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NATIONAL LABORATORY
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Laboratory Directed Research and Development Program

FY 2013 Annual Report

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Oak Ridge National Laboratory

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2013 ANNUAL REPORT

March 2014

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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 2013. The associated *FY 2013 ORNL LDRD Self-Assessment* (ORNL/PPA-2014/2) 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 'ensure America's security and prosperity by addressing its energy, environmental and nuclear challenges through transformative science and technology solutions'. 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. It allows ORNL, as well as other DOE laboratories, to improve its distinctive capabilities and enhance its ability to conduct cutting-edge R&D for DOE and WFO sponsors. R&D projects funded through LDRD support the following general goals:

- 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.

ORNL has established a program with four components to meet its LDRD objectives and fulfill the particular needs of the Laboratory: 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	~78% of program	~17% of program	~3% of program	~2% 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. Each year proposals are solicited to 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. 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 within each initiative. Each winter, the Deputy Director for Science and Technology issues a call for proposals. This year's call for proposal emphasized specific research priorities selected by management as being critical to the success of the following Laboratory initiatives.

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

The research priorities within the FY 2013 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 several focus areas that address critical issues associated with current and next-generation fission reactors, establishing leadership capabilities in fusion research, biofuel production, additive manufacturing applications, materials manufacturing processes, building efficiency R&D, and ecosystem sustainability. In 2013, $7.24 million of LDRD funds supported 21 projects in this area. FY 2013 LDRD investments were made in these projects to accomplish the following.
    - Virtualize processes and technologies to facilitate design and deployment of clean energy systems.
    - Improve the accident tolerance of nuclear fuels.
    - Integrate multi-physics and engineering simulation of fusions systems and develop novel plasma-material interaction testing capabilities to support future fusion research needs.
    - Support materials processing research and simulation capabilities for advanced manufacturing applications including large-scale additive manufacturing.
    - Develop R&D methods and technologies that support improved understanding of management practices that affect the long-term sustainability of natural resources and ecosystems.
- *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 2013, $9.40 million of LDRD funds supported 38 projects in this initiative. FY2013 LDRD investments were made in these projects to accomplish the following.
    - Develop novel neutron instrument sample preparation capabilities and probing techniques for investigating soft matter systems such as biomembranes.
    - Support materials R&D for energy applications including novel membranes for desalination, computation tools for understanding electron transport in meso-scale heterostructures, and identification of principles and methods for the design of improved catalytic pathways.
    - Advance hardware and software design tools to support extreme-scale computing including support of resilient architectures for "Big Data" applications.
    - Develop nondestructive methods for evaluating nuclear fuel cladding performance and perform advanced simulation to support research reactor operation with low enriched uranium.

- *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: development of hardware, software, and data analysis techniques that support cyber security advancement; development of technologies and analytical techniques to build biosurveillance capabilities; and advancement of scientific capabilities that address solution of "intelligence hard" problem sets. In 2013, $4.76 million of LDRD funds supported 11 projects in this initiative. FY2013 LDRD investments were made in these projects to accomplish the following.

    - Develop mathematical theories of control system vulnerabilities, techniques for high-throughput analysis of unstructured data, and virtualization of critical energy infrastructure systems for cyber security applications.

    - Improve metagenomic analysis and transcriptomic-based techniques for bio-threat identification and bioforensic analysis.

    - Development of software toolkits for the design, programming, and analysis of quantum computers.

- *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. Focus areas for this initiative included improved understanding of structure, dynamics and function of biological macromolecules; development of low-cost lignin-based carbon fiber; and strengthening of climate system modeling capabilities and climate data fusion methods. During the year, the Laboratory invested $6.67 million in 27LDRD projects. FY 2013 LDRD investments were made in these projects to accomplish the following.

    - Develop neutron-based methods for understanding metabolic and signaling pathways in plants and cross-corrolated techniques for investigating membrane interactions at the molecular level.

    - Define the R&D foundations for converting lignin to carbon fiber including characterization and modification of plant feedstocks, fractionation and purification of lignin components, and developing the scientific understanding and methods needed for lignin conversion to carbon fiber.

    - Develop stochastic subgrid modeling techniques for land-scale climate model and coupling of surface and subsurface hydrological process models.

To select the best and most strategic 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 2013, $35.33 million was allocated to the ORNL LDRD program to support 183 projects, 90 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	$28,063,228	$5,855,602	$1,278,599	$135,984
Number of projects	97	72	11	3
Number of new starts	49	35	5	1
Continuing (2nd & 3rd year of funding)	48	37	6	2
Average total project budget (1–3 years)	$669,602	$155,822	$388,105	$159,859
Average project duration	24 months	16 months	24 months	24 months

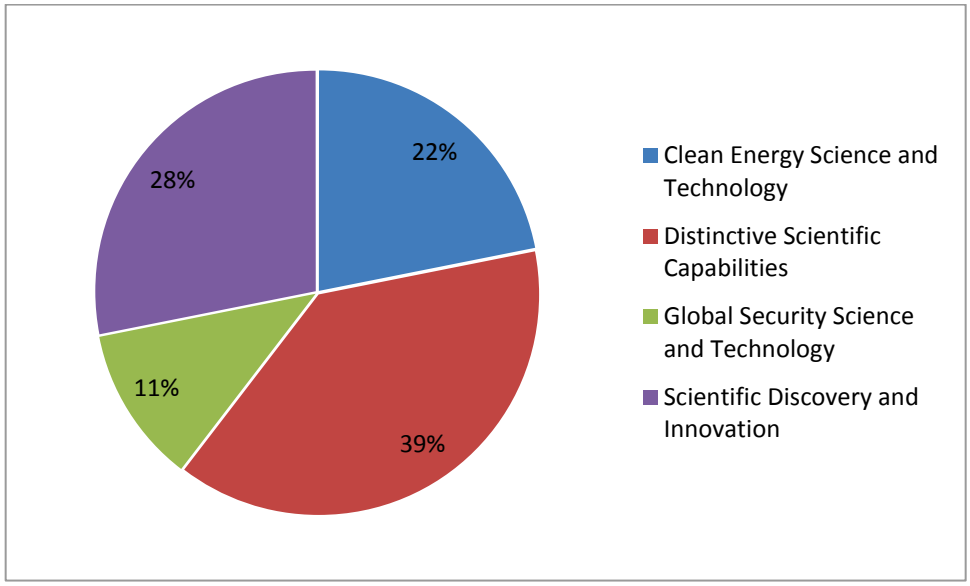

Fig. 1. Level of Director's R&D Fund investment in the Laboratory Initiatives for FY 2013.

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 to enhance 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 initiatives. 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 2013, $5.86 million of the LDRD program was apportioned to the Seed Money Fund to support projects, 35 of which were new starts (Table 2). The distribution of Seed Money Fund support by research division area is shown in Fig. 2.

