based on high-quality single-crystal or single-crystal-like Cu_2O films are expected to provide an ideal pathway for reaching or exceeding the DOE target.

Results and Accomplishments

In the first year (FY 2012), we have successfully fabricated high-quality Cu_2O films on $SrTiO_3$ single-crystal substrates and textured metallic templates via pulsed laser deposition. For epitaxial growth of Cu_2O films on textured metallic templates, NiW foils with multiple epitaxial oxide layers with a $SrTiO_3$ top layer are developed. The deposition space of $P(O_2)$ – the temperature region in which pure, epitaxial Cu_2O phase without any trace of CuO phase is formed – has been identified. Phase and microstructural analyses confirmed that epitaxial Cu_2O films are highly cube textures and have smooth surface structure. Epitaxial Cu_2O films at the optimum conditions exhibited excellent electronic properties with both high carrier mobility over 10^{16} cm^{-3} and high concentration in the range of 30–50 $cm^2/V{\cdot}s$.

06640

Development of High-Performance Lithium-Ion Hybrid Ultracapacitors

J. Nanda, S.K. Martha, J.M. Miller

Project Description

The goal of the project is to develop a lithium-ion hybrid ultracapacitor (LIHUC), a hybrid energy-storage device, which can sustain high-energy density of lithium-ion batteries with high-power density and cycle life of ultra-capacitors. We propose a unique 3D electrode architecture approach that combines a non-faradaic double-layer anode with a high-energy lithium-ion based cathode potentially doubling the voltage window and thereby increasing the energy density by a factor of 4 within a single cell configuration. Additional gain in energy density and cost is achieved at the cell level as the design allows an extremely thin cathode to achieve the overall power and energy density. The proof-of-principle experiment will enable us to demonstrate a hybrid energy storage system that exceeds the current goal of U.S. Advanced Battery Consortium (USABC) and provides four times higher energy density compared to the current state-of-the art ultra-capacitors (<7 Wh/kg).

Mission Relevance

The overall experimental goal is to fabricate a hybrid energy storage cell as mentioned above that has an operating voltage >4 V with a projected energy and power density of 40 Wh/kg and 650–700 W/kg at cell level with cycle life expectancy of $>10^5$.The successful completion of the project would contribute significantly to ORNL efforts in the area of energy storage by attracting follow-on funding from the DOE Office of Energy Efficiency and Renewable Energy (EERE)–Vehicles Technologies, since the research on high-energy and high-power electrodes is a high priority for this office. In addition to DOE, we will approach the Department of Defense (DoD) and the Advanced Research Projects Agency – Energy (ARPA-E) for the follow-on funding since development of ultra storage devices for large-scale energy generation systems is the priority of these agencies. This R&D project is also strategically aligned to the ORNL carbon fiber manufacturing facility built with funding support from EERE.

Results and Accomplishments

The main goal of this proposal is to design a LIHUC energy storage device based on $LiMn_{0.8}Fe_{0.2}PO_4$ lithium-ion cathode and graphene-based double layer anode on carbon fiber–based 3D current collector. To achieve these goals, the project was divided into three tasks:

1. 3D carbon fiber-graphene-based electrode fabrication

2. Incorporating high-energy lithium-ion intercalating cathode, $LiMn_{0.8}Fe_{0.2}PO_4$, for achieving high-energy density

3. New electrolytes for enhancing the cyclability of LIHUC battery-type electrodes at high current rates

The project only started during late August 2012 with a partial funding support to cover materials expenses and perform preliminary characterization of various carbon fiber supports that will form the basis of our proposed 3D electrode architecture. Scanning electron microscopy (SEM) and Raman microscopy studies were undertaken to determine morphology and degree of graphitization of carbon fibers. One of the chosen mats for our study comprise of fully graphitized fibers obtained from Applied Sciences Inc. These fibers have a uniform fiber diameter in the range of 8–10 microns. Furthermore, we have also undertaken cyclic voltammetry studies to determine the stability of such fibers against standard lithium-ion electrolyte solution EC: DMC (1:2)/ 1,2 M $LiPF_6$. Our results show that graphitic carbon fibers work well between the voltage range of 2.5–4.6 V without any detrimental corrosion or passivation film formation.

As a part of the FY 2013 effort, we are currently incorporating multilayer graphenes (MLG) on the surface of carbon fibers by chemical functionalization in order to fabricate hybrid anodes. Synthesis of high-capacity $LiMn_{0.8}Fe_{0.2}PO_4$ lithium-ion cathode will follow shortly.

06646

Development of Fiber-Reinforced Composite Thermoelectric Materials with Enhanced Reliability and Performance

H. Wang, J. Kiggans, P.A. Menchhofer, F. Ren

Project Description

Thermoelectric (TE) materials can directly convert thermal energy to electricity and vice versa. However, their application in power generation or solid state cooling is often hindered by their poor mechanical properties. In this project, a powder metallurgical approach is used to fabricate composite TE materials with fiber reinforcement. This project consists of three integrated components including fiber generation, composite fabrication, and performance characterization. Although generating fibers represents a great challenge for these materials, incorporating TE fibers into TE matrices is expected to maintain the thermoelectric performance of the base materials while improving the mechanical integrity. In addition, introducing a fiber/matrix interface may lead to new opportunities to further enhance the transport properties via interfacial engineering.

Mission Relevance

The goal of this research is to develop a new approach to fabricate robust TE materials, which can play important roles in generating electricity from waste heat sources such as automobile engine exhaust and industrial waste heat, as well as in developing new technologies to harvest energy from renewable sources including geothermal and solar. Therefore, the current project is relevant to DOE’s mission such that it will help to develop new materials technology for improving energy efficiency and utilization of renewable energies. Furthermore, further development of TE technology can benefit other government agencies including NASA, who is currently using thermoelectric generators for powering deep space probes, and the Army and Navy, who are developing portable sources for their field missions.

Results and Accomplishments

Since its start in August 2012, this project has made progress towards the fabrication of baseline material. A p-type bismuth antimony telluride ingot ($Bi_{0.5}Sb_{1.5}Te_3$) was synthesized from pure elements via melt method. The phase composition was confirmed by powder x-ray diffraction to be > 95% pure with trace amounts of oxides. Powder was then milled from the ingot and densified by a hot pressing technique. The hot pressing conditions were optimized over four trial runs to yield materials with relative densities > 96%. The hot pressed material exhibited a very repeatable thermoelectric performance as determined from measurements of Seebeck coefficient and electrical conductivity on two samples.

Given the short performance period in FY 2012, the main research efforts will be carried out in FY 2013.

06649

Titanium/Graphite/Graphene Composite Friction Materials

P. Menchhofer and J. Klett

Project Description

Powdered Graphite foam will be blended with powdered titanium and powdered graphene and pressed together to form a lightweight composite material with high thermal conductivities and high strengths, and will be compared to other friction materials. The temperature used in processing the composite is sufficient to sinter the titanium powder to form a continuous phase of titanium, yielding a graphite/titanium composite with high strengths and thermal conductivities. The extreme thermal conductivity of the graphite ligaments (more than 5× that of copper) yields thermal conductivities of the composites that are significantly higher than standard friction materials.

This new composite family has the potential to serve as a lightweight friction (rotor) material for heavy trucks, military vehicles, trains, and other large-scale applications. However, in order to be able to optimize the properties and thus obtain funding by other agencies such as the Department of Defense (DoD), the relationships between the powder size of the graphite foam and the titanium, ratios of constituents, and heat treatment conditions to the resulting thermal physical properties need to be characterized and understood. This is critical to understanding the phenomenon and mechanisms by which the mechanical strengths, friction properties, and thermal properties are enhanced (or degraded). This project will evaluate these constituent variables (powder size, concentrations, additives, and heat treatment conditions to start) and their effect on strength, thermal conductivity, density, and friction properties. An analysis of the data will be conducted to develop fundamental relationships and the mechanisms by which the resulting properties are affected. This will then be used to approach and secure funding from other government agencies as well as DOE transportation technologies.

Mission Relevance

One project goal is to demonstrate the potential for titanium-bonded graphite materials to be utilized in brake applications. The marriage of unique properties of both materials has the potential to significantly reduce weight while providing high strength and better performance at higher temperatures and in corrosive environments. Relevant to DOE and the Office of Energy Efficiency and Renewable Energy

(EERE) missions, these materials could offer the potential for reducing energy by light-weighting vehicles and by improving performance.

Results and Accomplishments

The project initial task 1A is focusing on materials characterization for the constituent powders being used in the investigation. Initial experiments to reduce the particle size of the ORNL graphite foam by grinding, ball-milling, and subsequent sonication have shown some favorable preliminary results. Powder samples of the chosen (CP Ti) and L1 Koppers ground graphite foam, as well as samples of graphene powder (Angstrom Materials), were observed before and after some minimal processing.

The initial efforts for the project have concentrated on the microscopic characterization of the starting materials, and the subsequent effects of minimal processing to these materials. Although too early in the project to draw any conclusions, the ground graphite foam powder may offer a unique morphology and aspect ratio that could be favorable for the final composites.

MEASUREMENT SCIENCE AND SYSTEMS ENGINEERING DIVISION

05903

Decoder-Assisted Frame Synchronization (FS) for Orthogonal Frequency Division Multiplexing (OFDM)–Based Data Communications Systems

M.K. Howlader and M.A. Buckner

Project Description

Emerging Internet protocol–based systems transmit their data in packets, and a subsequent loss of synchronization reduces the data rate due to the required retransmissions. We propose a novel approach for the rapid acquisition and detection of packet transmissions by buffering the entire packet. This approach is expected to lead to reduced complexity from the current synchronization approaches, where synchronization is achieved by using a longer header, by eliminating the separation of packet processing stages, and by improving the acquisition time by basing decisions on all of the data in the packet rather than just a few header bits. Removing the longer header will increase the data rate. Not only will the acquisition and detection be accomplished in a single step, but the acquisition process will be greatly enhanced through the application of all of the available information. Earlier results from our research on traditional non-OFDM based systems indicate that the probability of the false acquisition of packets can be reduced by several orders of magnitude with this approach. Our intent now is to expand the research to OFDM-based communications systems. The proposed research will explore code structures and hybrid decision matrices for the decoder to support joint FS and detection for OFDM-based systems.

Mission Relevance

The proposed research is based on a novel technique for FS. This technique offers unique contributions to the field of synchronization for communication systems. However, existing research results are not detailed enough to be considered for practical systems. There is a legitimate gap between the basic concept and the challenges for its application to practical systems. The proposed proof-of-principle research will bridge this gap by showing that the FS scheme can be applied to practical OFDM systems.

Robust, fast, energy-efficient communications is of interest government-wide, as well as in the commercial sector. Program managers in the US Department of Energy Industrial Wireless Program and Office of Electricity Delivery and Energy Reliability have shown interest in such communications systems, and these organizations are potential sponsors. Other potential sponsors for the developed technology include the US Departments of Defense and Homeland Security and the National Aeronautics and Space Administration. OFDM-based communication systems are already planned for many military, space, homeland security, and commercial applications.

Results and Accomplishments

We developed a theoretical basis for a noncoherent decoder-assisted frame synchronizer, a two-stage synchronization scheme based on the list-synchronization principle, for the serially concatenated coded differential modulation system in the burst OFDM transmission. We adopted the conventional minimum mean-square estimation rule based on the supplementary guard interval to provide a list of potential frame starting positions for the coarse synchronization in the time domain. We used the decoder-assisted methods to obtain more reliable final synchronization decisions for the fine synchronization in the frequency domain. Here, we developed a new synchronization method by fully exploiting the combination of different decoder information. We used the Matlab program for our simulation results. We achieved the main goals of the project: develop a decoder-assisted FS technique for OFDM systems, select the proper synchronization word and derive the required cost function, and develop a method for the decision at the second stage of the synchronization. We also achieved results for joint FS and channel estimation. Various optimizations of the decision matrices still need to be accomplished.

Synchronization information from the OFDM system has been used for a vehicle lane positioning technique based on joint frequency difference of arrival and time difference of arrival by measuring Doppler frequency.

Information Shared

P. Vallance and M. Howlader, “Automotive Geolocation Using Wireless Infrastructure in a GPS Denied Environment,” presented at the Virginia Tech Symposium on Wireless Personal Communications, June 1–3, 2011, Blacksburg, Virginia.

06250

Precision Long-Range Projectile Tracking

S. Rajic and P. Datskos

Project Description

The project entails proof-of-principle experiments and analysis to examine a novel optically based projectile tracking approach. The concept to be demonstrated is the basic feasibility of using the rotation of the projectile as the periodic source for a synchronous detection based tracking approach. The projectile itself will be completely passive in this approach and thus will contain no emitter, batteries, or electronics of any kind. This type of approach can provide covert projectile precision location information even in daylight hours that is presently not achievable. The successful completion of this project, along with additional follow-on funding, could lead to the elimination of a human spotter. Additionally, the information derived from such technology could be used to compensate the sight reticle to always be coincident with the projectile point of impact under any environmental conditions. Having detailed knowledge of a projectile’s location over a long range can also be useful in determining the environmental condition along that path. That information can be beneficial in several additional applications beyond projectile tracking.

Mission Relevance

The feasibility demonstration of this approach will support the DOE national security mission in many ways, such as providing a substantial capability increase to DOE special courier teams. The primary funding source, and beneficiary, for this technology would ultimately be the Department of Defense (DoD). Projectile tracking, and aim point compensation, is of great concern to all of the military services.

Results and Accomplishments

Key components have been procured and configured to provide empirical feasibility data. Reflectivity measurements were performed on these components by rotating a projectile mock-up with an embedded retroreflectors to determine signal-to-noise as a function of effective distance. Analysis was also performed to determine a theoretical signal-to-ratio with these initial commercial reflectors. The results indicate a S/N of 12 can be achieved at a range of 1600 m with an eye safe laser source.

06346

Growth of Large Area Single-Crystal Graphene

I. Vlassiouk, N. Lavrik, P. Datskos, G. Eres

Project Description

Graphene is an emerging one-atom-thick carbon material with potential applications ranging from photovoltaics and electronics to desalination membranes. In this project we propose to investigate the feasibility of growing large single-crystal graphene domains using ORNL's unique capabilities and experience in thermal processing.

We intend to use catalytic copper substrates and chemical vapor deposition technique (decomposition of carbon containing gases such as methane, acetylene, etc.) to produce graphene. They key innovation as well as the main challenge of the proposed effort consists of identifying growth parameters that lead to formation of defect-free single-crystal graphene domains with characteristic sizes of $1mm^2$ and above. Our main hypothesis is that such growth can be achieved and optimized by tuning deposition temperature and hydrogen pressure during graphene growth. The quality of the fabricated graphene will be characterized by a set of complementary techniques, including charge carrier mobility and thermal conductivity measurements.

The completion of the project will provide critical answers regarding the feasibility of large single-crystal domains of graphene suitable for a variety of electronic applications.

Mission Relevance

Graphene has a great potential in many DOE mission areas, such as biotechnology, energy-efficient devices, computing, composite materials, and waste treatment. In particular, graphene can potentially be employed as a substitute for expensive indium tin oxide (ITO) in solar cells, mobile devices, large displays, and other energy-related applications such as electrochromic windows. Graphene can be employed as a thermal management component, and could be the basis for new composite materials with remarkable properties. Thus, proposed ORNL capability to synthesize large graphene crystals will directly contribute to the successful accomplishment of DOE goals.

Results and Accomplishments

We have elucidated that optimal condition for atmospheric pressure chemical vapor deposition (CVD) synthesis of graphene with large domains corresponds to temperatures close to the melting point of copper, where the nucleation density is the lowest. The activation energy for nucleation is dramatically larger in atmospheric pressure CVD compared to that under the low-pressure conditions (9 eV vs 3eV), and we attributed this to copper evaporation rate dependence on the background pressure. At low pressure conditions, severe copper evaporation dictates the desorption rate of active carbon on the surface, while at atmospheric pressure, experimentally measured 9 eV activation energy is attributed to desorption energy of carbon clusters from the surface. High copper evaporation rates at the low-pressure synthesis conditions result in significantly greater catalyst roughness compared to the atmospheric pressure conditions. Because of these different mechanisms, atmospheric pressure CVD also shows opposite to the low-pressure CVD preference in nucleation densities on different crystallographic orientations of copper at low temperatures; that is, nucleation on (111) surface is three times higher compare to (100) and (101) copper surfaces. At any pressure conditions, the highest possible temperature should be used for the synthesis of large single-crystal graphene. Nearly millimeter (0.6 mm) hexagonal graphene domains were achieved and their single-crystal appearance was confirmed by LEED.

Information Shared

I. Vlassiouk, P. Fulvio, H. Meyer, N. Lavrik, S. Dai, P. Datskos, S. Smirnov, “Large Scale Atmospheric Pressure Chemical Vapor Deposition of Graphene,” *Carbon*, **2012**, in press, DOI: 10.1016/j.carbon.2012.11.003

06627

Systems Approach to Steganalysis

J.D. Allen, V.C. Paquit, X. Liu

Project Description

Our goal is to demonstrate that it is feasible to detect steganographic embeddings (i.e., secret messages hidden in digital images) using novel texture-based 3D steganalytic routines.

Steganography is the art and science of writing hidden messages in such a way that no one, apart from the sender and intended recipient, suspects the existence of the message. In an ever-growing world of digital media, sophisticated steganographic routines were implemented and improved to embed secret messages in seemingly innocent cover objects, in particular digital images, introducing distortion and artifact almost invisible to the human eye. Consequently, steganographic images are almost impossible to detect amongst the billions of images available on the Internet, and therefore can be used to create a covert communication protocol to bypass internet censorship. Existing signature-based, machine-learning, and statistical approaches are not sufficient in meeting the needs of intelligence and security communities due, largely, to the lack of accurate models. By investigating a novel detection method called Long-Range Correlation (LRC) which aims at understanding how the steganographic routines are modifying the image encoding, we expect this project to enable the near-term development of a robust steganalytic routine to detect state-of-the-art steganographic algorithms.

Mission Relevance

Often used by terrorists to create cover communications, steganography allows hiding messages and/or documents in digital media. Tools exist to extract hidden information from known-to-be steganographic media; however, over years steganographic routines have become increasingly hard to identify, and despite millions of dollars invested in this quest, the Department of Defense (DoD)/Intelligence Community does not have the tools or the resources to efficiently identify steganographic media amongst all of those present and exchanged over the Internet, making the development of a “steganographic data finder” a national security interest. Considering these facts, this proposal intends to investigate a unique approach for steganalysis, which if successful will put ORNL in a desirable position to lead steganalysis programs. In the longer term, we envision this technology as a key enabler for creating a fully tunable digital image forensics. These near-term and long-term plans provide for significant follow-on funding opportunities through collaboration with Intelligence Advanced Research Projects Activity (IARPA), Defense Advanced Research Projects Agency (DARPA), and the Air Force Research Laboratory (AFRL).

Results and Accomplishments

As a preamble it is important to note that changes to the team occurred during year one: (1) Dr. Allen left ORNL before the end of FY 2012, transferring the role of PI to Dr. Paquit, and (2) due to administrative problems to put the subcontract in place with FSU and the new research schedule resulting from this delay, Dr. Liu decided not to participate or pursue this project. As a result, starting in FY 2013, Dr. Paquit will be the only researcher from the original team working on the project, therefore taking over all the tasks associated with the project.

Year one was mainly focused on (1) understanding, compiling, and testing steganographic routines such as F5, Outguess, Perturbed Quantization PQ, and Modified Matrix Encoding MMx, (2) developing automatic 3D model generator with texture mapping to create our synthetic image database, (3) implementing image feature extraction algorithm on a GPU platform as we are expecting to analyze two databases of billions of images in order to find a handful of tempered images, and (4) identifying and preparing a large database of real images to be used in performance benchmarking.

Most of these tasks have been completed in year one. Year two will be focused on the study of the Long Range Correlation approach. Also, from our understanding of the steganographic routines and our expertise in image formation and JPEG encoding, we are planning to test additional image processing–based approaches that might be more suitable than the LRC.

06633

Digital Hydraulic Actuator

L.J. Love and R.F. Lind

Project Description

The proposed *digital hydraulic actuator* enables discretely variable cross section controlled by ORNL’s new multi-stage digital valves. The objective of this project is to develop a new energy-efficient control methodology for fluid-powered cylinders. Rather than controlling fixed displacement actuators (cylinders with a fixed cross section) with dissipative type controllers, we propose a variable displacement actuator controlled with digital control valves. To validate this approach, we will design and fabricate a variable displacement linear actuator controlled by a set of energy-efficient, high-flow digital control valves.

Mission Relevance

Fluid powered systems (pneumatics and hydraulics) are a fundamental component in manufacturing. While this is a large and diverse industry, there has been very little research and development in the fluid power industry since the 1960s. Fluid powered components consume between 2 and 3 Quads/year. The efficiency of fluid-powered systems is typically very low (less than 14%). Traditional hydraulic control is based on fixed sized pistons controlled by valves that throttle the pressures down to the required load pressure. These throttling losses account for approximately 40% of the losses in a hydraulic system. If successful, this technology will provide a pathway to more than double the net energy productivity of fluid-powered systems.

Results and Accomplishments

Activities this year have focused on simulation and design. Simulations show that by varying the effective actuator cross section (A, 2A, 4A or 8A) as a function of the load force (F), it is possible to control the piston chamber pressure. When driving a load, it is desirable to open the appropriate valves completely so that the chamber pressure is slightly under the supply pressure (Ps), thereby reducing throttling losses (the pressure drop between the supply pressure and piston chamber pressure). Likewise, when the load force is driving the actuator (the actuator is absorbing power), it is desirable to open the appropriate valves so that the chamber pressure is slightly greater than the supply pressure, thereby enabling the actuators to act like a pump (e.g., regeneration). SolidWorks computer-aided design models of the actuators and valves are complete. Valves have been manufactured and tested. Remaining activities will focus on fabrication, assembly, and testing. Applications of the technology include energy-efficient pneumatics and hydraulics for mobile systems (excavators, backhoes) as well as energy-efficient pneumatics in material handling.

Information Shared

L.J. Love, "Additive and Emerging Manufacturing Technologies and Their Impact on Fluid Powered Components," National Fluid Power Association Conference on The Future of Energy Efficient Fluid Power, Chicago, IL, Nov. 29–30, 2012.

06634

Image Analysis for Calibration and Comparison of Hyperspectral Retina Fundus Camera Data and Ocular Phenomena

T.P. Karnowski

Project Description

Our objective is to develop semi-automated software tools for the analysis and comparison of retina tissue for human and animal subjects with a hyperspectral retina camera. Since different physiological elements of animal and human eyes have different spectral responses, our primary scientific objective is to find and validate relevant animal models for various human retinal phenomena using these tools. Our proposed primary result is a comparison of the spectral response from several animal subjects with human subjects to find a close match to the spectral response of the human retina which can serve the vision research community as suitable animal models for this exciting new imaging modality. While some animal models are widely used in ophthalmology research, their validity in the hyperspectral domain is not known. Animal models are important in this research because once a suitable hyperspectral model is found, different experimental protocols can be established for studying the detectability of various phenomena in the hyperspectral modality.

Mission Relevance

The research made possible by this work will help maintain a vibrant US effort in the science of ocular disease and conditions, which will enhance American economic prosperity. In addition, the impact of this research, and related follow-on funding, will be research tools and animal models which will validate the use of this new imaging modality for a variety of detection tests for specialized ocular conditions, improving the ability of physicians to detect and cure blinding eye disease. This will benefit a variety of federal agencies ranging from the Department of Health and Human Services to the Department of Defense.

Results and Accomplishments

This project began in FY 2012 with a limited amount of funds ($10K, or roughly 5% of the total budget), and thus results and accomplishments are limited at this point in time. We have, however, spent some development time ensuring the software and research tools developed with this work can be ported to multiple environments to maximize usability, and we have also begun investigating the design of the software in a portable environment (ideally open source, such as Python). We have also begun the coding of an algorithm which can compare two HFC fundus images in a brute force fashion, using affinity matrices (which attempt to compress high-dimensional data using similarity measurements between spatially adjacent components). In addition, we have dealt significantly with programmatic issues for our collaboration with University of Southern California and Doheny Eye Institute and ensured our research is meeting ORNL Animal Tracking protocols.

06641

Adaptive Emissivity Surface Using Sub-Pixel Averaging

S.R. Hunter, P.G. Datskos, J.T. Simpson

Project Description

The project focuses on developing adaptive surface emissivity techniques that result in the control of the thermal radiation emitted from a variety of surfaces. The technique uses the finite spatial resolution of infrared imaging cameras to average, at the sub pixel level, the infrared power radiated and reflected from interlaced high- and low-emissivity structures located on the surface of the adaptive emissivity surface. The work in this project will demonstrate the feasibility of the technique and the conditions under which it can effectively alter the thermally emitted radiation from the surface in a number of different operating environments, thereby modifying the apparent emissivity of these surfaces while simultaneously managing the thermal load and waste heat generated by the underlying structures.

Mission Relevance

Traditional emissivity control techniques rely on pattern matching to make the reflected signal from a surface be as indistinguishable as possible from that reflected from background objects. However, these techniques do not work well in the infrared wavelength region as warm objects produce heat that must be dissipated into the environment. Simple changes in the emissivity of the surface to attempt to reduce the apparent temperature to close to that of the background are only partially effective as the heat generated by the surface must be dissipated through another high-emissivity surface or the temperature of the surface must increase to compensate for the reduced emissivity of the surface. The approach being explored in the present project involves the development of surface emissivity modification techniques that result in variable infrared power emission capabilities, allowing these surfaces to blend into the thermal background. The goal is to modify the apparent emissivity of surfaces while simultaneously managing the thermal load and waste heat generated by these structures. There are numerous of applications for variable emissivity surfaces, and we have contacts in several potential sponsor agencies that would fund research and development in this area once a proof-of-principle demonstration had been achieved. These potential sponsors cannot be listed here due to the sensitive nature of this work and its applications.

Results and Accomplishments

This project started in late July with an initial funding of $20,000 for FY 2012. This funding was primarily used for project kick-off activities (setting up project accounts, acquiring lab space, and supplies for the project) and obtaining an infrared camera that will be used to measure the apparent emissivities of the adaptive emissivity surfaces. Appropriate test targets are presently being designed and fabricated and will be examined under a variety of environmental conditions.

06642

Machine Vision for Underwater Explosive Ordnance Detection

T.P. Karnowski and R.A. Kerekes

Project Description

There is a growing yet unmet need by the United States Navy to automatically detect “proud” (i.e., resting on the seafloor) explosive ordnance (EOD) using side-scan sonar (SSS), particularly from autonomous underwater vehicles (AUVs). A proven automated technique based on machine vision and machine learning would provide benefits by reducing the time to detect and eliminate mines and improve mission effectiveness. Current methods are too labor intensive, requiring the detections in acquired images to be manually reexamined before decisions can be made to attempt to eliminate a particular specimen. In this project, we will analyze a new set of SSS images collected by Space and Naval Warfare Systems Command (SPAWAR) AUV experts using three main techniques: deep machine learning (DML), learning from signals (LFS), and image correlation methods. Our immediate goal is to validate these methods on a new test data set from SPAWAR, with the ultimate aim of producing sound, valid methods which can be deployed on an AUV with an embedded system to allow the autonomous detection of mine-like objects (MLO) and produce actionable intelligence (such as real-time detections of suspect objects at closer distances). If successful, we expect this effort to lead to additional funding to further test and deploy the detection system.

Mission Relevance

Our project and its follow-on efforts will advance the field of object detection in wide-area imagery, which is of high relevance to several DOE interests. A prime example is the National Nuclear Security Administration (NNSA) Nonproliferation Research and Development Office’s interest in computer-aided analysis of satellite imagery, which, by employing computationally efficient object detection techniques, could help analysts to locate potential areas of nuclear proliferation activity around the globe. This effort will directly benefit the Office of Naval Research, which seeks to improve the current state of computer-aided explosive ordnance detection and equip the US Navy with an improved ability to combat underwater mines. Our objective is to prove the viability of explosive detection using side-scan sonar, which we believe will generate significant interest from the Navy.

Results and Accomplishments

Our goals for 2012 included acquiring and characterizing a data set from Panama City Naval Surface Warfare Center (PC-NSWC) and reformatting an existing MLO data set acquired from SPAWAR to better create a testing/training set suitable for machine learning experimentation and research. We only acquired the PC-NSWC set in late September, and therefore this task has been moved to the start of FY 2013. We have been successful in reformatting the SPAWAR set into a group of 99 distinct MLO and roughly 200,000 background sections from the original 1425 background images. We then investigated some methods for unsupervised learning on the background images to characterize these components into groups of “uninteresting” elements. We implemented a spectral clustering method based on affinity matrices to investigate its utility as a clustering mechanism. Both these latter tasks are showing some progress but will require some sort of additional image transform (such as a Gabor filter or discrete cosine transform) to improve performance. Finally, we have begun to explore the portability of these algorithms to small embedded computer platforms such as Embedded Windows or open-source hardware solutions such as the Arduino, as the operational environment will be very low-power and low-payload constrained.

06643

Arrays of Piezoelectric Nanotubes Based on Polyvinylidene Difluoride

G. Polyzos, J. Simpson, D. Schaeffer, P. Datskos

Project Description

Polyvinylidene difluoride (PVDF) is a semicrystalline polymer that exhibits piezoelectric properties when the net dipole moment of all crystallites is oriented. Stress-induced polarization is an effective method for switching of the non-polar α phase into the polar-piezoelectric β-phase. The objective of the proposed work is to use a draw tower technique and fabricate arrays of aligned PVDF nanotubes. The fabrication of these piezoelectric arrays will be implemented by co-drawing PVDF and poly(methyl methacrylate) (PMMA). A bundle of aligned PVDF nanotubes will remain after dissolving the PMMA phase with acetone. The project aims to establish the proof-of-principle concept and define the limits in the length of the arrays in order to attain uniform and well-defined structures.