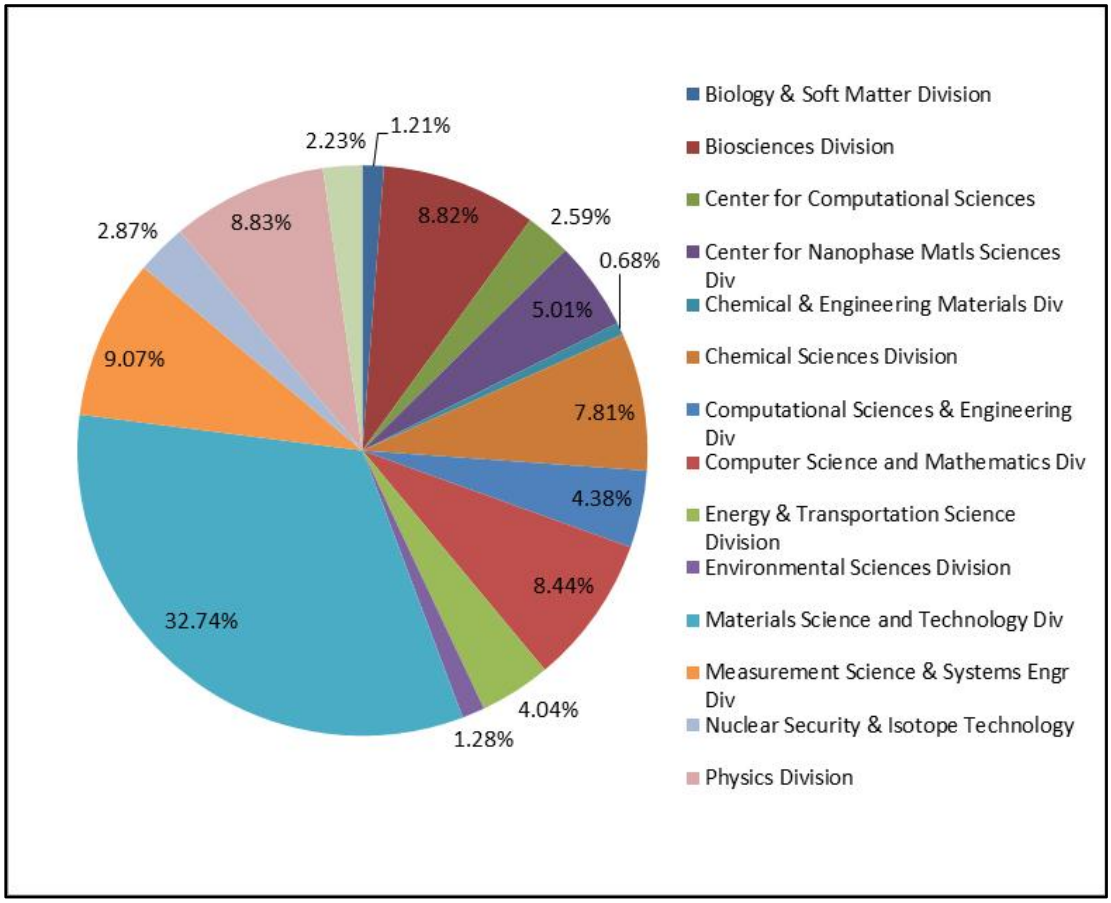

Fig. 2. Distribution of Seed Money Fund by research division for FY 2013.

Fellowship Fund

In FY 2013, 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 at ORNL provides an opportunity for outstanding scientists and engineers in life, physical, computer, computational, social sciences to 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 their doctorate degree. 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 2013, $1.41 million of the LDRD program was apportioned to the Fellowship Fund to support 14 projects—3 Weinberg and 11 Wigner Fellowship proposals.

Report Organization

This report, which provides a summary of all projects that were active during FY 2013, is divided into 12 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 2013. Publications resulting from the project are also listed.

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

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CLEAN ENERGY SCIENCE AND TECHNOLOGY

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, M.R. Alle, L.S. Sulewski, E.B. Freer, B.K. Daniel, K.A. Walker

Project Description

DOE-OE and DOE-SC workshops identified that 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 to trigger the smart grid's self-healing functions. ORNL will establish the feasibility, define the scientific issues, and demonstrate the solutions to important smart grid simulation problems only addressable within an exascale scientific computing application. This objective is accomplished by 1) using frequency recorders to establish a representative and scalable real-time data stream, 2) invoking ORNL signature identification algorithms, 3) modeling dynamically a representative region using an institutional cluster, measuring the scalability and computational benchmarks, and 4) constructing a prototype simulation for the system's concept of smart grid deployment. The ORNL enduring capability will 1) establish and demonstrate hardware in the loop testing network as a national resource, 2) develop data processing and simulation metrics to design a national capability justifying exascale applications, 3) demonstrate running dynamic models to design few-second self-healing is feasible, and 4) show simulated disruption data can be analyzed as cognitive patterns and visualized within a control room of the future concept.

Mission Relevance

Key to producing an enduring capability is future funding of 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 including both physical testing and exascale simulation 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 procured and set up a power grid emulator that was not only able to reproduce this testable data set but also benchmark cognitive analytic algorithms. 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 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 searching capability greater than 40 times faster. Utilizing compression, total data size is reduced from roughly 8.76PB to 7.01PB, a 20% 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 8000 measurements-per-second sampling rate, c) a sensitivity of 25 mHz within 80 ms, d) a timing system that can accurately time-stamp each measurement, and e) a system cost less than $1000 per copy.

Based on these design criteria, an interconnection capable emulator was designed and constructed in a high bay laboratory. Representative disruptions were ported through the complete analysis chain. The finished product was ported to a mock-up visualization capability suitable to demonstrate the efficacy of the new concepts for identifying and diagnosing impending disruptions and responding in time to keep the meter spinning.

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06085

Experimental Test of an Innovative Intense RF-Plasma Source

R.H. Goulding, J.B.O. Caughman, L.W. Owen, T.M. Biewer, J. Canik, G. Chen, S. Diem, Y.K.M. Peng

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 for MPEX. The MPEX device will provide data on materials and components needed both for ITER and the design of the 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 research and development (R&D) needed for "Materials in the Fusion Environment."

Results and Accomplishments

PhIX became fully operational in FY 2013. During this period, a new whistler microwave launcher was fabricated and installed, and hookups of all services to the experiment were completed, fulfilling objective 2 of the proposal. Experimental results obtained include the successful coupling of microwave power to the core of an overdense helicon-produced plasma using both electron Bernstein waves and whistler waves. The demonstration of such coupling was the primary goal of objectives 3 and 4 in the proposal. It was evidenced by increases in plasma density of up to 50% on axis in the target region of the device during the phase in which both helicon and microwave power were injected. In this region, as well as in the microwave coupling section of the device, the plasma density was clearly over-dense, being a factor of two or greater above the cutoff density for the 18 GHz microwaves (= 4×10^{18} m^{-3}) for O-mode launch. Densities measured in the helicon region were up to 5×10^{19} m^{-3}. Another important result, partially meeting objective 5, is that the modification of end boundary conditions caused by the addition of a downstream target did not reduce the plasma density produced in the helicon section. This target was initially stainless steel, with a carbon ring added later. Thin tungsten and molybdenum coupons were also placed in the target region, but these have not yet been removed from the device.

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06090

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

A. Naskar, J. Mays, M. Dadmun

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, 250 ksi) can be produced from commercial lignin feedstock. Successful demonstration of the proposed tasks will provide the technical basis for the DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Program to reinvigorate and expand its work on lignin-derived carbon fiber.

Mission Relevance

The DOE and its EERE 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 polyacrylonitrile 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. To date, 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 made major breakthroughs on (1) melt-spinning of softwood Kraft-lignin fiber (believed to be first report of such); formulations have 90–99% lignin; (2) stabilization of the fiber tow under stretching (50–300 %) condition within 8 hours, a conservative path (first report); and (3) flexibility of the fiber, as evidenced by the fact that it can be tied to standard carbon fiber tow by a knot (in order to apply axial stress). The group developed lignin characterization protocols and evaluated compatibility of lignin with various additives. The team is still working on optimization of conversion protocol. At this moment, the axial stress level corresponds to one-half of the desired one. Once we obtain good mechanical properties, we will demonstrate that this technology is applicable to source-neutral lignin chemistries.

To date, we have prepared lignin-based carbon fibers with 100–150 ksi tensile strengths and 7–8 Msi tensile moduli. Our protocol allows alignment of the pyrolyzed carbonaceous mass in fiber so that the modulus improves from 4 Msi to 8 Msi. It has been found that the fibers create more porosity at very high temperature pyrolysis, and that causes deterioration in mechanical properties. To address that issue, stabilized fibers with higher strengths need to be prepared.

During the summer of 2013, the ORNL team submitted a response to a request for information from the EERE program office of DOE regarding 'bBio-based carbon precursors'. We are expecting a future funding call in this area, and ORNL is now in well positioned to submit a proposal.

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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 US 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 has been collected for various hydride forms in zirconium and Zircaloy-4. Hydride reorientation system was used to generate radial hydrides at temperatures up to 400°C and internal pressures up to 3000 psi. Unique experimental setup for introducing and reorienting hydrides was developed, and first-ever 3-D simulations of hydride reorientation were performed.

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06129

An 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 that 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 project 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 US 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 experiment facilities 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 took 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 because of 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.

The research team created a prototype system that can be used to test the performance of the thermosyphon. A secondary coolant system is provided to simulate HFIR coolant flows, and power is provided by three rod-type heaters. The heaters are fully instrumented with thermocouples along the length, and the thermosyphon chamber has both thermocouples and pressure transducers. This facility will allow future researchers to qualify a thermosyphon design and test various transients that are required for a HFIR safety basis.

Information Shared

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06146

Science of the Plasma-Materials Interface at Extreme Conditions

F.W. Meyer, P.S. Krstic, M.E. Bannister, C.M. Parish, H.M. Meyer, III, H. Hijazi, 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 (DOE Fusion Energy Sciences) 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 .

Results and Accomplishments

In FY 2013 of this LDRD project, we have accomplished the following tasks:

1) We developed a new high-flux decelerated ion-beam capability at MIRF for this project capable of producing a helium ion flux > 10^{20}/m^2 at 50 eV and >10^{21}/m^2 above 2 keV.

2) We studied ordered helium nanofuzz precursor growth at 80 eV, and found, by EBSD analysis, grain-to-grain variations because of grain crystallographic orientation.

3) We investigated the energy, temperature, and fluence dependence of helium nanofuzz production and found that the critical flux decreases with increasing helium-ion energy, that an order to disorder (nanofuzz) transition occurs between 830 and 940°C, and that the helium nanofuzz layer growth is proportional to the square root of fluence.

4) By varying the incidence angle of the helium ion beam, we found that the nanofuzz tendrils grow toward the beam direction; sequential exposure at two different incidence angles (normal followed by 43°) showed a reduction of tendril density, suggestive of enhanced W sputtering (lawnmower effect).

5) Investigating the effect of high-dpa W self-ion predamage to simulate neutron damage, we found only qualitative changes: there was an increased number of surface pinholes at 50 eV and an increased void density in nanotendrils at 12 keV, but no major morphological changes.

6) We performed LAMMPS simulations of W self-ion damage and found that the defect density is not linear with damage dose but saturates at low fluences, which could help explain the previous observation.

7) In FY2013, this activity generated two invited talks, two conference presentations, and four research articles.

Information Shared

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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 a 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 Defense Advanced Research Projects Agency (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

The modified crystal plasticity code that contains soft slips modes to account for glide along the twin-matrix interface and hard modes to account for the strengthening due to nanotwins was used in the multi-objective optimization effort. The initial crystallographic texture in the polycrystalline microstructure was systematically varied through two parameters: the spread of the [0001] poles and the shift of the [0001] poles about the rolling direction, to capture the textures normally developed under shear rolling conditions. The twin width was another variable that controlled the strength of the alloy. Material failure was included in the deformation simulations by introducing a failure criterion based on a critical amount of shear strain and a critical amount of hydrostatic tensile stress exceeding in 10% of the elements. Multi-objective optimization was carried out by coupling the deformation simulations with an optimization routine based on simulated annealing. Three different criteria were used to evolve the initial population consisting of different textures and twin spacings. The simulated annealing procedure was carried out in parallel using the Titan supercomputer. The simulations showed that the optimization procedure was very effective in identifying specific locations in the parameter space where the combination of the strength and ductility were the highest. The presence of such attractive combination of strength and ductility in the parameter space was also verified using parameter sweep runs made using the DAKOTA toolkit in Titan. On the experimental front, friction stir processing of AZ31-titanium alloys containing different levels of titanium were carried out. The material was analyzed using analytical electron microscopy at the University of Virginia. The solubility of titanium in AZ31 was demonstrated in many samples. An invention disclosure based on the experimental work has been filed.

Information Shared

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06237

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

E.M. Pierce

Project Description

Describing the reactions that occur at the glass-water interface and control the development of an altered layer constitutes one of the main scientific challenges impeding existing models from providing accurate estimates of radionuclide release in safety assessments for geologic repositories. The altered layer (i.e., amorphous hydrated surface layer and crystalline reaction products) represents a complex region, both physically and chemically, sandwiched between two distinct boundaries—pristine glass surface at the inner most interface and aqueous solution at the outer most interface. The research objective is to develop an improved mechanistic understanding of the processes that control altered layer development in alumino-borosilicate glass. The specific aim is to advance our understanding of the processes involved in the formation of the amorphous hydrated layer (e.g., gel layer) and the impact the chemical composition of the glass has on layer development.

Mission Relevance

A major objective for the Department of Energy's (DOEs) 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

Because this project required linking of macroscopic reaction kinetics (e.g., altered layer development) to nanometer-scale interfacial process (e.g., silica condensation reactions), a combined experimental and computational approach was employed. The first objective was to add more features to an existing Monte Carlo (MC) code so that the simulations could guide future measurements. After adding the features, MC simulations of simplified borosilicate glasses showed that silica incorporated into the amorphous layer originates from solution as well as the surface, indicating that two mechanisms (i.e., condensation and repolymerization) are involved in the altered layer formation.

The following objective was to evaluate the role glass composition has on altered layer development by using five glasses in the Na_2O-Al_2O_3-B_2O_3-HfO_2-SiO_2 system that varied in the ratio of HfO_2/SiO_2 as a model. Results indicate that hafnium can have a significant effect on the bulk glass structure and the

dissolution and condensation rates during corrosion. Increasing hafnium content in alumino-borosilicate glass (1) results in a decrease in the dissolution because of the increased resistance to hydrolysis by the Hf—O—Si bonds in comparison to the Si—O—Si bonds; and (2) results from the increased residence time of low-coordination Si—O—Hf moieties at the glass surface and increases the density of anchor sites from which altered layers with higher silica densities can form than in the absence of hafnium.

These data have resulted in a focused effort to use in situ techniques to monitor the evolution of the amorphous layer using atomic force microscopy (AFM) and small-angle x-ray scattering (SAXS). The AFM measurements are providing information related to the surface roughness, topography, and composition (via correlation with the nano-mechanical properties of the altered surface), and the SAXS measurements are being used to gain insights on the pore structure. Both studies were initiated in FY 2013 and are being incorporated into a final manuscript as part of the project.

Information Shared

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06244

Demonstration of Electric Vehicle Dynamic On-Road Wireless Power Charging

J.M. Miller, O.C. Onar, M. Chinthavali, L. Tang, C.P. White, C.P. Coomer, S.L. Campbell

Project Description

This project was designed to showcase in-motion wireless charging of electric vehicles and to provide the foundation for future contactless energy delivery to electrified vehicles. Such energy delivery cannot be realistically accommodated using conductive charging; therefore, wireless power transfer (WPT) is the technology of choice. Wireless resonant power transfer for battery electric vehicle charging consists of a high-frequency (HF) inverter to excite a loosely coupled transformer. Primary and secondary side tuning effectively cancel leakage inductances resulting from loose coupling, thereby enhancing power transfer across large gaps of 100 to 200 mm. Vehicle side electronics consists of a diode rectifier and filter and can also be some form of power electronic converter. The result is delivery of filtered dc charging current to the onboard rechargeable energy storage system (ESS). Specific aims of the program are to demonstrate >97% coil-to-coil efficiency at reasonable power levels such as 3.3 kW and synchronism of the roadway coil sequencing with vehicle motion. The ORNL system is unique in three aspects. (1) The

coupling coil geometry is fully compatible with stationary WPT charging and exhibits coupling coefficient characteristics on ORNL's 0.25 m^2 coil that are better than a commercial 0.35 m^2 coil. In fact, the charge in-motion vehicle may stop, or park, over one roadway coil and charge as if stationary charging in a garage. (2) Grid side regulation of charging power facilitates high rate charging of the vehicle battery pack, effectively a dc fast charge rate, and with minimal onboard complexity. (3) The implementation of dynamic tracking, or coil sequencing strategy, confines the WPT magnetic field to the confines of the vehicle-mounted secondary coil.

Mission Relevance

Wireless charging is viewed by DOE and many in the automotive field as the enabling technology for mass-scale electrified transportation and the level of vehicle onboard ESS mass and volume reduction necessary to realize an affordable electric vehicle. If charge in-motion is adopted, onboard ESS can be reduced since most propulsion energy could be delivered the vehicle while in motion. This benefit is amplified by the shear convenience and ease of use of WPT, and it is the type of technology advance needed to make battery or plug-in vehicles acceptable to the average household. While dynamic charging provides the impetus for affordable mass-scale electrified vehicles, it also places a burden on future highway planners regarding the need for durable in-highway power transfer coils and their attendant dc power supply. In the ORNL dynamic WPT future concept, this dc power distribution would be buried in the roadway median with grid connections at various intervals. The U.S. DOT Research and Innovative Technologies Administration (RITA) has been apprised on the construction and durability aspects of WPT integration into roads.