Mission Relevance

There is an enormous interest and numerous applications associated with scalable piezoelectric nanostructures. The project established the scalability and capability within ORNL to fabricate aligned piezoelectric nanostructures. This will allow ORNL to build on existing infrastructure and make an impact in the field. The achieved structures can be utilized in many strategic applications such as energy storage (i.e., capacitors), separation devices, nanoelectronics, nanoactuators, and piezoelectric sensors. The Defense Advanced Research Projects Agency (DARPA), the National Institutes of Health (NIH), and DOE’s Advanced Manufacturing Program are potential sponsors of future efforts.

Results and Accomplishments

Piezoelectric fibers were drawn utilizing existing infrastructure. Two PVDF grades were successfully tested, and indefinite long fibers were obtained. For each grade the drawing temperature and speed were defined by employing drawing theoretical models. In order to obtain a uniform fiber with well-defined cladding, the maximum reduction in the diameter of the preform is 40 times for each draw. This technique can be applied for fabricating arrays of piezoelectric fibers or tubes. The advantage of this method compared to existing technologies is the ability to scale and perfectly align the fabricated structures.

06647

Remote Chemical Detection Using IR Microcalorimetric Spectroscopy and Quantum Cascade Lasers

P. Datskos, M. Morales, L. Senesac, N. Lavrik

Project Description

We propose to demonstrate detection of chemicals using infrared (IR) microcalorimetric spectroscopy that utilizes quantum cascade lasers (QCLs) at a standoff distance of 10 meters. Calorimetric spectroscopy uses (IR) micromechanical thermal detectors and an IR excitation source. The technique involves two main steps. In the first step, the chemical is allowed to interact with the surface of a microcantilever thermal detector. In the second step, a photothermal spectrum is obtained for the molecules adsorbed on the detector surface, by scanning a broad infrared (IR) wavelength region using quantum cascade lasers as the illumination sources. The temperature change in the active detector region is proportional to the number of photons absorbed, which, in turn, is proportional to the amount of sample species adsorbed on the detector surface. The microcantilever thermal detector will be at a standoff distance of 10 meters and will be illuminated by tunable quantum cascade lasers (QCLs).

Mission Relevance

The ability to detect and identify chemicals remotely is very important to many applications and is a highly desirable capability for many potential sponsors. For example the Department of Defense and the Department of Homeland Security have ongoing requirements about the detection of explosives. Our present approach will provide such capability in those cases in which the microcantilever can be placed near the location of the chemical. With the aid of an optical system, the cantilever will be exposed to the IR photons and with be interrogated remotely.

Results and Accomplishments

We have investigated an IR microcalorimetric spectroscopy technique that can be used to detect the presence of trace amounts of target molecules. The chemical detection is accomplished by obtaining the IR photothermal spectra of molecules adsorbed on the surface of uncooled thermal micromechanical detectors. IR microcalorimetric spectroscopy requires no chemical specific coatings, and the chemical specificity of the presented method is a consequence of the wavelength-specific absorption of IR photons from tunable quantum cascade lasers due to vibrational spectral bands of the analyte. We have obtained IR photothermal spectra for trace concentrations of RDX and a monolayer of 2-mercaptoethanol, over the wavelength region from 6 to 10 μm. We found that in this wavelength region both chemicals exhibit a number of photothermal absorption features that are in good agreement with their respective IR spectra. The results of this study demonstrate that this technique has potential to become a powerful analytical tool that can be used to detect and identify trace amounts of chemicals. The sensitivity of the described method can be further improved (by at least an order of magnitude) by increasing the sensitivity of the thermal detector. For example, by decreasing the thickness of the thermal detector an improved IR response can be achieved. Therefore, we believe a combination of tunable QCL IR sources and cantilever thermal detectors enables the implementation of photothermal spectroscopy for chemical detection and identification of many target compounds with greatly improved sensitivity and selectivity.

06648

Implementation of an Optical Properties Measurement System for Whole Intact Scattering Samples

J.S. Baba

Project Description

A proof-of-concept solution to the image degrading effects of scattering is proposed. It utilizes a backreflection geometry implementation of the integrating sphere approach to capture a sample's wavelength-dependent response to interrogating radiation. The novelty is that it permits whole, intact sample optical properties characterization using an integrating sphere by obviating the need for thin micron slicing. As such, fragile or brittle materials not suitable for slicing can be characterized via this method, and the variability of heterogeneous samples can be accommodated more extensively. Additionally, the critical information obtained can be used to solve the inverse problem of radiation transport in the highly scattering sample medium. Successful implementation will allow for more accurate standardized characterization of whole, intact sample materials that would otherwise be impossible.

Mission Relevance

Optical properties characterization of whole intact scattering materials, particularly for fragile or brittle materials, will provide critical data for computational modeling of sample response to interrogating and/or propagating radiation. This is applicable to the Department of Energy thrusts in radiation delivery, exposure, and effect measurement and monitoring, and scientific investigations that entail high-energy radiation imaging of biologic and novel engineered materials. We plan to pursue follow-on funding opportunities through the Center for Nanophase Materials Sciences.

Results and Accomplishments

A proof-of-concept system setup was implemented, and experiments were conducted to validate the technique. We are still running standards and analyzing the results to quantitatively establish the degree of success.

PHYSICS DIVISION

05868

Irradiation Effects in the Graphene-Based Electronics

P.S. Krstic and F.W. Meyer

Project Description

The objective of the project is to conduct theoretical research to further fundamental understanding of the mechanisms of radiation interaction with graphene and graphene-based electronics. We study (1) the microstructural evolution, chemical composition, and electronic structure variation of freestanding graphene (mono- or multi-layer graphite) upon irradiation, (2) variation of electronic properties of the graphene-based devices under irradiation, and (3) defect behaviors and their effects on structural and electrical properties and device performance. The defects induced by irradiation are studied by methods of classical molecular dynamics by defining the chemical and structural changes of graphene for various kinds of impact particles (H, H_2, C, CH_4 and isotopes) and various ranges of impact energies (1–1000 eV). The change of electronic and band structure, in particular the conductance as a function of the radiation damage, is quantified by the quantum methods of electron transport.

Mission Relevance

Understanding radiation interaction with graphene and graphene-based electronic devices will lay the scientific foundation to develop radiation-tolerant graphene devices, which is of interest to space and missile systems and nuclear security applications. If successful, this research will open the opportunity to transfer unique electronic structure information on a graphene layer upon irradiation into its unique conductance signatures, toward application in an ultrasensitive single-particle or few-particles detector. The control and manipulation of molecules, one of the primary missions of the DOE Office of Basic Energy Sciences (BES), will lay the scientific foundation for the development of radiation-tolerant graphene devices, which is of interest in space and Department of Defense (DoD) missile systems, as well as to the National Aeronautics and Space Administration (NASA).

Results and Accomplishments

The microstructural evolution, chemical composition, and electronic structure variation of a freestanding single graphene sheet upon irradiation of H, D, T (hydrogen isotopes) and H_2 (hydrogen molecule), in the energy range 1–1000 eV, for normal and grazing angles of impact particle incidence, and for various vibrational excited H_2 molecules, have been analyzed. Statistical analysis of these simulations, for thousand of impacts per point in parametric space (energy, angle, particle, particle state), has determined the yields of the various dynamic processes, like reflection, transmission, sputtering, and sticking. In addition, the potential of graphene was mapped across the surface, and the yields were explained. It was concluded that the results obtained by the standard hydrocarbon classical MD potentials, REBO and

AEREBO, do not provide satisfactory data for the hydrogen chemistry with graphene, as well as for the transmission and reflection probabilities (due to the existence of unrealistic barriers in these potentials). Using tight-binding Density Functional Theory (DFTB), the new potentials of H-graphene were developed, and applied quantum-classical molecular dynamics to calculate new data for H-sticking, H reflection and transmission, as well as changes of the graphene HOMO-LUMO graph due to the H-impact (0.1–200 eV), indicating significant changes in the graphene conductivity and its ability to sensitively respond to the particle energy and type (chemistry). These important results are being published in *Nanoscale Research Letters*, along with two publications with A. Allouche (refereed also in 5869) in Carbon, which partially checked our DFTB results by first-principles DFT calculations.

Information Shared

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05869

Modeling of the Plasma-Material Interface

P.S. Krstic, P.R. Kent, J.H. Harris, D.L. Hillis, F.W. Meyer, C.O. Reinhold

Project Description

This project will develop an innovative theoretical-computational capability for simulations of processes at the Plasma-Material Interface (PMI) to help guide research on present and future linear and toroidal PMI experiments. We envision development of a capability to build and validate predictive models for both ion-beam-surface interactions and more complex plasma-surface interactions. The leading component of the proposed research will be development of classical molecular dynamics interatomic potentials for fusion-relevant composite surfaces (Li, C, H) and (W, C, H, He) and their validation with the available experimental beam-surface interaction data. However, in the case of Li-H-C (ionic solids), the quantum-classical approach is attempted (based on the tight-binding Density Functional Theory) to describe chemistry in the surface. In the transition to plasma irradiation studies, we will validate the models using the existing data from the plasma PMI machines, like PISCES B (UCSD), NSTX (PPPL), and beam surface experiments (Purdue).The work will provide a foundation for predictive science of the PMI and will integrate theory with available plasma surface and beam surface measurements to validate models for surface phenomena.

Mission Relevance

The walls of magnetic fusion reactors must sustain large particle and heat fluxes, which present a major challenge to achieving controlled fusion power. A recent panel report to the Fusion Energy Sciences Advisory Committee (FESAC07) found that of the top five critical knowledge gaps for fusion, four involve the PMI. Fusion community REsearch NEeds Workshops (RENEW09) in 2009 have recommended new PMI research programs and facilities to advance the science and technology of plasma-surface interactions. A valid simulation of the PMI in the big fusion reactors (ITER, DEMO) can save billions of dollars in the long term through a predictive scientific approach.

Understanding the effects of energetic particles on materials is of great relevance to the Department of Defense (DOD), the National Aeronautics and Space Administration (NASA), and the Nuclear Regulatory Commission (NRC).

Results and Accomplishments

Development and validation of potentials for the systems containing (Li, C, O, H) as well as (W,H,He,C,O) were accomplished. Using the Electronegativity Equilization Method (EEM) (Eric Yang, student of Purdue, HERE student), we developed and applied an algorithm for calculation of position dependent fractional charges of the mixed cluster of Li-C-H atoms. We have also developed an algorithm for fitting of the short-range, bond-order (BO) potentials, based on the Tersoff-Brenner approach (Jonny Dadras, graduate student of UT, who graduated in Novemeber 2011, Paul Kent). These were completed in collaboration with H. Witek (Taiwan) and S. Irle, K. Morokuma and S. Moeda (Japan). The complete potential is being validated with experiments at Purdue and NSTX(PPPL) and verified against the first-principles DFT calculations (Alain Allouche, external collaborator, CNRS, France).

This project has resulted in nine publications in peer-refereed journals and also enabled theoretical studies on the tungsten damage under ion bombardments in the LDRD 6416, "Science of the Plasma-Material Interface at Extreme Conditions" (PI F. W. Meyer).

Information Shared

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05906

Development of a Novel Electron Dynamics Simulation

C.O. Reinhold

Project Description

We have developed a considerable fraction of a multiple electron dynamics simulation that can add explicit electronic phenomena like multiple charge transfer, ionization, and Auger processes to the widely used method of molecular dynamics simulation. As a proof of principle, we started applications of this method to treat the dynamics of all electrons in C_{60} interacting with a multiply charged ion. The theoretical approach will provide a new computational tool to study ion-grain interactions. It will also open up the possibility for other follow-on work to integrate electronic and molecular dynamics for applications such as description of dusty plasmas, intense X-ray or laser interaction with molecules, and nano-patterning of surfaces by highly charged ions.

Mission Relevance

This work is of interest to the DOE Office of Fusion Energy Sciences because of the growing importance of understanding the formation and interaction of dust in fusion and other laboratory plasmas. Interest from the DOE Office of Basic Energy Sciences is likely in simulation of the coupled dynamics of electrons and ions following irradiation of molecules by intense pulses at the new Linac Coherent Light Source or from laboratory-based ultra-intense lasers. Of broader interest, an electronic and molecular dynamics simulation would impact science that requires more explicit treatment of electrons than is currently possible involving electron transfer among molecules, electron-driven reactions, and electron ejection. The work is directly applicable for seeking follow-on funding from NASA because of the need for ion-grain modeling for an important component of the cosmic rays entering our solar system, the creation of the building blocks of planets, and the kinetic chemistry of pre-stellar clouds.

Results and Accomplishments

In the second year, the project was active only briefly due to the departure from ORNL of David Schultz, the original PI, by the end of FY 2011 and Carlos Reinhold in December 2011. During this final stage of funding, we put a few finishing touches on the computer code that was started during the first year. Work was focused on the development of a prototype electron dynamics code that could be tested against a comprehensive set of experimental data for the simplest interacting systems. As a proof of principle, we started applications to treat the dynamics of 360 simultaneous active electrons in C_{60} interacting with multiply charged ions for which several recent experimental data for distant collisions and penetrating collisions are available. These data provide a much more strenuous test of the simulation than those initially envisioned in the proposal.

06261
Technique for Elimination of Excited States from Atomic and Molecular Ion Beams

Y. Liu, M.E. Bannister, C.C. Havener, C.R. Vane

Project Description

Interactions of atomic and molecular ions with electrons, neutral atoms and molecules, surfaces, and photons play a major role in the dynamics and structure of many plasma and chemical environments. Fundamental experimental studies of these interactions are often complicated by the presence of an uncharacterized population of excited states, including long-lived metastable atomic states and vibrationally excited molecular states. Outside the United States, complex and expensive magnetic and electrostatic storage rings are used to produce “cool” atomic and molecular ion beams. There are no such facilities dedicated to atomic and molecular ion studies in the United States. This project investigates the feasibility of producing ground-state atomic and molecular ion beams without the need for such expensive facilities. We propose to eliminate the excited states in atomic and molecular ion beams using a gas-filled radio-frequency quadrupole (RFQ) ion cooler. To demonstrate the proof of concept of this technique, atomic and molecular ions with significant populations of excited states will be injected into a RFQ ion cooler filled with proper buffer gas. The excited states can be suppressed in the ion cooler through decay or by collisions with the buffer gas that preferentially destroy excited-state ions. Upon exiting the ion cooler, the ions will be sent to experimental stations where the degree of suppression of the excited states in the ion beams will be measured by state-selective photodissociation or by electron-ion interactions that have been shown to be very sensitive to the excited-state population of the target atomic and molecular ions.

Mission Relevance

Production of controlled-state ion beams will facilitate experiments on fundamental ion interactions, allowing direct comparison with state-of-the-art theoretical predictions. This project supports the DOE Office of Basic Energy Sciences mission to understand fundamental interactions of charged atoms and molecules with electrons, atoms, molecules, and surfaces that are important to many applications such as fusion energy, plasma processing of materials, atmospheric physics, and astrophysics. In many space environments such as nebulae and interstellar clouds, molecular ions exist in very low vibrational states. Thus, the technique investigated in this project could be well suited as an input for a wide variety of electron-, ion-, cluster- and photon-impact experiments of significant interest to NASA.