Results and Accomplishments

The ORNL in-motion wireless charging experimental system consists of an energized roadway track of six primary coils, a coil sequencing electronics box, a high-frequency inverter and isolation transformer box with controller, Zlinx radio communications, and a power supply. A Global Electric Motors (GEM) electric vehicle was modified with a WPT secondary coil beneath its chassis, mounted midway between its wheel base, plus secondary electronics, filter, and dc contactor to its ESS pack. A light pole mounted to the rear of the GEM vehicle provides visual indication of captured power when the vehicle is driven across the primary coils.

How it works: Primary coils are embedded flush into roadway fiber plates, series connected in pairs, and with a single tuning capacitor per pair to set the center frequency. When the GEM front tires interrupt a photo sensor, the coil sequencing electronics connect that pair to the high-frequency (HF) power inverter and signal its controller to an enabled state. HF current then flows from the power inverter through the HF isolation transformer, the sequencing contactor, the series tuning capacitor, and into the primary coils. The GEM chassis-mounted secondary coil couples with the ensuing HF magnetic field, dictated by relative alignment between this secondary coil and the roadway primary coils, then rectifies the HF current, and routes the filtered dc power via another set of contactors to the vehicle ESS high-voltage (HV) battery pack. The transferred energy is supplied to the HV bus and is used to charge the HV battery and/or propel the vehicle. As charging takes place the GEM light pole illuminates, signaling the amount of received power. Similarly, on the primary coil sequencing box, another light pole signals the amount of power delivered. Then, as the GEM vehicle traverses the next set of coils, the sequencing logic requests a HF inverter inhibit, the initial roadway coil contactor is de-energized, and the in-coming coil set contactor is energized. When this sequencing is accomplished, the HF inverter is enabled and the next coil set is energized, repeating the process. This same procedure occurs for the remaining coil set, and for any number of additional coils in an energized track. The HV battery charge current and pack voltage are available at the Zlinx radio for communication back to the grid side controller.

Results: Energized demonstrations show that the coil sequencing is crisp, with out-going coil de-energizing complete within 0.2 ms and in-coming coil energizing complete within 1.4 ms. The fast quenching of coil current occurs because the HF inverter, when inhibited, places the dc link voltage directly across the coil and thereby quickly absorbs its stored energy. During the turn-on phase, the coil current rings up according to the quality factor of the tuned circuit. The ORNL team also implemented both primary and secondary side power smoothing using electrochemical capacitors. ORNL in collaboration with experts at ElectroStandards Laboratory (ESL) experimented with lithium-capacitor (LiC) storage on the roadway side power inverter to smooth power drawn from the grid. Similarly, carbon ultracapacitors manufactured by Maxwell Technologies were used in the GEM vehicle to smooth power flow to the vehicle HV battery pack. Such local energy storage can be either passive parallel as the carbon ultracapacitor plus battery, or active parallel as with the lithium-capacitor plus buck/boost converter and HV grid power.

More in-depth details and results from the in-motion wireless charging program will be reported on in subsequent annual report and publications.

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06414

Assembly of Functional Microbial Communities

D.A. Pelletier, M.J. Doktycz, G.J. Van Berkel, G.B. Hurst, D.J. Weston, S.T. Retterer

Project Description

This LDRD project aims to advance our knowledge of how microbial cells function as part of a complex community to carry out beneficial activities such as bioremediation, bioenergy production, prevention of disease, and sustainable agriculture. We propose a novel approach to elucidate the underlying principles that will ultimately enable engineering a synthetic microbial community for performing desired functions. We will perform experiments aimed at discovery of compatible interactions between microbial isolates, quantitative assessment of identified interactions, followed by modeling multispecies interaction networks and corroborating model predictions. The long-term goal of these efforts is to determine genetic and molecular factors that are important to dynamic microbial interactions and ultimately lead to predictive understanding of complex ecosystem functions.

Mission Relevance

This LDRD project is directly relevant to the DOE's Biological and Environmental Research (BER) program that seeks to understand "how genomic information is translated to functional capabilities, enabling more confident redesign of microbes and plants for sustainable biofuel production, improved carbon storage, or contaminant bioremediation." Microbial communities are the bases for numerous functional attributes observed in managed and natural environmental systems. Importantly, functional microbial communities are at the fundamental level of future efforts to manage and/or design sustainable ecosystems. Consequently, the fundamental knowledge resulting from the proposed efforts has a potential broad range of applications in human health, sustainable biomass production, carbon sequestration, and bioremediation. Additionally Dr. Pelletier as PI, along with a large group of Co-PIs, has been awarded a DOE Joint Genome Institutes community sequencing project entitled "Defining the functional diversity of the *Populus* root microbiome" that will allow us to sequence the genomes of 400 bacterial isolates. We currently have <50 genome sequences of microbes we are utilizing in this project, but through this collaboration with JGI we will have access to an order of magnitude more genomic data from strains known to be present within this ecosystem to aid in model development.

Results and Accomplishments

In order to uncover compatible interactions between microbes, we have developed a multi-tiered approach to determine phenotypes and assess both one-on-one interactions as well as interactions in multi-member communities. For the initial phase of the project, we selected 96 phylogenetic and metabolically diverse bacterial strains, isolated from a common ecosystem. We then developed a minimal medium that supports growth of the majority (~80%) of these strains. This defined minimal medium allowed us to manipulate medium constituents, such as the phosphorous and nitrogen source. Utilizing this medium, we have identified several strains with the ability to release phosphorous from organic and inorganic forms of phosphorous. Utilizing our one-on-one interactions approach, we have identified interacting pairs of

microbes with positive and negative growth effects. We have carried out preliminary studies of several molecules involved in cellular communication and microbial interactions across different ambient mass spectrometry platforms in the Organic and Biological Mass Spectrometry group. Phenazines are produced by *Pseudomonas* and other bacterial species and play multiple roles in interactions between the bacteria and the environment. Using laser desorption combined with LESA (liquid extraction surface analysis), phenazine-1-carboxamide was detected on colonies of GM17 grown on agar. Additional measurements of phenazines on GM17 colonies were performed using spatially resolved thermal desorption interfaced with mass spectrometry. A tandem mass spectrometry signal corresponding to loss of ammonia from the parent ion (m/z 224 -> m/z 207 transition) provided confident identification of the phenazine-1-carboxamide production from *Pseudomonas* sp. GM17, which had been hypothesized based on genome sequence data. While primarily a year 2 task, we have initiated our modeling efforts and are on track to define community assembly rules and testable predictions. Initial results from phosphorous solubilization assays, one-on-one interaction screens, and microbial genome sequence are currently being used to develop metabolic models for interacting microbes.

Information Shared

"Multimodal Imaging: AFM and Chemical Imaging Mass Spectrometry on One Platform" is in preparation.

06468

Development of Carbon Fiber-Based Products from Natural and Modified Plant Lignin

T.J. Tschaplinski, G.A. Tuskan, N. Labbe, D. Baker, J. Bozell, T. Rials, A. Ragauskas, A. Naskar

Project Description

The potential to use lignin as a feedstock for production of carbon fiber and new chemicals is limited by meeting the purity specification. This proposal aims to isolate purified lignin using a combination of enzymatic and chemical purification approaches, coupled with determination of the optimum lignin characteristics for carbon fiber production. Numerous available enzymes plus known selective chemical separation methods will aid in this process. Plant materials will include available herbaceous and woody biomass, progressing to transgenic switchgrass (*Panicum*) from Noble Foundation (NF) and natural variant poplar (*Populus*) from ORNL that greatly vary in syringyl/guaiacyl (S/G) ratio. Source-neutral lignin processing methodologies will be applied to understand the effect of lignin chemistry and structure on the properties of precursor feedstocks and carbonaceous materials. Chemical processing and characterization will include lignin monomer, dimer, and polymer isolation, polymerization of isolated polymers, fabrication of filaments from lignin derivatives, pyrolysis of precursors, and testing of carbonaceous materials. The target outcome is the establishment of procedures to reproducibly create unique lignin-derived precursor materials with potentially new properties. The project will focus on testing of previously unavailable lignin that can result in new raw materials for polymerization and processing into new products derived from renewable biomass resources.

Mission Relevance

The nascent carbon fiber industry aims to deliver high-strength fibers that are tolerant of elevated temperatures with low thermal expansion. These characteristics are required for advanced composites used in aerospace, wind-power, and automotive applications. Currently, carbon fibers are produced from

non-renewable, expensive polymer precursors, such as polyacrylonitrile (PAN) and/or petroleum pitch. The resulting fibers have excellent properties but are too expensive to encourage widespread demand for carbon fibers in high-volume, industrial, energy-efficient applications. Alternative precursor polymers, such as lignin by-products from the biorefinery and pulp and paper industries, have not yet met the property specifications defining high-value carbon fiber product. Developing a dedicated, renewable source of acceptable precursor polymer feedstocks that yields acceptable fiber properties would be transformational, helping to maintain U.S. technological leadership in a key energy sector and revolutionizing the carbon fiber industry. Abundant, renewable, and inexpensive sources of carbon precursor molecules, such as lignin in woody plant biomass, can potentially reduce the final costs by about two times, compared to fibers produced from expensive synthetic precursors, such as PAN.

Results and Accomplishments

Black cottonwood poplar *(Populus trichocarpa)* extreme wood chemistry variants were identified in the Genome-wide Association Study (GWAS) at Clatskanie, Oregon, with Syringyl/Guaiacyl (S/G) ratios ranging from 2.29 to 1.36. Fourteen high (5) and low (9) S/G ratio clones were harvested, shipped to ORNL, dried for 2 weeks at 70°C, debarked, chipped, and milled (as needed) for carbohydrate removal for lignin by 1) enzyme preparations and 2) Organosolv prior to fiber spinning. Four carbohydrate enzyme digests of the BESC standard poplar and seven Organosolv lignin extracts of variant *P. trichocarpa* clones have been prepared for C-fiber spinning. The Organosolv lignin extracts performed better than those generated by enzyme digestion, with the former protocol presently being optimized by modifying solvent conditions to adjust the extent of cleavage of β-O-4 linkages using the BESC standard poplar clone. Of the *P. trichocarpa* clones tested thus far, one clearly has superior performance characteristics with respect to carbon fiber characteristics. By resequencing all of the poplar clones in the GWAS population and searching for variants (early stop codons, late stop codons, frameshifts, etc.) in the key genes controlling lignin formation, we have identified clones that are homozygous for the 16 unique deletions in seven genes that control the flux of carbon to the lignin pathway and have blocks early, middle, and late in the pathway. These clones should have a wide array of lignin-quality phenotypes (variant) that will be characterized. By being natural variants, these clones may prove to be more effective and stable in producing tailor-made lignin than that produced by transgenesis. These natural variants have the added benefits that they can be rapidly scaled up by clonal propagation by industrial partners, and can be established in plantations without the need for lengthy APHIS paperwork approvals that transgenic clones would require. An additional 14 of such variant poplar have been collected from the Placerville, California, study and are being processed at ORNL.

06469

New Measurement Technology for Physical and Biological Characterization of Fundamental Carbon Cycle Processes in the Subsurface Environment

P. Fuhr, R. Kisner, P. Hanson, T. McIntyre, C. Schadt, J. Warren

Project Description

This project involves the development of a novel multi-measurement probe, enabling field experiment manipulations that uncover linkages between biogeochemical cycling within ecosystems, controlled laboratory experiments, and mechanistic process representations within models. The goal is to better understand the interplay among soil physical and chemical characteristics, microbial activity, and biogeochemical processes in response to varying environmental conditions. Simultaneously monitoring

multiple factors affecting carbon cycle processes will enable experiments that uncover key mechanisms for model development and validation. The proposed new multifunction probe will supply unprecedented measurement and sampling capabilities within the soil profile of intact ecosystems and laboratory mesocosms, providing data that significantly improves understanding on spatial and temporal scales. The new multi-measurement probe will consist of a cluster of optical fibers, supplemented by a unique ORNL sensor design that integrates electrical wires within optical fibers (wibers). The multi-functional probe cluster will provide a platform for multiple, complementary measurement techniques including 1) optical UV-VIS-IR-NIR absorption spectroscopy, 2) optical thermometry, 3) optical fluorescence spectroscopy, 4) Raman spectroscopy, and 5) electrical impedance spectroscopy. This suite of measurements collectively enables the simultaneous observation of gaseous species concentrations, temperature distributions, dissolved organic matter, and availability of nitrogen-containing compounds.

Mission Relevance

Accurate prediction of the evolution of climate system requires high-resolution simulation of land processes in the Earth system models. The fate of organic soil carbon under changing environmental conditions is a major uncertainty in the models, and has strong feedbacks on climate forcing. The DOE Office of Biological and Environmental Research has been and will continue to make large investments through SPRUCE, NGEE and other related effort to better understand the processes behind net carbon storage pathways in soils and the interplay between atmospheric and terrestrial ecosystems.

Results and Accomplishments

- Design and construction of peat bog measurement column with uniform spacing gas extraction locations and ambient conditions gradient variation capabilities.
- Design and development of fluorescent oxygen-sensing probe capable of subsurface installation and measurements.
- Integration of multiple sensing techniques and sampling methodologies in a well point probe design with interior scaffolding for structural support.
- Development of novel multipoint calibration techniques and support equipment for the aforementioned devices and systems.
- Design, deployment, and operation of a wireless communication backhaul network for the transport of measurements obtained from multiple field locations throughout the ORNL property to R&D laboratories on the ORNL campus proper.

Information Shared

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06471

Diabatic Void Fraction Measurements in Channels with Small Hydraulic Diameters Using Neutron Imaging

P.J. Geoghegan

Project Description

The goal of this project is to use neutron imaging to accurately measure refrigerant void fraction inside small hydraulic diameter channels. This would result in improved heat exchanger (HX) designs, which are crucial for improving the efficiency of heating, ventilation, air-conditioning, and refrigeration equipment (HVACR) for buildings. The energy savings for HX improvements is estimated at 1.0 Quads annually. Typical HVACR equipment employs two HXs involving two-phase flow. In order to effectively design and optimize the HXs for maximum system efficiency, design engineers rely on heat transfer and pressure drop correlations with accuracies of ± 20% and several iterations of testing for accurate modeling. Neutron imaging will provide improved measurements of void fraction, which will enable design engineers to eliminate months of testing to develop accurate HX models. Neutrons are relatively insensitive to aluminum while being strongly scattered by hydrogen atoms. These two facts ensure a reasonable image contrast in neutron-imaged HX devices. The proposed work will also lead to the development of a predictive tool in linking the real performance of HVACR systems to theoretical models – enabling robust fault detection and diagnostics (FDD) to maintain equipment efficiency.

This project has been broadened to include neutron imaging of operating heat pipes embedded in additively manufactured parts for applications such as engine and compressor cooling to increase the lifetime of the part and improve the thermodynamic efficiency. It is hoped that this work will promote Additive Manufacturing by overcoming heat transfer limitations in titanium- and nickel-based alloyed parts.

Mission Relevance

Energy efficiency is as an important energy resource that allows the United States to meet future energy needs and contributes to reducing carbon emissions. Short of major advances in energy production and conservation efforts, the United States faces growing threats to its national and economic security. HVACR systems account for over 32% of the energy consumed in commercial buildings. Since HVACR is the major commercial-building energy consumer, the Department of Energy (DOE) is aggressively targeting efforts to develop low-energy commercial-building heating and cooling systems.

Improved HX design provides opportunities for compactness, increased efficiency, and refrigerant charge reduction. These benefits provide excellent opportunities to meet new emission reduction goals. First the HX compactness would require less material to manufacture, and hence less carbon emissions. The improved thermal performance would result in lower approach temperature, thus improving the system efficiency by up to 10% and lead to less carbon emissions associated with system operating energy. The refrigerant charge reduction would result in smaller direct emissions.