Results and Accomplishments

The excited atomic and molecular ions can be reduced or eliminated in a RFQ ion cooler by two means: (1) natural radiative decay to the ground state for short-lived metastable ions with lifetimes on the order of milliseconds; (2) preferential quenching in charge-transfer collisions with selected buffer gas. Molecular H_2^+ and D_2^+ and atomic C^{2+} ion beams were selected for the proof-of-principle experiments. A Colutron electron-impact ion source was used to produce H_2^+ and D_2^+ ion beams with vibrationally excited ions. The H_2^+ or D_2^+ beams were extracted from the ion source, mass selected, and then injected into a RFQ ion cooler filled with hydrogen buffer gas. Vibrationally excited H_2^+ or D_2^+ ion ions have significantly larger charge-transfer cross sections with H than the ions in the ground state and therefore could be preferentially quenched in collisions with the buffer gas in the cooler. The ions transmitted from the cooler were irradiated by a laser beam at a proper wavelength to detect the vibrationally excited H_2^+ and D_2^+ ions by photodissociation into atomic H^+ and neutral H atoms or D^+ ions and D atoms, respectively. By measuring the neutral fragments, the degree of suppression of the excited ions were determined. Successful elimination of the excited states is indicated by suppression of the neutral signals. This has been observed for both H_2^+ and D_2^+ ion beams with a laser at 532 nm for photodissociation and when the RFQ ion cooler was operated at sufficient buffer gas pressures. The 532 nm laser can dissociate the excited H_2^+ and D_2^+ions in $v > 2$ vibrational states. Therefore, the absence of photodissociation signal indicates that the cooled H_2^+ and D_2^+ beams may be in the $v = 0$ and 1 states only, with the higher excited states eliminated in the RFQ ion cooler.

Atomic C^{2+} ions from an electron cyclotron resonance (ECR) ion source were also injected into the ion cooler filled with He buffer gas. The C^{2+} beam contained metastable ions in the 2s2p $^3P_1°$ excited state which have a short lifetime of about 9.7 ms and larger cross sections for electron capture in He gas than the ions in the ground state. Thus, the metastable ions may be removed in the ion cooler by natural decay and/or by preferentially quenching in charge-exchange collisions with He buffer gas. The degree of suppression of the ^3P metastable states was determined by measuring the electron-impact ionization cross sections. Gas attenuation measurements using He buffer gas in the cooler, with no RF or deceleration fields present, established a metastable fraction of 0.49 ± 0.03. Subsequent ionization cross sections were measured to be lower when the metastable ions were preferentially quenched by the He gas in the cooler. Measurements continue to improve statistics.

06621

Optimization of Light Collection Efficiency from Liquefied Noble Gases

V. Cianciolo, R. Allen, Y. Efremenko, P. Huffman, P. Mueller, S. Penttila

Project Description

An experiment (nEDM@SNS) has been proposed to measure the neutron electric dipole moment to an unprecedented level of precision at the Spallation Neutron Source (SNS) Fundamental Neutron Physics Beamline. As articulated in Nuclear Science Advisory Committee recommendations to the Department of Energy (DOE) and the National Science Foundation (NSF), this experiment is considered a very high priority by the US nuclear physics community due to its potential to shed light on the physics responsible for producing matter in the aftermath of the Big Bang. One outstanding technical issue is the ability to extract the experiment’s optical signal, originating from neutron capture events in liquid helium. We propose to carry out an experiment to measure the optical signal strength in a system closely approximating the proposed experiment. Successful completion will significantly increase the chances for nEDM@SNS approval, with the associated MIE, long-term programmatic effort, and a high degree of visibility for ORNL and the SNS on a high-priority precision-frontier nuclear physics experiment.

Mission Relevance

Information gained in this work will be of general interest for experiments funded by the DOE Office of Nuclear Physics (NP). Immediate impact will be felt by an experiment to measure the electric dipole moment of the neutron – an experiment of high priority to DOE-NP and the National Science Foundation.

Results and Accomplishments

Activities so far have focused on the fabrication, assembly, and testing of the experimental apparatus. At this point, the apparatus is nearly complete: (1) the support frames for the dewar and the dewar insert have been completed, (2) the dewar passed a liquid nitrogen leak test and heat load test, (3) the dewar insert pieces have been fabricated and are awaiting final welding, (4) the optically isolated power supply has been completed and successfully tested, (5) the cryogenically modified photomultiplier tubes have been purchased and successfully tested, (6) the internal lightguides have been fabricated, (7) the Data Acquisition System assembled and tested, and (8) alternative silicon-based photosensors have been obtained and passed initial testing.

We expect that after the dewar insert welding has been completed the other components will be assembled onto the insert for warm, then cryogenic tests. Results will inform the design of optimized light collection systems for liquefied noble gas scintillation detectors of interest to a number of high-energy and nuclear physics experiments.

06635

Prototype of Compact Calorimeter Module for Beam Test

K.F. Read, T. Awes, C. Britton, D. Silvermyr, P. Stankus

Project Description

The objective of this project is to prepare a prototype of a calorimeter module and associated readout ready for subsequent testing at an accelerator test beam. The authors of this proposal previously were awarded funding for a DOE Lab 11-450 proposal in Nuclear Physics to develop a novel Application-Specific Integrated Circuit (ASIC) for readout of next-generation compact calorimeters to pursue high-priority scientific goals of the DOE Office of Nuclear Physics as well as compact detectors for homeland security applications. This project serves as the first demonstration of the performance of this ASIC in a realistic detector prototype. Successful completion of this project will significantly increase the likelihood that our developed readout solution will be chosen for the CERN Large Hadron Collider (LHC) ALICE Experiment Forward Calorimeter, which is a ~$15 million future detector project with a large expected scientific impact. Such real-world demonstration of the ASIC performance is very relevant to detector upgrades being considered for the PHENIX Experiment at the Brookhaven National Laboratory Relativistic Heavy Ion Collider.

Mission Relevance

As articulated in the recent Nuclear Science Advisory long-range plans and recommended Department of Energy (DOE) and National Science Foundation (NSF) milestones, heavy ion nuclear physics addresses critical research questions. One of the primary research areas in nuclear physics is the creation and study of nuclear matter under extreme conditions of high-energy density and temperature. Fundamental nuclear physics research is and always has been a core capability of ORNL. The subfield of heavy-ion nuclear physics has entered a new high-precision era yielding a wealth of new discoveries concerning a novel state of matter consisting of a plasma of quarks and gluons. In addition to directly responding to scientific goals of the DOE Office of Nuclear Physics through its relevance to the ALICE and PHENIX experiments, this project also supports the DOE Office of Science mission to apply and benefit outside applications, in this case compact, rad-tolerant, affordable, high-channel count imaging for homeland security.

Results and Accomplishments

In the first 4 months of this 12 month project, we performed simulations, finalized specifications, and purchased needed components. Simulations were used to optimize the thickness of the silicon sensor and tungsten absorber layers, as well as the dimensions of the overall prototype. A custom ORNL ASIC separately developed as part of a precursor project was submitted and received. Specifications of silicon sensor wafers were finalized after completing simulations, meeting with collaborators with past experience, and discussions with Hamamatsu Corporation. Vendors capable of cost-effectively supplying satisfactory machined tungsten layers according to mechanical tolerances and chemical composition were identified.

In conjunction with colleagues at CERN, specifications were finalized for a custom Scalable Readout System (SRS) appropriate for readout of this prototype.

Mechanical drawings of the prototype were prepared to finalize connector and integration specifications. Design work for both the sensor board and the summing board was started.

Information Shared

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REACTOR AND NUCLEAR SYSTEMS DIVISION

06256

Development of a Thermal-Hydraulics Simulation Tool for High-Fidelity Analysis of Transients in Small Modular Reactors

E.L. Popov, P.K. Jain, A.S. Joshi

Project Description

The aim of this project is to develop a parallel, three-dimensional lattice Boltzmann method (LBM)–based turbulent flow simulation code capable of handling computer-aided design (CAD) geometries and relevant boundary conditions (e.g., flow inlets and pressure outlets). The developed software—called PRATHAM (**P**a**RA**llel **T**hermal **H**ydraulic simulations using **A**dvanced **M**esoscopic Methods)—will then be used to demonstrate LBM's applicability, accuracy, and scalability for realistic nuclear applications. PRATHAM uses both the time-explicit single and multi-relaxation (SRT/MRT) LBM schemes to simulate turbulent flows and is designed to support a parallel coupled multiphysics solver (i.e., by possibly coupling it with ORNL's Denovo deterministic particle transport code and AMP fuel performance code). The deliverable of this project at the end of FY 2013 will be a parallel and scalable thermal-hydraulics code that is able to simulate time-dependent turbulent/laminar flows in realistic nuclear geometries, and a demonstration model for the ORNL's Small Advanced High-Temperature Reactor design.

Mission Relevance

The successful completion of this project will provide ORNL with a key and fundamental capability to support advanced R&D related to small modular reactors (SMRs) as well as future needs of key sponsors. In particular, it will put ORNL in a position to develop multiphysics simulation activities for SMRs using novel state-of-the-art methods. Once the proposed capability is successfully demonstrated, additional funds are expected to become available from sponsors to support specific programmatic interests and the needs of several different agencies. Proposed simulation framework for SMRs would be directly relevant and applicable to the DOE Office of Nuclear Energy (NE) mission and would potentially benefit from the above programs. In addition, successful demonstration of an advanced nuclear simulation capability will also attract potential industrial collaborations, especially from the leading SMR vendors, such as Babcock and Wilcox (mPower), Westinghouse, and General Electric (Prism), which could provide funding through cooperative research arrangements.

Results and Accomplishments

The work on the project during the reporting period was very intensive, and more than planned was achieved. Practically the work scope on the mesh generation (modification of CartGen software) committed in the project was completed during this year. In addition, a parallel version of the code

(CartGen++) was developed, which was not proposed in the original plans. Provided below is a short summary of the milestones achieved during FY 2012.

LBM Software (PRATHAM): (1) reorganization of the 3D MRT lattice-Boltzmann code written using FORTRAN-90 into multiple files and folders; (2) addition of the unstructured mesh option for SILO post-processing; (3) added midway bounce-back scheme for handling complex boundaries; (4) addition of the Smagorinsky LES model; (5) addition of the SRT model; (6) addition of outflow boundary condition; (7) adding in a restart feature; (8) added a check to calculate dfdt (steady state convergence); (9) added in a feature to use externally specified geometry (from CartGen); (10) simulations: 2- and 3-D Lid cavity-driven flows; 2- and 3-D flow around cylinder (vortex shedding test); simulation of 3-D flow inside a circular pipe on JAGUAR, massive parallel computing, initial code runs performed on 6912 cores.

Mesh Generator (CartGen): (1) code modification to make it work with the *gfortran* compiler; (2) changes of the subroutine for reading in binary STL files; (3) addition of a subroutine to write the voxel color for use as input to PRATHAM; (4) development of a boundary tagging approach; (5) debugging the algorithm to make it work for all geometries; (6) add in a feature to write output in SILO format (instead of VTK and PLT); (7) convert the output-file-writing segment of code from serial to parallel using MPI; (8) Basic algorithm in CartGen rewritten in C++; (9) optimization of data structures to save memory (compared to CartGen); (10) converted the algorithm to parallel using MPI; (11) mesh written using XDMF for "light" data and binary for "heavy" data; (12) a Python script is written to combine XDMF files and create a "global" XDMF file for post-processing.

Information Shared

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J. Nathan Cantrell, Eric J. Inclan, Abhijit S. Joshi, Emilian L. Popov, and Prashant K. Jain, "Extending a CAD-Based Cartesian Mesh Generator for the Lattice Boltzmann Method," ANS Winter Meeting, November 11–15, 2012, San Diego, CA, USA.

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Jaime A. Mudrich, "Development of a Parallel, 3D, Lattice Boltzmann Method CFD Solver for Simulation of Turbulent Reactor Flow," Student Summer Internship Technical Report, DOE FIU S&T Workforce Development Program, 2012.

Eric J. Inclan, "Development of a Preprocessing Software for Lattice Boltzmann Fluid Dynamics Solver," Student Summer Internship Technical Report, DOE FIU S&T Workforce Development Program, 2012.

06645

Inverse Sensitivity/Uncertainty Methods Development for Nuclear Fuel Cycle

G. Arbanas, M.E. Dunn, M.L. Williams

Project Description

Sensitivity/uncertainty (S/U) analysis propagates uncertainties in input nuclear data to uncertainties in reactor performance parameters ("responses"). We propose to solve the inverse sensitivity/uncertainty (IS/U) problem, in which the desired response accuracy is specified, and the required accuracy of input data is determined, subject to minimizing the cost of data measurements. Integral and differential data measurements will be combined for the first time into a unified cost minimization framework; this presents new conceptual and computational challenges. The envisioned solution would find optimal combinations of integral and/or differential data measurements necessary to attain the required accuracies of responses. Our IS/U solution will be the first ever applicable to thermal and intermediate systems. The proposed IS/U solution methodology will address the implicit neutron resonance self-shielding effects essential to accurate modeling of thermal and intermediate systems.

Mission Relevance

This project is relevant to DOE/NE Fuel Cycle R&D (FCR&D) Program and the DOE Nuclear Criticality Safety Program (NCSP) managed by NNSA/NA-162. The FCR&D Nuclear Data Program (NDP) is responsible for nuclear data needs across the advanced fuel cycle applications areas. Its Technical Program Director provided a letter of support stating that ORNL will have an opportunity to obtain FCR&D support to investigate, quantify, and prioritize differential nuclear data needs. The NCSP NDP provides support for the measurement, evaluation, testing, and publication of neutron cross-section data for nuclides of key importance to nuclear criticality safety analyses.

Results and Accomplishments

The funding for this project was initiated in late July 2012 when $30,000 was allocated for the FY 2012 effort. We have built and studied relatively simple but non-trivial prototypes of the Inverse Sensitivity/Uncertainty method. These prototypes helped us to determine that DAKOTA (Design Analysis Kit for Optimization and Terascale Applications, dakota.sandia.gov) toolkit ought to be capable of minimizing cost functions that (in our applications) could easily become functions of tens, or even hundreds, of thousands of data points. We have started to integrate DAKOTA into the SCALE (Standardized Computer Analyses for Licensing Evaluation) by reusing SCALE libraries that provide methods for reading sensitivity data formatted files and the nuclear covariance data files, both of which are needed to define the IS/U problem. We have also decided that our first realistic, yet simple, application of the IS/U method would be on the Flattop-25 integral benchmark experiment and are in the process of implementing it.

SUMMARIES OF PROJECTS SUPPORTED THROUGH LABORATORY-WIDE FELLOWSHIPS

WEINBERG FELLOWSHIP

05921

An Investigation into the Synthesis and Annealing of Iron-Based Superconductors under High Magnetic Fields

O. Rios, A. Safa-Sefat, G.M. Ludtka, M.A. McGuire

Project Description

The state of the art in synthesis and processing of class II superconductors has recently made significant advances; however, there have been limited yet promising studies on processing of these materials under extreme conditions, specifically high magnetic fields. The current study investigates the structure, microstructure, and interrelated electrical properties of iron-based superconductors, reaction sintered and/or annealed, under high magnetic fields with the aim of increasing the critical current density at or below the critical transition temperature. It has been well established that magnetic ordering is deeply rooted in the underlying mechanism behind high-temperature superconductivity; therefore, it is expected that the synergistic action of the high magnetic fields and thermal energy will facilitate the growth of crystals that exhibit improved magnetic order below the critical temperature T_c (for superconductors) or Neel temperature (for antiferromagnets). Of the known high-temperature superconductors, the iron-based pnictide class of materials should most strongly respond to magnetic processing due to the strong magnetic properties of the iron atoms electronic structure.