Titanium- and nickel-based alloys are forming the cornerstone of Additive Manufacturing (AM). Both have great strength but low thermal conductivity. By addressing and overcoming the heat transfer limitations of these alloys, AM parts will achieve greater thermodynamic efficiency (turbines, engines, etc.) and have improved lifetimes due to lowered thermal stress. This effort relates directly to the Advanced Manufacturing Office of the DOE, which was established to reinvigorate manufacturing in the United States through Additive Manufacturing.

Results and Accomplishments

I successfully neutron imaged a horizontal boiling flow of the refrigerant isopentane in a square 4mm × 4 mm channel of an aluminum HX. The neutron images were translated into a vapor fraction (void fraction) image based on a successful calibration of the refrigerant isopentane at the CG1-D beamline at the High Flux Isotope Reactor (HFIR) at ORNL. Peak heat and mass fluxes reached 167 kW/m^2 and 800 kg/m^2s, respectively, achieved by a dedicated flow loop apparatus. This data is being correlated with corresponding sensor measurements and is currently being employed to validate Computational Fluid Dynamics (CFD) boiling flow models on the TITAN supercomputer.

I have designed an additively manufactured heat pipe to cool a 100 W heat source. The evaporative wick that provides the capillary driving force is fabricated as part of the additive build. It was manufactured at the Manufacturing Demonstration Facility at ORNL. This heat pipe is currently being tested and is scheduled for beamtime at HFIR in February of 2014. Neutron imaging of the operating wick will provide valuable information such as the 2D porosity of the wick, the vapor (void) fraction within the wick, and the working fluid level of the compensation chamber. This will be complemented by thermal imaging and sensor measurements.

Information Shared

Invention Disclosure 201303213, DOE S-124,818 entitled "Heat Pipe Embedded During Additive Manufacturing."

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. Warren, J. Kumar, A. Jensen, A. Walker, D. Maddalena

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 Community Land Model (CLM4) will define the relative sensitivity of tropical forests to elevated CO, 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 Next Generation Ecosystem Experiment (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, field measurements were conducted at the Parque Natural Metropolitano and Gamboa in September 2012 and at Parque Natural San Lorenzo, Gamboa, and Parque Natural Metropolitano in January–February 2013. Cranes were used to access tree canopies at two sites to obtain leaf gas exchange measurements in closed tree canopies to complement ground-based measurements. 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 CLM4 may not be well suited for tropical species, and 3) mesophyll conductance significantly limits photosynthesis in tropical species. An initial implementation of a phosphorus limitation mechanism has been incorporated into CLM4 for global simulations. Site-level and global simulations employing a mesophyll conductance mechanism were performed, and a paper is now available for early on-line access. An initial eco-regionalization has been completed for the tropics by clustering different sets of globally gridded data, and a manuscript descrbing the resulting representativeness analysis is being developed.

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, Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 24, 2012.

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, Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 24, 2012.

Y. Sun, L. Gu, R. E. Dickinson, S. G. Pallardy, J. Baker, Y. Cao, F. M. Damatta, X. Dong, D. Ellsworth, D. van Goethem, A. M. Jensen, B. E. Law, R. Loos, S. C. V. Martins, R. J. Norby, J. Warren, D. Weston, K. Winter, "Asymmetrical effects of mesophyll conductance on fundamental photosynthetic parameters and their relationships estimated from leaf gas exchange measurements," *Plant Cell Environ.*, 2013, doi:10.1111/pce.12213.

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F. M. Hoffman, R. Norby, X. Yang, L. Gu, A. M. Jensen, J. Kumar, D. M. Maddalena, Y. Sun, A. P. Walker, J. M. Warren, and D. Weston, "Model-Inspired Science Priorities for Evaluating Tropic Ecosystem Response to Climate Change – Part II: Model Simulations and the Implications for Field Experiments," poster presented at ORNL LDRD Poster Session, Oak Ridge National Laboratory, Oak Ridge, Tennessee, September 25, 2013.

06546

Process Optimization and Control for Additive Manufacturing by Integrated Computational Materials Engineering (ICME)

Z. Feng, J. Chen, W. Zhang, L. Zheng, R. Dehoff

Project Description

Additive Manufacturing (AM) is an emerging, revolutionary manufacturing technology for fabricating intricate and complex-shaped components with demonstrated dramatic improvement in energy efficiency and cost-effectiveness. This proposal aims to develop the integrated computational materials engineering (ICME) framework to provide the fundamental insights of the complex physical and chemical processes and their interactions involved in AM. Moreover, it seeks to demonstrate the quantitative predictive capability of the ICME model to guide effective development of new approaches for AM process optimization and control and to address the critical issues in the current AM technology. The ICME model will consider diverse physical phenomena including particle melting, fluid flow, heat transfer, non-equilibrium phase transformation, solidification, and residual stress and part distortion. Built upon the proposing team's extensive modeling capability on fusion welding, an analogous process to AM, the proposed model will capture the AM-specific phenomena, for example, power, heat source and molten pool interactions. Furthermore, taking advantage of ORNL's world-leading measurement and characterization capability, the model will be experimentally validated to ascertain the effect of process parameters on the microstructure and properties of finished products. The effectiveness of the ICME framework for AM process control and optimization will be demonstrated at the ORNL's state-of-art AM facility.

Mission Relevance

It is not a mere coincidence that the two recent independent reports from DOE's Advanced Manufacturing Office and Institute for Defense Analyses (IDA) featured the AM technology as an emerging advanced manufacturing technology with dramatic potential to change the future of manufacturing. Indeed, this is a part of the Administration's Advanced Manufacturing Partnership (AMP) to develop transformational manufacturing technologies and innovative materials, a grand effort led by National Institute of Standards and Technology (NIST), Departments of Defense, Energy, and Commerce, and National Science Foundation. Furthermore, AM technology is a key component of the National Network for Manufacturing Innovation (NNMI) with a proposed $1 billion federal investment from mandatory funding. Even though it has the high potential to revolutionize the future manufacturing, the AM technology is still in its infancy in the grand scheme of broad industry applications. Several grand challenges in AM technology need to be solved such as scaling up size of production runs, producing large parts, and increasing speed of production. In order to develop the next generation of AM process, a more holistic and integrated approach toward process control and optimization is urgently needed.

Results and Accomplishments

In FY 2013, the first year of the project, the R&D efforts have been focused primarily on the development of major model blocks of the ICME framework for AM. The electron-beam-based powder-bed AM process was chosen as the basis for the model development. Experimental work related to identifying key process variables was also carried out.

The project took advantage of existing ICME modeling capabilities developed at ORNL over the past several decades for fusion welding, which shares commonality with the AM process in many key aspects such as the process characteristics and physics involved (solidification, microstructure evolution, stress,

and distortion). The adoption of these existing modeling tools allowed us to concentrate on the development of key sub-models to capture the unique features in AM to speed up the entire modeling framework development, and, at the same time, to integrate various sub-models and an optimizer into the ICME of AM. In FY 2013, we successfully developed the framework for the following sub-models that were unique to AM: (i) evolution of powder material attributes such as the thermo-physical properties as the powder particles go through heating, sintering, melting, solidification and cooling; (ii) the electron-beam and powder particle interaction describing the energy absorption in the powder from the high-energy electrons; (iii) the heat transfer in the powder bed AM process to adequately simulate the layer-by-layer powder addition and the buildup of the solidified part, an unique feature of the AM process; (iv) the thermal-mechanical simulation of the addition of the powder and the changes of material states to compute the stress evolution and deformation process during AM, and the formation of residual stresses, distortion, and quality of the part.

Information Shared

J. Chen, L. Zheng, Z. Feng, and R. Dehoff, "Prediction of material thermal properties and beam-particle interaction at meso scale during electron beam additive manufacturing," MS&T'13, October 27–31, 2013, in Montreal, Canada.

J. Chen, L. Zheng, Z. Feng, and R. Dehoff, "An integrated computational model for additive manufacturing process to predict the residual stress distribution," MS&T'13, October 27–31, 2013, in Montreal, Canada.