Mission Relevance

Historically, superconductors are key energy materials that are important to the DOE mission and national security. A fundamental understanding of the underlying mechanisms behind superconductivity and how the material properties are affected by the synthesis and processing conditions is vital to the design of the next generation of materials. The current study investigates a relatively unexplored process variable (magnetic fields) that is state of the art in industrially transferable technologies. The results of this study are expected to help establish ORNL's expertise in the advanced high magnetic field processing and synthesis of superconductors, thus better positioning ORNL in the soliciting future industry participation and technology transfer through the DOE Office of Energy Efficiency and Renewable Energy Industrial Technologies Program (EERE-ITP) and future Office of Basic Energy Sciences (BES) initiatives.

Results and Accomplishments

We developed the methods and apparatus as well as designed and conducted elevated-temperature high-magnetic-field experiments that resulted in superconductors exhibiting up to a 59% increase in diamagnetic shielding. A high-frequency induction furnace capable of processing iron-based superconductors (SC) under high magnetic fields was designed and integrated into the ORNL 9T superconducting magnet, providing a unique capability at ORNL. Thus far we have magnetically annealed several iron-based superconductors with promising results indicated by magnetic susceptibility measurements. Initially, reaction-sintered samples of $LaFeAsO_{0.90}F_{0.10}$ and $CeFeAsO_{0.88}F_{0.12}$ were annealed at 1300°C under a 9T field in an inert atmosphere. The magnetic susceptibility in both these samples decreased from -0.75 to -0.85 ($4\pi\chi$) (13% decrease) and -0.85 to -1.0 ($4\pi\chi$) (18% decrease), respectively. These results indicate that the advanced processing yields materials that are more "perfectly" diamagnetic. Additionally, synthesis was performed on two pressed pellets of constituents of $NdFeAsO_{0.88}F_{0.12}$. In order to establish a controlled baseline, both samples were pressed from the same batch of components and then reaction sintered either with or without a magnetic field. The orientations of the pellets within the superconducting solenoid magnet were held constant throughout the experiment. The Meissner effect below the critical temperature was enhanced in both the parallel and orthogonal to the field directions, and reductions in susceptibility from -0.17 to -0.27 (emu/g) or a 59% improvement were found in the parallel direction. A modified magnetic synthesis experiment was performed on the $NdFeAsO_{0.88}F_{0.12}$ superconductor based on the promising results found in FY 2010. This experiment included controlled rapid cooling rates to kinetically limit the formation of lower temperature structures during slow cooling. The Meissner effect during the superconducting transition was slightly improved, and the transformation temperature was consistent. X-ray diffraction revealed that the quality of the crystal was improved, and there was no detectable diffraction from impurity phases remnant from the unreached precursors. Susceptibility measurements under a 1000G field revealed two distinct magnetic transitions. Additionally, the microstructure was investigated by scanning electron microscopy (SEM) and limited transmission electron microscopy (TEM). The goal was to link the modified electronic and magnetic properties with the crystal structure, microstructure, and morphology. The results of this study are expected to help establish ORNL's expertise in the advanced magnetic processing and synthesis of iron-based superconductors. The technology developed within this study is compatible with other material systems and has led to subsequent studies in magnetic materials and functional materials that would otherwise have not been possible. This study has led to the submission of two invention disclosures with patent applications in preparation. Sufficent data and analysis was generated for a publication that is expected in the near future.

05935

First-Principles Calculations and Computational Thermodynamic Modeling on Zn-S and Sn-S to Support Identifying Thermal Decomposition Pathways for Fabricating a New Photovoltaic Material, Cu_2ZnSnS_4

D. Shin

Project Description

Cu_2ZnSnS_4 (CZTS) has recently gained great interest as an inexpensive candidate photovoltaic material; however, the complex chemistry of Cu-Zn-Sn-S makes the optimization of a high-efficiency CZTS synthesis process difficult. Computational thermodynamic modeling of Cu-In-Ga-Se played an important role in identifying thermodynamic decomposition pathways for the $Cu(In,Ga)Se_2$-based photovoltaic devices production, and similar benefits are expected for CZTS. Current thermodynamic models for the Cu-Zn-Sn-S system are limited to Cu-Zn-Sn and Cu-S, but due to the high sulfur content of CZTS, thermodynamic modeling of Zn-S and Sn-S are necessary. Thermochemical measurements, such as heat capacities and formation enthalpies, directly affect the thermodynamic modeling quality and are thus preferred, but available data for Zn-S and Sn-S are only limited to phase equilibrium data. Evaluating thermodynamic parameters with only the phase boundary data may satisfy the relative Gibbs free energy among the phases to reproduce experimental phase boundaries, but they may be completely incorrect and hamper reliably extrapolating their energies to higher order systems. First-principles calculations in this regard can provide thermochemical properties of sulfides to supplement scarce experimental data, and I propose a hybrid computational thermodynamic investigation, that is, a thermodynamic modeling and first-principles study on Zn-S and Sn-S.

Mission Relevance

Currently available photovoltaic materials are chalcogenide based, and their usage of toxic (Cd) or expensive (In and Te) elements are projected to restrict the production of these solar cells. Thermodynamic modeling of Zn-S and Sn-S will eventually provide insight into the production of nontoxic and inexpensive new photovoltaic materials based on CZTS, and will help garner new funding opportunities from DOE, for example, the Office of Energy Efficiency and Renewable Energy (EERE) focus on solar energy technologies program.

Results and Accomplishments

The primary FY 2012 effort focused on the thermodynamic modeling of the binary sulfide phases in the Sn-S system. Available Gibbs free energy descriptions for the solid phases in Sn-S, SnS, SnS_2, Sn_2S_3, and Sn_3S_4 have been taken from the SGTE (Scientific Group Thermodata Europe) substance (SSUB) database. The thermodynamic description for the liquid phase for SnS was also taken from the SSUB database, and interaction parameters for the liquid phase have been evaluated to reproduce the experimentally observed two miscibility gaps for the liquid phase in this system with an associate model. Thermodynamic model parameters for all the phases in the Sn-S system have been optimized to reproduce experimentally observed phase boundary data.

05978

Advance Technology for High-Current Electromagnetic Isotope Separation

B.J. Egle

Project Description

The 2009 Nuclear Science Advisory Committee (NSAC) Isotope Subcommittee recommended as a top priority the reestablishment of domestic stable and radioactive isotope enrichment capabilities in the United States. Electromagnetic isotope separation was identified as the separation technology that is the most flexible and capable of high enrichment for a majority of the elements in the Periodic Table. This project’s overarching goal will be to investigate transformational technologies for key systems for the electromagnetic separation of stable and radioactive isotopes. The primary aim is to develop an ion source that is capable of approximately 100 mA of usable ion current with a lifetime greater than 250 hr. The deliverable for this project is a preliminary design for a prototype electromagnetic isotope separator that incorporates novel features compared to current electromagnetic isotope separation (EMIS) systems.

Mission Relevance

The Department of Energy’s Office of Science, Office of Nuclear Physics (DOE-NP) has received the recommendations of the 2009 NSAC isotope report to reestablish a domestic stable isotope enrichment capability. One of the recommendations may require 3 to 6 high-current (100 mA) EMIS. In addition to isotope separation, the new ion source technology developed in this project will be directly applicable to ion implantation equipment that is widely used in the semiconductor equipment industry, which, in North

America, is estimated at $4 billion annually. The development of innovative ideas to advance the mature technology of EMIS will provide ORNL with a competitive advantage to respond to anticipated funding calls from DOE and may lead to potential licensing of technology to industry.

Results and Accomplishments

The Nonambipolar Electron Driven Ion Source (NEDIS) was conceived and developed during this Weinberg Fellowship LDRD project. It was determined early in this project and during the related and concurrent 10 mA EMIS experimental project that the present state-of-the-art high-current, heavy-ion ion source technology was the primary hindrance to improved EMIS performance. The NEDIS was designed to specifically address the limitations of the present class of ion sources used for EMIS, the Freeman and Dempster ion sources. The failure-prone hot filament of the two previous sources has been replaced with a radiofrequency (RF)-driven, high-current electron gun. The RF-driven system is estimated to have a lifetime greater than 1000 hr, compared to the 40 to 120 hr lifetime of the hot filament systems. A new feedstock introduction system has been investigated that will increase the throughput of the EMIS instrument by reducing the amount of contaminants that are introduced into the source plasma with the feedstock. The scope of this Weinberg Fellowship project was limited only to concept development and design. A separately funded proof-of-concept experiment to fully verify the NEDIS concept and design features was recently started as a follow-on to this LDRD ($250K). A request for further follow-on funding has been submitted to a DOE-NP Isotopes Research, Development, and Training proposal call ($1,030K over 2 years) to upgrade the existing 10 mA R&D EMIS instrument to a 100 mA production prototype using these concepts. Additionally, an idea for an advanced concept for mitigating ion beam space-charge was uncovered during the literature review for this project. The development and testing of this advanced method of space-charge mitigation has been funded in a FY 2013 to FY 2014 Director’s R&D LDRD project.

Information Shared

An invention disclosure has been submitted for the NEDIS concept.

05979

Light Water Reactor TRISO Particle-Metal-Matrix Composite Fuel

K. Terrani

Project Description

This project evaluated the feasibility of an advanced light water reactor (LWR) nuclear fuel concept that offers exceptional reliability, high power rating, and ultra-high burnup levels. The main concept involves incorporating the established benefits of tristructural isotropic (TRISO) coated fuel particles into LWRs in the most effective manner. To achieve this goal, a novel fuel design was proposed where the fuel rod design is fundamentally altered: instead of fissile/fertile pellets clad in zirconium alloy tubing, the fissile/fertile-material encapsulated in TRISO particles is directly dispersed in a matrix of zirconium alloy to form an integral rod that contains multiple barriers to fission product release and eliminates the thin-walled cladding. The work performed under this project identified applicable processing methods and parameters for fuel rod fabrication. This work aimed at providing a knowledge foundation specific to this fuel concept with regards to fabrication, in-pile behavior, and reactor physics aspects. Accordingly, the foundation to enable moving past laboratory-scale experiments to small- and large-scale irradiation testing of this innovative fuel concept for its eventual full-scale deployment has been put in place.

Mission Relevance

This research was well aligned with DOE Office of Nuclear Energy's goals defined in the Fuel Cycle R&D (FCRD) and LWR Sustainability programs. Specifically, the Advanced Fuels Campaign (AFC) in the FCRD program has begun including this fuel concept in its portfolio of fuel concepts. This fuel concept effectively addresses the needs identified by the AFC for advanced LWR fuels—a revolutionary fuel design that offers exceptional reliability, higher operational margins, and improved accident performance.

Results and Accomplishments

Initially the fuel form was fabricated by hot-pressing. The fuel consisted of surrogate TRISO particles (where the uranium-bearing fuel kernel is replaced with zirconia) dispersed in a pure zirconium metal matrix. Some basic processing parameters (temperature, pressure, duration) were established through this early study. After this step, hot-isostatic-pressing was used to fabricate fuel-rod segments in a more representative cylindrical shape. Various TRISO particles with outermost layer coatings of pyrocarbon, silicon carbide, and zirconium carbide were incorporated into the zirconium metal matrix using this process. The fabrication method readily produced a fully dense matrix hosting the fuel particles without any damage to them. Extensive characterization of the fuel system via electron microscopy was performed. A phenomenological model for in situ growth of a ZrC coating layer on the surface of the particle (with a graphite outermost layer) embedded in the Zr metal matrix was developed. The model was in good agreement with various experimental data points from multiple fabrication trials. A successful proposal to Advanced Photon Source at Argonne National Laboratory was submitted, and a micro X-ray diffraction study at the particle-matrix interface was completed to identify the various phases that form during the fabrication stage. The most notable accomplishment was irradiation testing of fuel rods containing surrogate TRISO particles in the Oak Ridge National Laboratory's High Flux Isotope (HFIR). The fuel rods were fabricated to the exact cross-sectional geometry of pressurized water reactor fuel rods with a length of 55 mm. The rods underwent irradiation in the flux trap in HFIR for one cycle (equivalent to ~1.5 years in LWR environments) and were successfully extracted from the core and disassembled in the hot-cell; no signs of deformation were observed.

Information Shared

K.A. Terrani, J.O. Kiggans, L.L. Snead, "Fabrication and preliminary evaluation of metal matrix microencapsulated fuels," *J. Nucl. Mater.*, **427**, 79 (2012).

K.A. Terrani, L.L. Snead, J.C. Gehin, "Microencapsulated Fuel Technology for Commercial Light Water and Advanced Reactor Applications," *J. Nucl. Mater.*, **427**, 209 (2012).

K.A. Terrani, L.L. Snead, J.O. Kiggans, G.L. Bell, "Metal Matrix Microencapsulated Fuel Technology for LWR Applications," *Transactions of TopFuel 2012*, Manchester, United Kingdom, September 2012, Paper A0128.

05980

Intelligent Advanced Propulsion Systems

A. Malikopoulos

Project Description

The necessity for environmentally conscious vehicle designs, in conjunction with increasing concerns regarding US dependency on foreign oil, has led to significant enhancement of the propulsion portfolio of vehicles with new technologies. Hybrid electric vehicles (HEVs) have attracted considerable attention for their potential to achieve greater fuel economy than vehicles powered only by internal combustion (IC) engines (conventional vehicles). The main advantage of HEVs is the existence of two individual subsystems, thermal [(IC) engine] and electrical (motor, generator, and battery), that can power the vehicle either separately or in combination. The overarching goal of the proposed research was to develop intelligent supervisory control algorithms which could continuously direct HEV operation toward the most fuel-efficient operating point, regardless of the driver's particular driving style. The approach was based on stochastic control theory, reinforcement learning, and game theory. The predicted benefits of implementing the methods developed here include substantially increased HEV fuel economy for all types of driving styles, while still meeting stringent emission standards.

Mission Relevance

The research conducted in this project aims to reduce the discrepancy between posted gas mileage estimates and actual mileage in HEVs by providing feedback to the vehicle control systems as well as to the driver to enable global improvements in fuel economy and emissions. Successful implementation of these concepts will enable the true fuel economy of HEVs to be increased while still meeting emission standards. Thus the expected outcome is directly consistent with the Department of Energy (DOE) mission to promote scientific and technological innovations that advance the national, economic, and energy security of the United States.