06551

Lignin-Based Carbon Fiber Composites Manufacturing Processes Investigation

R.E. Norris, N.C. Gallego, F. Xiong, A.M. Clark, D.C. Webb

Project Description

Work in demonstrating approaches for manufacturing composites with lignin-based carbon fiber will significantly advance the impact of ORNL's low-cost carbon fiber research and will position ORNL as a world leader in low-cost carbon fiber composites. Cost-effective manufacturing methods that can immediately exploit low-cost carbon fiber approaches being introduced by ORNL are essential to facilitate the widespread implementation of carbon fiber parts in high-volume applications. This project is part of the larger integrated lignin LDRD program in which related efforts are addressing means for selecting the most appropriate lignin feedstocks, isolating and purifying those feedstocks, spinning the lignin into precursor, and converting the precursor into carbon fiber to provide the final lignin forms for processing into composites. In this project, potential large-scale processing methods and achievable composite properties for manufacturing carbon fiber composites from low-cost lignin-based precursors are being demonstrated. Product forms made using minimal development resources and projected to be among the first available utilizing lignin from the ORNL Carbon Fiber Technology Facility (CFTF) are being utilized for this demonstration. In demonstrating cost-competitive high-performance methods for manufacturing carbon fiber components, ORNL is positioned for expanded research opportunities with industrial and federal partners.

Mission Relevance

DOE has identified broader implementation of carbon fiber-based composites as a strategic investment area for a number of energy mission areas including automotive lightweighting and other applications. The development and demonstration of means for lowering the cost of both the carbon fiber as well as composite manufacturing processes are critical to success. Lignin-based carbon fiber precursors are very attractive for several key reasons: 1) lignin precursors are projected to be among the least expensive of any of the alternative precursors ORNL has identified, 2) lignin is a renewable resource available in quantities adequate to supply large-volume mission areas of DOE interest, and 3) lignin cost is relatively unaffected by the price of oil, unlike all of the other precursors currently under consideration. Combining ORNL's widely recognized carbon fiber initiatives with processes for exploiting the fiber in composites having attractive cost and performance enhances DOE's potential for success.

Results and Accomplishments

During this period, the project team has produced the first known composite articles constructed with lignin-based carbon fiber reinforcement. It was also the first time ORNL has carbonized lignin mat materials with carbonization demonstrated both in small batch ovens as well as at the CFTF. Significant progress was achieved in understanding of requirements and effects of the carbonization process on the resultant fiber characteristics and properties. For example, the fibers themselves were found to have a large number of voids, and other work in the LDRD program indicates the materials currently available for composite manufacturing are likely not capable of producing attractive strength or modulus enhancement in composites. This issue is being addressed as the project is entering its second year. Even with limitations of the existing materials' capabilities, significant progress has been shown in manufacturing composites, as modulus advantages (2–3X) were shown at a strength equivalent to neat resin strength. Improvements in resin wet-out and fiber/resin compatibility are necessary to get the best properties from these composites, and these issues are also being addressed as the work progresses toward utilizing tows and mats from proxy materials to represent processing characteristics and properties of lignin-based carbon fiber that is forecast to be available later next year by the LDRD program. Several potential partners in the composites industry have expressed interest in collaborating to support this initiative as appropriate materials become available.

Information Shared

None.

06558

Low-Cost, Multi-Sensor Wireless Platform for Smart Buildings

P.C. Joshi, P.T. Kuruganti, S.M. Killough, C.E. Duty, P.L. Fuhr, E.A. Vineyard

Project Description

DOE's Building Technologies Program's (BTP) mission is to deploy building technologies and practices that can reduce U.S. energy use. Buildings consume up to 40% of the energy produced in the United States and advanced low-cost sensors and controls have the potential to reduce the energy consumption of the buildings by 20–40%. This project will design, build, and package next generation wireless sensors using printable electronic technologies having the following components: (1) multi-modal sensors, (2) active/passive circuit elements, (3) antenna, (4) radio frequency (RF) electronics, and (5) photovoltaic cells. While several discrete circuit elements have been demonstrated, there are key technological barriers

to developing printable wireless sensor systems. The proposed research will address the development of a multi-sensor platform with a specific focus on temperature and humidity sensors, and printed RF antennas for monitoring in smart buildings. The integrated sensor system is aimed at bringing together the elements of functional sensors on low-cost substrates, multi-parameter detection, data processing, wireless communication, and energy harvesting. We envision the evolution of this system towards fully printed integrated "peel-and-stick" sensors for smart buildings. The materials R&D and flexible infrastructure, including low-temperature material processing and printing technologies, are the core strengths of ORNL that meet the technology demands at both extremes: material innovation and manufacturability.

Mission Relevance

The proposed research addresses the main goal of energy efficiency related to buildings, manufacturing, and process industries and establishes a core capability to print fully integrated wireless sensors requiring innovations in key areas. The aim of the advanced sensor platform development is to establish a high degree of coordination among complexity, functionality, innovation, and expected benefits. Successful demonstration of the system with key components will provide a powerful platform that can revolutionize ubiquitous monitoring applications for improving energy efficiency. Ultra low cost of manufacturing serves as the driver for deployment. This research aligns with the missions of DOE's Building Technologies Program (BTP) and Advanced Manufacturing Office (AMO). The proposed integrated multifunctional sensor platform will address a multiplicity of energy functions for buildings technology while paving the path for integrating non-energy functions such as safety and security. Although the focus of the present R&D is the development of a multifunctional sensor platform meeting the needs of future smart buildings, other functions that have economic benefits to the industry and consumer will emerge while influencing the investment decisions of the funding organizations. Process and discrete manufacturing industries have applications for the technology described above for improving energy efficiency through ubiquitous process visibility. The proposed research will position us to play a competitive role in the thin film and flexible sensor technology areas. (By 2021 the market will be worth $44.3 billion, as compared to the current level of $2.2 billion; Source: IDTechEx.)

Results and Accomplishments

The proposed R&D attempts to exploit the novel materials, low thermal budget pulse thermal processing, and low-cost, additive printing techniques for the realization of a multifunctional sensor platform. We have reached all the major technical goals proposed for the first year of the project. Specific accomplishments include the following:

- Drop-on-demand inkjet printing of silver conductive lines below 100 µm resolution using nanoparticle (size <150nm) inks with 10 pL drop volume.

- Integration of high-performance temperature (sensitivity: 1.02×10^{-3}/°C) and humidity (sensitivity: 0.50 pF/%RH) sensors on flexible substrates.

- Printed antenna design with return loss below -10 dB in the investigated frequency range of 2.0–5.5 GHz.

- Demonstrated printed antenna, sensor, and driving-circuit integration on flexible polyimide and paper substrates.

- A requirements document was developed to review sensor standards and codes that regulate new construction and retrofits for residential and commercial buildings to aid in energy efficiency. Some of the energy standards that were discussed include American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) Standards 90.1, 90.2, 55, 62.1, and 189.1, International

Energy Conservation Code (IECC), International Building Code (IRC), and National Fire Protection Association (NFPA) 5000 code.

Beyond meeting the technical goals for the first year, the team has focused on activities that prepare the project for successful execution of the second year objective: system-level integration. The main material and thin film development and device integration tasks include (1) Sensor co-integration; (2) system-level characterization; and (3) integrated system demonstration. Beyond these goals we have a stretch goal of incorporating a photovoltaic cell, energy storage, and an organic light emitting diode into the system.

Information Shared

P. T. Kuruganti, S. M. Killough, and P. C. Joshi, "Miniature Wireless Sensors as Printable Components," oral presentation at the 59th International Instrumentation Symposium, Cleveland, OH, May 13–17, 2013.

P. T. Kuruganti, S. M. Killough, P. C. Joshi, E. A. Vineyard, and P. Hughes, "Low-Cost Wireless Sensor Networks for Building Applications Using Novel Materials and Energy-Efficient Communication Techniques," oral presentation at Intelligent Building Operations Workshop, Boulder, CO, June 20–22, 2013.

P. C. Joshi, M. Shao, K. Xiao, P. T. Kuruganti, S. M. Killough, and C. E. Duty, "Low temperature integration of metal oxide thin films for flexible electronic applications," oral presentation at the American Vacuum Society 60th International Symposium & Exhibition, Long Beach, CA, October 27–November 1, 2013.

ORNL Invention Disclosure DOE S-No. S-124,540, 2962_IDSA, "Low-Cost Printable Wireless Sensors for Buildings Applications."