Results and Accomplishments

The primary component of this research was directed at the HEV system control. HEVs were modeled as cooperative multi-agent systems in which the subsystems (i.e., IC engine, motor, generator, and battery) were treated as autonomous intelligent agents. The agents jointly interact to maximize HEV overall operation (e.g., fuel economy and emissions). In this context, the HEV interacts with its environment and obtains information enabling it to improve its future performance; namely, optimizing specific operational control criteria while satisfying the system's physical constraints. Computational intelligence, or rationality, can be achieved by modeling the HEV and its interaction with its environment (the driver) as being composed of actions, perceptions, and associated costs (or rewards). This interaction-based approach portrays the learning process as a progressive enhancement of the HEV's "knowledge" regarding the control policy that minimizes the accumulated cost with respect to the HEV's operation. A widely adopted paradigm for this type of interactive modeling is the completely observable Markov decision process (MDP). The problem of optimizing the power management in HEVs was thus formulated as sequential decision-making under uncertainty where an intelligent system, the HEV, is faced with the task of efficiently selecting optimal control actions in several time steps to achieve long-term goals. A theoretical and mathematical modeling framework was developed based on an extensive literature review of more than 80 archival publications covering key results on stochastic optimization and control theory with an emphasis on infinite-time controlled Markov chains. This framework was used to construct a set of algorithms that direct HEVs to operate at their *instantaneous equilibrium operating point*, which ensures maximum overall fuel efficiency for any particular driving style.

A second part of the research was directed at the impact of driving style. The variation in fuel consumption for different driving styles is significant, so developing a means of improving driver behavior to maximize fuel economy provides a significant opportunity to reduce fuel consumption in existing fleets. In an effort towards understanding the impact of various driving styles on fuel economy, two main issues were investigated: (1) those driving factors that have a major impact on fuel economy and explicitly quantify their impact and (2) the characteristics of an optimization framework that can be used to optimize a driving style with respect to these driving factors through driver feedback. The contributions of this part of the research effort were (a) identification and justification of key driving factors that can provide an efficient indication of transient engine operation deemed characteristic of high fuel consumption, (b) construction of a set of polynomial metamodels that explicitly represent the relationship between fuel consumption and the identified driving factors, (c) formulation of an example optimization problem that can be used to study various driver needs and preferences, and (d) development of a driver feedback system that can provide visual instructions to the driver to alter his/her driving behavior. Providing feedback in this fashion gives drivers the opportunity to evaluate their driving behavior and learn how to improve their driving styles based on their own preferences.

The research work completed here has established a foundation for future funding opportunities and collaborations with the Vehicle Technologies program at the DOE. In particular, the expansion of this work, that is, to ultimately develop autonomous intelligent propulsion systems capable of learning their optimal operation in real time while the driver is driving the vehicle, was proposed to the Vehicle Technologies program at DOE and was granted $400,000 for the fiscal years 2012 and 2013. The invited lectures and seminars given in academia and scientific community aimed at enhancing reputation in this area. Furthermore, the theoretical and simulation results produced and related publications are expected to attract the attention to industry in the near future.

Information Shared

Conference Publications:

A.A. Malikopoulos and J.P. Aguilar, "Optimization of Driving Styles for Fuel Economy Improvement," Proceedings of 2012 15th International IEEE Conference on Intelligent Transportation Systems, Anchorage, AK, September 16–19, 2012.

A.A. Malikopoulos, "Equilibrium Control Policies for Markov Chains," Proceedings of the 50th IEEE Conference on Decision and Control and European Control Conference, Orlando, Florida, December 2011.

A.A. Malikopoulos and D.E. Smith, "An Optimization Model for Plug-in Hybrid Electric Vehicles," Proceedings of the 2011 Technical Conference of the ASME Internal Combustion Engine Division, Morgantown, West Virginia, Oct 2–5, ICEF2011-60028.

ORNL Invention Disclosures:

A.A. Malikopoulos, "Driver's Feedback System," DOE S-Number: S-124,487, ORNL Invention Disclosure No. 201202913.

ORNL Reports:

A.A. Malikopoulos, *Intelligent Advanced Propulsion Systems*, ORNL summary report.

A.A. Malikopoulos, *PHEV Emissions and Control Strategy*, ORNL final report.

Invited Lectures:

A.A. Malikopoulos, Average Cost Criterion in Controlled Markov Chains: Enabling Theoretical Framework for Optimal Solution Characterization, Seminar in the Aerospace Robotics and Embedded Systems Laboratory, MIT, June 18, 2012, Cambridge, MA.

A.A. Malikopoulos, Dual Constrained Optimization of the Average Cost in Markov Chain, Seminar in the Department of Aerospace, University of Michigan, April 30, 2012, Ann Arbor, MI.

A.A. Malikopoulos, Equilibrium Control Policies for Markov Chains Subject to Total Variation Distance Uncertainty, Colloquium in the Department of Mathematics, University of Tennessee, February 24, 2012, Knoxville, TN.

A.A. Malikopoulos, Stochastic Control and Optimization for Eco-Driving Feedback Technologies, Seminar in the Department of Electrical Engineering, University of Texas, October 24, 2011, Austin, TX.

A.A. Malikopoulos, Self-Learning Identification and Stochastic Control for Autonomous Intelligent Propulsion Systems, Colloquium in the Department of Mathematics, University of Tennessee, April 27, 2011, Knoxville, TN.

A.A. Malikopoulos, Self-Learning Identification and Stochastic Control for Autonomous Intelligent Propulsion Systems, Seminar in the Department of Mechanical Engineering, University of Tennessee, March 24, 2011, Knoxville, TN.

Professional Presentations:

Optimization of Driving Styles for Fuel Economy Improvement, 2012 15th International IEEE Conference on Intelligent Transportation Systems, Anchorage, Alaska, September 16–19, 2012.

Self-learning Control for Eco-Driving Technologies, Presentation to General Motors Global Research & Development, National Transportation Research Center (NTRC), Knoxville, Tennessee, June 11, 2012.

Self-Learning Control for Advanced Propulsion Systems, Cummins Inc., Columbus, IN, May 23, 2012.

ECO-Driving Panel: From Habits to Research, ORNL Earth Day Lunch and Learn Seminar, Oak Ridge, Tennessee, April 16, 2012.

Stochastic Optimal Control for Advanced Propulsion Systems, 2012 DOE Crosscut Workshop on Lean Emissions Reduction Simulation (CLEERS), University of Michigan, Dearborn, MI, April 30–May 2, 2012.

Equilibrium Control Policies for Markov Chains, 50th IEEE Conference on Decision and Control and European Control Conference, Orlando, FL, December 14, 2011.

An Optimization Model for Plug-In Hybrid Electric Vehicles, 2011 Fall Technical Conference of the ASME Internal Combustion Engine Division, Morgantown, WV, October 4, 2011.

Driver Feedback Technologies for Enhancing Eco-Driving Ethics, Presentation to Bosch, National Transportation Research Center (NTRC), Knoxville, Tennessee, July 25, 2011.

Self-Learning Identification and Stochastic Control for Autonomous Intelligent Propulsion Systems, 2011 DOE Crosscut Workshop on Lean Emissions Reduction Simulation Workshop (CLEERS), University of Michigan, Dearborn, Michigan, April 19–21, 2011.

Press:

M. Millikin, “Oak Ridge researcher developing autonomous intelligent engines capable of real-time calibration based on driver behavior,” *Green Car Congress*, May 24, 2012. http://www.greencarcongress.com/2012/05/malikopoulos-20120524.html

M. Millikin, “ORNL researchers propose optimization framework for use in real-time feedback systems to improve driving styles with reduced fuel consumption,” *Green Car Congress*, October 3, 2012. http://www.greencarcongress.com/2012/10/malikopoulos-20121003.html

06234

A Current-Source Boost Inverter-Based Power Electronic Interface for Grid-Connected Photovoltaic Applications

O.C. Onar

Project Description

This study focuses on utilization of a current source-inverter as a single-stage power electronic interface for the grid-connected photovoltaic (PV) system applications. Conventionally, PV systems require two or three stages in order to connect them to the grid. All of these conversion stages increase the overall losses and result in lowered conversion efficiency. Moreover, each conversion stage requires a number of power electronic components along with the passive power components, which increase the overall cost. The objective of this study is to reduce the cost, size, and volume of the inverter and increase the efficiency through a new design and control system.

The objective of this study is to utilize a current source inverter with an input inductor instead of an electrolytic DC link capacitor–based voltage source inverter. Current-source design helps control the input current of the inverter, hence providing maximum power point tracking (MPPT) and is able to boost the voltage without a need for a boost dc/dc converter or a transformer, as is the case with the voltage-source inverter.

Specific aims and the plan statement consist of computer modeling and analysis, control system design and development for simulations, comparison with conventional configurations, and experimental validation. In computer modeling, the models of the PV module, inverter, and the control system will be developed using MATLAB&Simulink and SimPowerSystems physical modeling tools. The proposed control system design will include maximum power point tracking through the input current control and output voltage regulation with grid synchronization through a single-phase phase-locked-loop (PLL) system. During the comparison with conventional inverters, the operational characteristics of the proposed single-stage inverter will be compared to the other existing grid interconnection schemes. During the experimental validation phase, an experimental setup will be built in order to validate the applicability and feasibility of the proposed grid interconnection system.

Mission Relevance

The proposed project is highly relevant to the DOE missions on energy resources and environmental quality. Since most transportation energy is imported from foreign countries that are unstable politically and economically, solar residential applications will enhance the national energy security and independence, as more plug-in electric vehicles will be powered from domestically generated clean energy sources. As America’s need for energy grows, the proposed project is capable of meeting the challenge by establishing a cost-effective and highly efficient solution for the widespread commercialization of PV power generation. This would enhance the diversity of the energy sources and greatly reduce the dependence on fossil-fuel-operated power plants and imported oil as well. In addition, DOE aims to harness the power of the earth itself to meet the energy needs. Advances in solar will allow the United States to take the advantage of clean, abundant energy for both residential and transportation energy demands. Since the power demand of buildings is increasing and plug-in vehicles will introduce a new demand, the grid infrastructure will need to be modernized in the near future. However, switching to locally generated power can reduce the modernization costs of transmission and distribution infrastructures while also eliminating the possible capacity additions to the current conventional power plants.

Results and Accomplishments

The model of the PV system has been completed. The model’s voltage, current, temperature, and solar irradiance characteristics have been verified with a few manufacturer datasheets, and the model has been fine tuned. The electrical equivalent circuit model of the PV has been completed as well in MATLAB&Simulink. A brief review of most of the available MPPT techniques has been completed, and a method that automatically responds to the changes in both irradiance and temperature has been implemented within current-source inverter. A single-phase phase-locked-loop implementation of the inverter has been completed for synchronizing the PV inverter with the grid. The single-phase space-vector pulse width modulation (SVPWM) has also been created for the inverter’s switching sequences and implemented within the proposed control system. Simulations carried out and results have been documented.

06235

Real-Time, Portable Neutron Spectroscopy Using a Filtered and Moderated Semiconductor Detector Array

M.J. Harrison

Project Description

Project goals included the design, construction, and testing of a novel neutron spectrometer in bench-top prototype form. The design of the prototype was based on the concept of incorporating an array of uniquely filtered and moderated neutron detectors into a single, portable package. The neutron detectors comprising the array are each uniquely filtered and moderated such that they each efficiently detect incident neutrons of a different energy. This, in effect, creates a neutron spectrometer that can be utilized to determine an unknown neutron spectrum in the manner used by existing Bonner spheres spectrometers (BSSs). Contrary to BSSs though, the filtered array neutron spectrometer (FANS) prototype is designed to be readily portable, weighing roughly 15% of a commercial, off-the-shelf (COTS) BSS system and being an even smaller fraction of the volume.

Mission Relevance

Detection and identification of special nuclear material (SNM) is a critical mission of DOE. The development of a rugged, handheld instrument capable of not only detecting a neutron source but also identifying the source based on its spectral signature will provide field operations personnel on-site capabilities far exceeding the current technological limit. The work will be most meaningful to the DOE Office of Nonproliferation Research and Development (NA-22). Other agencies likely to benefit from the development of the proposed instrument include the Department of Homeland Security, specifically the Domestic Nuclear Detection Office, and the Department of Defense, specifically the Defense Threat Reduction Agency. Each of these agencies has been tasked with SNM detection goals similar to those of DOE's National Nuclear Security Administration for their respective departmental operations.

Results and Accomplishments

A thorough computational investigation was conducted to determine the effectiveness of using several alternative materials for neutron energy filtration. After a review of nearly 40 elements, it was found just ^{6}Li, ^{10}B, Gd, and Cd were suitable energy filters, all four being high-pass filters. Based on these results, a second computational effort was performed to identify what combinations of these four filter media, high-density polyethylene (HDPE) moderating medium, and their respect geometries provided the optimal detector response curves. Basically, the ideal geometries produced the most "peaked" detector response function as determined by their likelihood ratios. After sifting through several million potential filter/moderator combinations, the top 1000 geometries were then taken as candidates for incorporation into the array. The third and final computational effort focused on optimizing the total amount of joint entropy, as defined in information theory, an array of 12 of any of the 1000 candidates could produce. The resulting optimized array was then compared to the performance of a COTS BSS, and it was found that the FANS array was expected to provide slightly more information (~9.5 bits) about a given neutron spectrum than a COTS 12-member BSS (~9.1 bits).

Upon completion of the above discussed computational work, a working prototype instrument was designed and fabricated to match the specifications of the optimized array. The fabricated components were then assembled into a single core detection module (CDM) package of size and weight reasonable for being considered portable. The CDM was wired to its associated electronics for pulse processing and spectrum acquisition.

Finally, the working FANS prototype was experimentally compared to a COTS BSS using a bare ^{252}Cf neutron source. After numerous calibrations and performance checks, it was determined that the prototype FANS device was capable of neutron spectroscopy approximately as well as the COTS BSS. Interestingly, the FANS prototype performed its measurements roughly 30 times faster than did the BSS, but performed spectrally equivalent. Also of note was the fact that the FANS prototype, though not originally designed to do so, was capable of providing rudimentary gamma-ray spectroscopy in addition to neutron spectroscopy. No such known portable instrument is capable of this. The count rate data measured from a bare ^{252}Cf source showed good agreement with theory, and a pulse height spectrum from one element of the array showed the feasibility of also performing gamma spectroscopy simultaneously.

Information Shared

A presentation was given at the 2011 IEEE Nuclear Science Symposium held in Valencia, Spain, in late October 2011. An accompanying paper was submitted and published.

M.J. Harrison, Q. Cherel, M. Monterial, “Design of a moderated multidetector neutron spectrometer for optimal specificity,” *2011 IEEE Nuclear Science Symposium and Medical Imaging Conference* (NSS/MIC), pp.4787–4794, Oct. 23–29, 2011.

06264

Advanced Electron Microscopy Studies of Energy-Related Catalysts

D.A. Cullen and K.L. More

Project Description

Catalysts play a crucial role improving the efficiency, sustainability, and quality of energy production streams. The effectiveness of any catalyst depends on fundamental properties such as activity, selectivity, and durability. Improvements in catalyst efficiency and stability hinge on obtaining a complete understanding of the nature and behavior of active sites operating at the nanoscale. The recent advent of aberration-corrected scanning transmission electron microscopy (AC-STEM) has allowed researchers to finally visualize the individual active sites within these catalysts. This research initiative aims at utilizing AC-STEM and complementary analytical techniques to robustly characterize important energy-related catalysts. We proposed to study two specific systems, hydrodesulfurization (HDS) catalysts and the bimetallic/monolayer-shell catalysts, in the development of advanced electron microscopy techniques and methods towards understanding catalyst functionality. Once developed, these unique methods, which include in situ microscopy, electron holography, secondary electron (SE) imaging, and through-focal-series (TFS) imaging, will then be applied to other key catalysts for energy technologies.

Mission Relevance

In alignment with the mission of ORNL and the Weinberg Fellowship, this project seeks to promote innovation in energy technologies by developing/optimizing and applying the Å-scale imaging and analytical capabilities of AC-STEM to catalyst characterization. This research directly benefits Fuel Cell R&D within the Energy Efficiency and Renewable Energy Program (EERE). The primary collaborator on this research is 3M, an important industrial partner in the DOE Fuel Cell Technologies Program. In fact, this project was one of only two projects funded as part of the recent DOE Funding Opportunity Announcement on research and development of fuel cells for stationary and transportation applications.

Results and Accomplishments

The project began with a brief study of HDS and bimetallic catalyst systems, which resulted in one co-authored publication. The bulk of the research then turned to ruthenium and iridium oxygen evolution reaction (OER) catalysts decorating platinum-coated nanostructured thin film (NSTF) catalysts developed by 3M Company for fuel cell electrodes. These electrodes were examined before and after testing under severe start-up/shutdown and cell reversal conditions. Aberration-corrected STEM, energy dispersive X-ray spectroscopy (EDS), and secondary electron imaging were used to directly image the as-deposited catalyst layers, and showed that Ir catalysts preferred to epitaxially coat the platinum layer. Changes to the catalyst morphology under different test conditions and catalyst loadings, such as catalyst coalescence and dissolution, were correlated to electrochemical tests results. Key results included direct imaging of the as-deposited catalyst morphology, identification of catalyst deactivation and dissolution routes under different testing conditions, and tracking of dissolved catalysts throughout the membrane electrode assembly. The work has resulted in several presentations, including two invited presentations, at Electrochemical Society meetings, Microscopy and Microanalysis and the Electrochemical Energy Storage and Conversion Forum. A poster highlighting this work was awarded third place at the Fuel Cell Seminar and Exposition in Orlando, FL. This collaboration with 3M has resulted in new funding through a second 3M collaboration under DOE FOA-0000360 Project CEHT017: “High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications.” (PI: Andy Steinbach, 3M). This LDRD-funded research effort has also lead to a Work for Others (in progress) with the Automotive Fuel Cell Cooperation and attracted new users from the University of Central Florida and the Florida Solar Energy Center to the ShaRE User Program.

Information Shared

D.A. Cullen, K.L. More, K.S. Reeves, G.D. Vernstrom, L.L. Atanasoska, G.M. Haugen, and R.T. Atanasoski, “Characterization of durable nanostructured thin film catalysts tested under transient conditions using analytical aberration-corrected electron microscopy,” *ECS Transactions* **41**, 1099 (2011).

R.T. Atanasoski, L.L. Atanasoska, D.A. Cullen, G.M. Haugen, K.L. More, and G.D. Vernstrom, “Fuel Cells Catalyst for Start-Up and Shutdown Conditions: Electrochemical, XPS, and STEM Evaluation of Sputter-Deposited Ru, Ir, and Ti on Pt-Coated Nanostructured Thin Film Supports,” *Electrocatalysis*, accepted for publication.

R.T. Atanasoski, L.L. Atanasoska, and D.A. Cullen, “Efficient Oxygen Evolution Reaction Catalysts for Cell Reversal and Start/Stop Tolerance” in M. Shao ed., *Electrocatalysis in Fuel Cells: A Non and Low Platinum Approach*, Chapter 22, Springer, to be published March 2013.

L. Meng, D.A. Cullen, K. Sasaki, N. Marinkovic, K.L. More, and R.R. Adzic, “Ternary Electrocatalysts for Oxidizing Ethanol to Carbon Dioxide: Making Ir Capable of Splitting C-C bond,” *Journal of the American Chemical Society*, accepted for publication.

06348

Universal Sensing Platform for Autonomous Data Correction in Building Technologies

C.C. Castello

Project Description

Sensors are used heavily at Oak Ridge National Laboratory (ORNL) to help analyze energy-saving building technologies at the component, system, or whole-building level. However, issues arise such as missing and corrupt data. Data acquisition activities at ORNL have shown up to 14.59% of missing data from data logger and sensor failure. This rate does not even include data inaccuracy from sensor fouling and calibration error. Current methods used for correcting such data discrepancies are technically inadequate and not sufficiently automated. Therefore, I propose to utilize advanced statistical methods, filtering mechanisms, and machine learning techniques specific to the data, to facilitate an autonomous and scientifically defensible method for the correction and reporting of sensor data. Furthermore, based on findings of investigated algorithms, I proposed to design a universal sensing platform (USP) for data validation and correction in real time. The ultimate goal is to design a universal device capable of being connected to a wide variety of sensors, to validate and correct data on a hardware level.

Mission Relevance

The U.S. Department of Energy's (DOE) Office of Energy Efficiency & Renewable Energy (EERE), which sponsors research dealing with energy efficiency in (1) homes, (2) buildings, (3) vehicles, (4) industry, and (5) government, would be our main target for further sponsorship. The goal of DOE's EERE is to build a network of research and industry partners to produce innovative, cost-effective energy saving solutions for residential and commercial buildings. Sensor data validation fits into this goal by ensuring complete and accurate datasets that are used to analyze and characterize energy-saving technologies for buildings. These datasets are also used for energy management and control systems which require quality data for proper operation.

Results and Accomplishments

The principal investigator (PI) has currently completed the study of four techniques dealing with statistical methods for data validation. These techniques include (1) least squares, (2) maximum likelihood estimation, (3) segmentation averaging, and (4) threshold based. Results will be presented at Energy Informatics 2012 in Atlanta, GA, which will take place October 6, 2012 (Castello and New, 2012). Implementation of these methods uses observation windows which define a subset of samples, size o, that are used to generate a model. Validation and correction occur for each successive observation window within the sensor dataset. Temperature, humidity, and energy data are used from ORNL's ZEBRAlliance Project, which built four energy-efficient homes for research purposes in Oak Ridge, TN. These homes are fitted with hundreds of sensors to characterize each home's performance and technologies being used. Based on the different types of data that were tested, the threshold-based method performed best with temperature ($\sigma=2$), humidity ($\sigma=2$), and energy data ($\sigma=1$).

Results are currently being generated for filtering techniques and machine learning techniques. It is the PI's goal to publish one conference and/or journal paper for each validation type. After results have been generated, the data validation technique resulting in the highest fault detection rate with minimal complexity will be utilized to design a universal sensing platform (USP) using electronic design automation (EDA) tools. The design focus of the USP is on a low-cost, robust sensor validation module to connect a variety of different sensors.

Information Shared

C.C. Castello and J.R. New, "Autonomous Correction of Sensor Data Applied to Building Technologies Utilizing Statistical Processing Methods," Energy Informatics 2012, accepted for publication.

WIGNER FELLOWSHIP

05908

Low Dimensional Multiferroicity

X. Xu

Project Description

Multiferroic materials exhibit more than one ferroic order simultaneously and thus have many advantages over other materials. For example, multiferroic materials are promising for high-density and energy-efficient information processing and storage, and possibly solar energy harvesting, because of the multiple ferroic orders and the coupling between them. The big challenge is to find a multiferroic material with a high ordering temperature, large polarization, and strong coupling. One promising way of achieving this overarching goal is to study the existing material and improve its properties by tuning the chemical substitution, structure, and dimensionality. Among many means, tuning dimensionality provides great opportunities: (1) the quantum size effect changes the electronic structure of the nanoparticles drastically compared with the bulk counterparts; (2) the surface and edge states not only give large strain that can tune the materials' properties or even stabilize the phases that are not stable in bulk case but also introduce completely new states; and (3) nanoscale materials allow the possibility of manipulating the individual domains (domain walls), whose dynamics are critical for application. So far, little research has been done on nanoscale physics of multiferroics because the former is mostly concentrated on a relatively simple system. Our objective is to grow high-quality epitaxial multiferroic thin films and tune/study their properties at low dimensionality. This will not only bring more insight into the mechanism of multiferroicity but also help realize the desired material properties.

Mission Relevance

The field of multiferroics is so interesting for fundamental science and commercial application that it was selected by *Science* magazine as one of the top seven "Areas to Watch" in all of science for 2008. Successful fabrication of new types of low-dimensional multiferroics will open up a whole set of new opportunities for fundamental scientific research as well as device making. For example, taking advantage of the unique material tailoring in low dimensions is promising for improving the functional properties of multiferroics. Moreover, multiferroics are promising for a new candidate of solar energy harvesting materials with more efficiency and tunabilities.

Results and Accomplishments

$LuFe_2O_4$ was successfully fabricated, and a full PLD growth diagram was published. This work led to the discovery of a strain-stabilized material that has coexisting ferroic states at room temperature, $LuFeO_3$.

This work is currently under review, but initial results confirm ferroelectric switching and an antiferromagnetic ordering at room temperature. Work is currently under way to investigate whether these properties are connected, which would introduce this material as only the second-known room temperature multiferroic. Several funding packages were submitted for external funding in the form of DOE funding grants, but none were accepted. The PI left ORNL in 2012.

Information Shared

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05910

Advanced Algorithms and User Interfaces for Personalized Data Mining of Biomedical Images and Literature

S. Xu

Project Description

With the exploding size of biomedical literature and images published to date, finding biomedical knowledge relevant to one's research interests and professional practice in a timely manner is becoming increasingly challenging. In this project, we will design and implement intelligent query- and behavior-based algorithms and user-friendly interfaces to facilitate biomedical knowledge discovery through accurate and timely access, selection, delivery, and personalized recommendations. Our project goals can be broken down into the following three phases: in Phase I, we will develop advanced image text extraction methods; in Phase II, we will develop user-friendly interfaces for accessing biomedical knowledge, aiming at fostering more natural human-computer communications during an end user's knowledge access process; and in Phase III, we will look for new opportunities to promote biomedical knowledge access through fusing knowledge from multiple sources. Overall, this project aims at developing novel computational tools and methods for facilitating access to and discovering knowledge from biomedical document and image collections.

Mission Relevance

The primary research on this project will focus on developing advanced image and text search models, ultimately merging unique techniques into a powerful software environment for data access and mining. This work is of strategic interest to DOE and in an area of growing science focus at ORNL: Knowledge Discovery. This research area is the science agenda thrust of the Computational Sciences and Engineering Division and has direct relevance to DOE interests in national security, energy assurance, and basic science. The successful achievement of this research will also result in direct impact across several directorates at ORNL, with important practical applications to the National Institutes of Health (NIH) and the Department of Defense (DoD).

Results and Accomplishments

We developed an advanced biomedical image text extraction method that processes biomedical images published in literature for identifying the embedded text. In studying the effectiveness of this new algorithm, we evaluated its performance on a set of manually labeled random biomedical images and compared its performance against other state-of-the-art text detection algorithms.

Generating personalized document summaries that observe the preferences of individual readers was one area of study. We proposed a new personalized document summarization method, which observes a user's reading behaviors, including user facial expressions, gaze positions, and reading durations, during his or her past reading activities to infer the user's personal reading preferences. The result of this comparative study shows that the algorithm can produce superior personalized document summaries to those from peer methods.

We proposed a personalized webpage re-ranking algorithm by exploring a user's dwell times in his/her previous readings over individual documents. The algorithm first models concept word level user dwell times. In order to understand a user's personal interest, according to the estimated concept word level user dwell times, the algorithm then infers a user's potential dwell time over a new document. Based on the inference results, the algorithm can re-rank webpage search results in a personalized way. Rankings produced by this algorithm were compared with rankings generated by popular commercial search engines and a recently proposed personalized ranking algorithm. The results clearly show the superiority of this method.

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05911

Optical Characterization of Bacterial Dynamics in a Microfluidic Environment

A. Kumar

Project Description

Bacterial motion represents an extremely rich class of dynamical behavior. Bacteria can respond to a variety of external stimulants, and one recently discovered bacterial motility response termed electrokinesis is present in the proximity of a redox active surface. However, a proper understanding of this motility response and its dependence on concomitant processes is lacking. Such lacunae in our understanding impede progress in the noninvasive control of microbal processes. Hence we propose a research plan which leverages microfluidics and advanced optical characterization to explore this dynamical behavior. A microfluidic system optimized for real-time characterization will be developed. Additionally, two-color velocimetry, total internal reflection microscopy, and optical tweezing will be developed to explore microbial systems. These developments will be used for elucidating electrokinesis and its dependence on various parametric conditions. Such fundamental investigations into bacterial motility are expected to contribute to very relevant issues of alternative energy generation and biological remediation.

Mission Relevance

Fundamental understanding of microbial systems is relevant to the DOE mission of scientific discovery and innovation. Such understanding is expected to benefit prevalent renewable energy systems and environmental remediation projects, and thus the project is also relevant to the DOE mission of energy security. Specifically, the proposed investigation is expected to appeal to the Department of Energy Office of Biological and Environmental Research (DOE-BER).

Results and Accomplishments

During FY 2012, progress was made in the study of bacterial dynamics under the influence of externally imposed environmental conditions. Miniaturized microfluidic platforms were constructed for the investigation of fluid flow on microbial aggregation and dynamics. It was found that flow structures generated either through fluid-structure interaction or through opto-electric methods, can be used to direct microbial aggregation on surfaces.

These studies were complemented with analytical and numerical analysis studies to understand the influence of the externally imposed conditions on bacterial transport and dynamics. These studies have enabled the development of models that explain the experimentally observed behavior of microbes. Together, the experimental and numerical studies are enabling the real-time monitoring of aggregative bacterial dynamics and influence of external factors on such dynamics.

Information Shared

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05913

Studies of Charge Particle Emitters at the Limits of Bound Nuclei

K.A. Miernik

Project Description

The exotic isotopes at and beyond the limits of bound nuclei will be investigated using charge particle spectroscopy and beta-decay methods. Measurement of properties such as emitted particle energy and the characteristic half-life allow us to study the evolution of nuclear structure of very exotic nuclear systems that are not accessible with other techniques.

The super-heavy nuclei will be investigated at the Joint Institute for Nuclear Research at Dubna (Russia) and at the Heavy-Ion Research Laboratory at Darmstadt (Germany). New two-proton emitters will be studied with the Optical Time Projection Chamber based on Gas-Electron Multiplier technology at the National Superconducting Cyclotron Laboratory at Lansing, Michigan. Novel detection techniques will be developed at ORNL and applied to facilitate the studies of these very rare nuclei.

Mission Relevance

One of the main scientific missions noted in the 2007 U.S. Long-Range Plan for Nuclear Science is the identification and understanding of the limits of the periodic table of elements as well as understanding of nuclei at extreme proton-to-neutron ratios. The experiments on nuclei beyond the two-proton drip line and in new super-heavy nuclei are particularly well suited to this mission statement. The research on radioactive nuclei, particularly on new chemical elements, is relevant to DOE activities by promoting science about and expanding human knowledge on atomic nuclei. In addition, the study of rapid neutron capture (r-process) nuclei reveals the formation of elements in explosive nucleosynthesis events such as supernovae.

Results and Accomplishments

The two-proton radioactivity study has been successfully accomplished for the doubly magic nucleus ^{48}Ni. The experiment was performed at the National Superconducting Cyclotron Laboratory at Michigan State University (Lansing, Michigan) in March 2011. It yielded the first unambiguous detection of two-proton emission from ^{48}Ni. The key to this accomplishment was a novel Optical Time Projection Chamber (OTPC) detector as well as a rotating target device developed at ORNL and the University of Tennessee.

An experiment searching for the new super-heavy element Z=120 was initiated in April 2011 at the GSI Helmholtz Centre for Heavy Ion Research, Darmstadt, Germany. This was an attempt to produce the new element Z=120 using ^{54}Cr beam and ^{248}Cm target material originating from ORNL. A dedicated digital data acquisition system developed by the ORNL–UTK collaboration was shipped to GSI and successfully integrated with the analog data acquisition system used at the SHIP recoil separator facility. A crucial feature of this change is the ability of the new system to detect sub-microsecond decay half-lives of this new element. The remaining 100 out of 130 days total allocated beam time are subject to the scheduling of GSI accelerator's time.

The aim of an experiment started in April 2012 in JINR Dubna, Russia, was to produce Z=117 nuclei in a fusion reaction of ^{48}Ca beam and ORNL-furnished ^{249}Bk target material in order to better investigate the properties of isotopes of this recently discovered element. During the campaign the digital data acquisition system was shipped and installed at JINR and will be used in future experiments together with a new detector system, built and tested at ORNL, that includes a large, highly segmented Double-sided Silicon Strip Detector.

In June 2012 an experiment to understand the decay properties of ^{6}He was performed at CERN, Switzerland. The OTPC detector was used to track the very rare (10^{-4} %) beta-delayed deuteron emission through the simultaneous observation of an alpha and deuteron particle emitted from a common vertex. The low energy part of the deuteron spectrum measured in this experiment will be studied in an attempt to probe the halo structure (^{4}He + n + n) of the ^{6}He by its beta decay properties.

The studies of r-process nuclei were enriched by half-life measurements at the limits of known isotopes around ^{78}Ni, performed during HRIBF campaigns in 2011 and 2012.

Information Shared

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05981

Algorithmic Challenges in Computational Science on the Path from Petascale to Exascale

M. Berrill

Project Description

Modern computers allow for a complex simulations and capabilities. Future computations at exascale will allow for increased capabilities to explore large domains and new physics but present significant challenges. This work focuses on two problems that deal with some of these issues.

First, we deal with the challenge of simultaneously achieving high resolution over a large domain. Adaptive mesh refinement (AMR) presents a unique opportunity to achieve this goal. By constructing a series of mesh refinements, the desired resolution in one region can be achieved while maintaining a coarse grid in regions where high resolution is not necessary. This results in a significant computational savings allowing for large problems. We demonstrate this by adding AMR capabilities to an existing Magneto-Hydrodynamic (MHD) simulation pixie3d.

Second we explore adding new physics with different spatial and temporal timescales to a nuclear fuel simulation. In a nuclear fuel rod, the oxide layer can affect the thermodynamics and mechanical properties of the rod but presents unique challenges. In particular, the spatial scale of the oxide is 10^{-5} m on a rod ~3 m in length. Additionally, the initial grow is dominated by short timescales, while the final oxide thickness is accumulated over the entire lifetime of the rod. We explore mixed domain and meshes using the Advanced Multi-Physics (AMP) infrastructure package being developed at ORNL.

Mission Relevance

By working on improving the algorithms and underlying scaling limitations, a significant impact on a number of petascale problems can be made. If the efficiency of the model is increased significantly, then it is possible to simulate current problems that would not otherwise be possible. In extended MHD, this can easily lead to discoveries that will help to improve fusion plasmas, such as the conditions in ITER; in climate modeling, it may be possible to better understand weather patterns and climate change that might affect our future. Additionally, many other problems may also be accessible, though these improvements as a wide variety of problems have the common need for high spatial accuracy, large simulation times, a variety of timescales, and large-scale modeling.

Results and Accomplishments

Efforts of my R&D targeted two primary areas: nuclear fuel simulations and plasma modeling. A potential problem for nuclear fuel is oxide growth on the cladding. This oxide growth reduces the heat flux, resulting in higher cladding temperature, and serves as a site for additional corrosion. To date, understanding the oxide growth has relied on experimental measurements and simple 1D models. While these models can predict the oxide growth for a given set of conditions, they cannot account for the growth on the full clad, which experiences a variation across the entire surface. To address this I coupled an oxide growth model with a full 3D nuclear fuel model (AMP). This consisted of a relatively simple 1D model that has good agreement with existing models and results, solved for each point on the surface of a 3D simulation of a nuclear fuel rod. With the design of a new mesh interface in the AMP package, a surface mesh is automatically generated on the exterior of the clad of a nuclear fuel simulation using DenovoMP. Solution transfer is then automatically handled by using the same grid for the surface as the volume mesh for the thermal transport. This allows us to efficiently handle the different spatial scales involved from the oxide thickness $\sim 10^{-5}$ m to the full rod length ~3 m.

Many existing plasma models are able to accurately model complex problems in 3D but are limited in the size/resolution of the problem they can handle because of the computational requirements in solving the magneto-hydrodynamic equations. To address this limitation, I worked on integrating Adaptive Mesh Refinement (AMR) using the Structured Adaptive Mesh Refinement Application Infrastructure (SAMRAI) into pixie3d. This has allowed for both hi-resolution and large spatial domain computations. We have AMR working both explicitly and implicitly with dynamic regridding. Implicit solvers were necessary for long-time simulations involving magnetic instabilities and have proven successful. A vector potential formulation was needed to ensure a divergence-free magnetic solution minimizing artificial artifacts from the coarse-fine interfaces. Dynamic regridding was recently completed with tagging based on current density and successfully flows of the current in the plasma simulations. The results have been presented in several conferences.

Information Shared

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05983

Novel Nanotoxicology Studies Using Noninvasive Real-Time Microscopy and Spectroscopy for Physical and Chemical Characterization of Materials and Live Biological Systems

L. Tetard

Project Description

As the interests in developing novel engineered materials and the natural extension to associated nanotoxicological effects continue to rise, a parallel development of a metrology toolbox that can contribute to the structural and chemical characterization of such nanosystems is needed. A crucial component in dealing with systems at the sub-micrometer scale is the ability to measure the sought properties and response of a given sample with (1) high spatial and temporal resolution, (2) minimum disturbance, (3) subsurface visualization, and (4) molecular recognition. These abilities can offer a detailed understanding of these complex systems by enabling quantitative study of their structural, physical, and chemical properties. Recently one such characterization tool has been preliminarily demonstrated to offer a unique approach to noninvasive, nanoscale, subsurface visualization of biological materials. Enhanced to operate in an aqueous environment and combined with a novel IR spectroscopy capability, this new powerful tool can be applied to a number of important research issues in nanotechnology, including specifically the environmental and health effects of nanomaterials on living systems. The proposed research will encompass the following. (1) Begin a research initiative to study nanotoxicity in living systems exposed to nanomaterials at the cellular level using a unique subsurface microscopy technique with integrated spectroscopy. In this objective, plant and animal cells, as well as engineered and naturally occurring nanoparticles, will be targeted. (2) Advance the state of knowledge in nanoscale subsurface imaging and spectroscopy. This objective will be composed of instrument enhancement and investigations of known fabricated nanostructures to provide "standards" for future theoretical analysis of the complicated signals from the proposed technology.

Mission Relevance

While the synthesization and application of nanomaterials are generating great excitement, the safety of nanomaterials to humans, animals, and the environment is also being treated with gravity. In order for the toxicological, epidemiological, and environmental impacts of nanomaterials to be understood and controlled, it is of paramount importance to have the ability to characterize, quantify, and track the nanomaterial within the biological or environmental system in real time. However, given the small dimension of the nanomaterial, its characterization is difficult, if not impossible, using traditional analytical tools. Recognizing the lack of analytical tools to assess exposure impact, guide manufacturing specifications, and verify desired end-product functionality, one of the nine grand R&D challenge areas identified by the National Nanotechnology Initiative (NNI) is Nanoscale Instrumentation and Metrology.

The premises of this work have offered great insight to the nanotoxicology community by demonstrating the ability of our instrument to localize engineered nanoparticles of various sizes and composition inside animal cells. In addition, it holds a great potential for fundamental research or applied material research, relevant to the missions of the Department of Energy (DOE), the National Institutes of Health (NIH), the Department of Defense (DoD), Defense Advanced Research Projects Agency (DARPA) or the National Science Foundation (NSF).

Results and Accomplishments

Subsurface imaging

Further developments of the Mode Synthesizing Atomic Force Microscope (MSAFM) and applications of the concept of virtual resonance to imaging were investigated. We performed measurements on a variety of soft matter samples (cells, polymers, tissues) and also worked in collaboration with North Eastern University to improve the modeling of the concepts at play in MSAFM. A series of subsurface standards are being fabricated and characterized to assess the subsurface parameters of the technique. Further investigations of our findings related to potential applications in sensors were also performed.We are in the process of publishing our results in a series of articles.

Molecular recognition

The implementation of high-resolution spectroscopy using our MSAFM platform lead to a new technique called hp-MSAFM. The patent was reviewed this year and is now pending.

The platform was adapted to accommodate laser illumination (QCL) and infrared broadband illumination (FTIR). The two configurations are now used to characterize samples of interest to various DOE and NIH programs (plant cells, stems, animal cells, polymers, metal nano-islands, etc). Progress has been reported through multiple invited presentations and has led to a new proposal submission.

In the meantime, a macro-scale spectroscopy technique was developed (pump-probe) for standoff detection and characterization.

Living systems

A series of developments were initiated, including the continued design of a new liquid cell for imaging and consideration of new probes for the measurements. We are also designing standards samples that would mimic the living system for a precise calibration of our techniques.

Through a new collaboration at the University of Tennessee, a new platform is now available for increased capabilities with respect to liquid imaging.

Information Shared

Invited speaker, MRS Meeting, Boston, December 2011
Presentation, Nature Bionanotechnology conference, Miami, February 2012

Presentation, Future of Instrumentation Workshop, Oak Ridge, November 2011
Invited talk (Thomas Thundat), Scanning Probe Microscopy Conference, Canada, May 2012
Invited speaker, BESC workshop, Riverside, January 2012
Poster Presentation, BESC retreat, Asheville, July 2012
Invited speaker, FIB 2012, St. Simons Islands, October 2012
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06668

Stimuli-Responsive Polymer Materials with Switchable Interfaces

V. Bocharova

Project Description

The goal of this research is to develop novel approaches to the design and implementation of switchable interfaces based on polymer ‘‘brushes’’ that are capable of sharp and reversible conformational and chemical changes controlled by an external signal (“smart” materials). We will focus on the synthesis and characterization of mixed polymer brushes capable of switching their conductive properties (electron transport) in response to pH signal. As part of this work, mixed polymer brushes will be prepared on highly ordered pyrolytic graphite (HOPG) and characterized by neutron scattering, light scattering spectroscopy, ellipsometry**,** atomic force microscopy (AFM), scanning electron microscopy, electrochemistry, and contact angle measurements. Results from the experimental studies will provide valuable insight to understand the relation between restructuring and electron transport in mixed polymer brushes upon change in pH. Knowledge about conductive behavior in mixed brushes will be applied to the problem of electron transport in the energy-harvesting devices (e.g., enzymatic biofuel cell). In general, this project will bridge the synthesis of well-defined molecular architectures, their characterization and optimization, and their application to an enzymatic biofuel cell.

Mission Relevance

Application of new stimuli-responsive materials capable of switching their conductive properties (electron transport) in response to pH signal in energy-harvesting devices will be evaluated. This is aligned with DOE energy mission by addressing energy challenges through transformative science and technology solutions. We are proposing to apply new stimuli-responsive materials for the problem of efficient conversion *of biomass to energy* in enzymatic biofuel cell. Research on enzymatic biofuel cells will provide the foundation to facilitate development of a *green energy technology* capable of producing clean, sustainable electrical power.

This research focused on development of new switchable interfaces capable of extreme conformational and chemical changes on receiving an external signal. It would be of interest to various agencies (including the Department of Energy, the National Institutes of Health, and the Department of Defense) providing support to programs that require "smart" materials, biosensors, drug delivery systems, micro-nanoactuators, regenerative systems, and tissue-mimicking platforms.

Results and Accomplishments

We have started with fabrication of mixed polymer brushes on the planar conductive surfaces that are capable of changing their conductive properties (electron transport) in response to pH stimulus. In the processes of fabrication and characterization of brushes we became closer to understanding of how molecular weight, composition, and method of preparation are affecting the switching behavior of the brush. We intend to use the obtained knowledge to fabricate a mixed polymer brush with sharp, reversible, complete, and stable transition between non-conductive and conductive states in response to pH.

Information Shared

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06671

Artificial Antennae: Investigating the Optical Properties of Fluorescent Metallic Nanocluster Assemblies in Order to Harvest Solar Energy

J.K. Sharma

Project Description

Recently the attention of mankind has turned towards the need of finding and harnessing sources of clean and renewable energy, for example, solar energy. Among the solar energy harvesting systems, structurally organized and functionally integrated artificial antenna systems that mimic natural photosynthesis in harvesting solar energy are highly attractive. However, the photostability and organization of chromophores are the challenging issues that reduce stability and efficiency of these antenna systems. To address the photostability issue of chromophores, I will synthesize highly photostable chromophores, that is, fluorescent metallic nanoclusters. DNA scaffolds, which provide surface points with nanoscale separation, will be employed to organize these chromophores with absolute control over inter-nanocluster distance and organizational geometry to achieve maximum solar energy absorption. These optimized assemblies of chromophores will be employed to achieve maximum energy transfer to photovoltaic materials (e.g., porphyrin–fullerene: dyads) for designing new solar energy harvesting devices and enhance the efficiency of the existing devices.

Mission Relevance

This research will lead towards developing new solar energy harvesting devices and enhancing the efficiency of the existing solar energy harvesting devices. Since solar energy is clean and available in abundance, this research excellently matches with the DOE mission of increasing energy security and improving environment quality. Specifically, the investigation of collective optical properties of fluorescent metallic nanoclusters fits well with the mission of the Materials Sciences and Engineering Division (http://science.energy.gov/bes/mse/) of the Office of Sciences of the Department of Energy. Similarly, this research matches to the Advanced Reseach Projects Agency (ARPA) proposal call (https://arpa-e-foa.energy.gov/) for new strategies to convert solar energy into electricity or fuel.

Results and Accomplishments

Since I began in the middle of September 2012, progress has been made. We have designed a strategy to organize nanomaterials at macroscale with nanoscale precision and control, which is highly desirable for achieving commercially viable products using organized nanomaterials. Currently, we are working on the synthesis of silica nanorods, which will be employed for developing antireflective coatings for solar cells to enhance the solar energy harvesting. Working in the same direction, we are initiating experiments to investigate the interactions of fluorescent metallic nanoclusters with other nanomaterials, which are commonly employed in solar cells, for example, metal and semiconductor nanoparticles. These investigations will provide us information about the compatibility of fluorescent metallic nanoclusters in real solar cell settings.

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