06562

Low-Cost Tailored Carbon Nanocomposites for Polymer Additive Manufacturing

C. Duty, A. Naskar, S. Ozcan, V. Kunc, H. Tekinalp, L. Love, I. Ivanov

Project Description

Additive Manufacturing (AM) is quickly becoming a mainstream manufacturing technique for complex and custom components and may soon provide the foundation for securing America's advanced manufacturing future. However, the strength of AM materials (specifically polymers) must be increased in order to meet the mechanical requirements of functional parts. This project will increase the strength of polymer AM components by developing a carbon nanofiber composite material system that is compatible with Fused Deposition Modeling (FDM). ORNL has developed a process for fabricating carbon nanofibers using technology from Hills, Inc., who has commercialized "thin plate" extrusion dies for multicomponent fiber spinning. We will leverage the Hills technology to produce continuous carbon nanofibers with a tailored geometry and composition to be treated and dispersed in a polymer matrix for AM. The use of high-aspect-ratio (L/d) and small-diameter filaments will produce mechanical properties superior to those of 5–10 μm diameter carbon fibers typically produced from the same precursor. The ability to produce high strength polymer composites with AM will uniquely position ORNL in this space and will lead to significant follow-on projects through DOE's Advanced Manufacturing Office as well as key industrial partners such as Stratasys, Boeing, Lockheed Martin, and Northrup Grumman.

Mission Relevance

This project supports the objectives of DOE's Advanced Manufacturing Office by exploring developments in AM and carbon fiber composites to improve time-to-market and product performance for advanced materials and complex components.

Results and Accomplishments

Significant progress has been made related to precursor fiber spinning during the initial portion of this project. The mutli-component single-shot extrusion equipment was delivered in November 2012, and homo-component extrusion was demonstrated in January 2013. Initial experiments in conjunction with Hills, Inc., have demonstrated the co-extrusion of linear low-density polyethylene (LLDPE) with polylactic acid (PLA) at 200°C to obtain island-in-a-sea composite fibers consisting of island filaments of LLDPE of 500 nm diameter. The fiber bundle was then washed in tetrahydrofuran (THF) to remove the PLA fraction and produce submicron-diameter LLDPE carbon precursors. The LLDPE fibers were stretched more than 100% using a fiber-stretching unit and stabilized in sulfuric acid through a sulfonation bath under various processing conditions, and the degree of sulfonation was analyzed by thermal analysis. Initial experiments for carbonization of the precursor materials are under way.

In order to evaluate the impact of second-phase materials on strength, ABS-carbon fiber composite specimens were prepared. In order to show the importance of the fiber size and L/D ratio on composite properties, two different fiber lengths (½ and 1 in.), and therefore two different L/D ratios (2540 and 5080), were chosen. The reinforcing carbon fiber, with an average fiber diameter of 5 µm, was added to the ABS at 10 wt%. Both ultimate tensile strength and the elastic modulus dramatically increased with the addition of carbon fibers, and with an increase in L/D ratio of these fibers, a tensile strength comparable to that of aluminum 6061 alloys was achieved.

Information Shared

None to date.

06654

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

T. Rogers, A. Naskar, C. Eberle, D. Miller

Project Description

Lignin-based carbon fibers are of great interest to industry across the globe. Lignin is an abundant, renewable raw material and is the only known potential carbon fiber material that 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, converting it to carbon fiber will require some investment, and without a market for those fibers, there has been no incentive for potential lignin suppliers to make those investments.

ORNL, in partnership with GrafTech International, has recently demonstrated that lignin-based carbon fibers can be produced at the laboratory scale that meet the technical requirements for thermal insulation. However, the lignin used in those experiments is not currently being produced at commercial scale. This

proposal will outline a path in which ORNL will work to identify, secure, and test alternative sources of lignin from both bio-refineries and pulp and paper manufacturers so that companies such as GrafTech International, and other companies in the future, can begin producing lignin-based carbon fibers at the commercial scale.

Mission Relevance

DOE has identified broader implementation of carbon-fiber-based composites as a strategic investment area for a number of energy mission areas including automotive lightweighting and other applications. The development and demonstration of means for lowering the cost of both the carbon fiber as well as composite manufacturing processes is critical to success. Lignin-based carbon fiber precursors are very attractive for several key reasons, primarily because 1) lignin precursors are projected to be among the least expensive of any of the alternative precursors ORNL has identified, 2) lignin is a renewable resource available in quantities adequate to supply large volume mission areas of DOE interest, and 3) lignin cost is relatively unaffected by the price of oil, unlike all of the other precursors currently under consideration. Combining ORNL's widely recognized carbon fiber initiatives with processes for exploiting the fiber in composites having attractive cost and performance enhances DOE's potential for success.

Results and Accomplishments

During this period, the project team has identified an appropriate lignin source with which to work going forward. Domtar Paper has implemented Metso's LignoBoost system at its Plymouth, North Carolina, pulp plant in an effort to increase the efficiency of the plant's recovery boilers. As an added benefit, the LignoBoost system creates a purified lignin stream that is suitable for carbon fiber precursor. Domtar is willing and able to supply ORNL with ton-size quantities of purified lignin in an effort to develop high-value markets for lignin.

The project team has reduced the stabilization time for lignin-based carbon fiber mat from 10 hours to 4 hours. The team has also tested concentrations of different additives in an effort to pelletize and melt-blow the Domtar lignin into a non-woven carbon fiber precursor mat. The project team was able to melt-blow a 100 kg sample of carbon fiber precursor mat from Domtar lignin at the Carbon Fiber Technology Facility.

ORNL is working with collaborators from UT-Knoxville and Georgia Tech to understand molecular changes that occur during thermal processing of lignin. This understanding will help us to develop better processing conditions that help to build structural order in lignin precursor and its carbon derivative.

Information Shared

None.

06735

Reducing Environmental Impacts of Hydrofracturing by Subsurface Co-Precipitation of Barium and Radium

A.G. Stack, L. Delmau, G. Rother

Project Description

Hydraulic fracturing is playing a dramatically increased role in natural gas and oil production in the United States, but environmental issues are currently delaying its development. Dissolved barium is one of the most significant toxic contaminants in brines produced from this activity, and radium is the primary naturally occurring radioactive material. We propose a novel approach to significantly reduce the toxicity and radioactivity of produced waters by inducing radium-containing barite precipitation directly in subsurface geologic formations. The focus of this proposal is to conduct proof-of-principle studies of a) the efficiency of radium incorporation during barite precipitation under subsurface conditions; b) the effect of pore-confinement in geologic media on the rates and locations of barite precipitation; and c) the applicability of models for predicting the performance of in situ precipitation schemes..

Mission Relevance

Due to the environmental issues related to hydrofracturing and its growing share of energy production, we anticipate growing interest by DOE and private industry. The likely DOE sources of future funding include the Fossil Energy (FE) Program, which last year funded projects ($28 million) "aimed at addressing the technical challenges of producing natural gas from shales and tight sands, while simultaneously reducing environmental footprints and risks" (from FE homepage). The Office of Basic Energy Sciences, Geoscience Research Program funds fundamental aspects of mineral growth, pore-size effects on precipitation phenomena, and multiscale modeling. Thus, this LDRD effort will help poise us for future funding. Finally, in recent years our neutron and X-ray scattering studies of porosity/permeability distributions in shales and other geologic formations have attracted interest by companies involved in oil, gas, and geothermal energy production.

Results and Accomplishments

In the 8 months this project has been funded, we conducted experiments and are disseminating results and initiated new collaborations. We obtained core samples of the Marcellus shale and conducted treatment experiments with added sources of sulfate to promote barite ($BaSO_4$) formation. In a suite of experiments, we determined that pure water does not produce significant barium from ground Marcellus shale samples, but 1 N HCl does produce significant barium (the acid used in hydraulic fracturing). We found that 1 N H_2SO_4 does not produce significant barium, indicating that there is the potential to use sulfuric acid in place of HCl to mitigate barium contamination in produced water. We obtained isotopes of radium and barium, developed a protocol for their analysis, and made measurements of the efficacy of radium incorporation into barite and barite's rate of formation. We found that nearly all radium can be incorporated into barite. To study the effects of barite precipitation on porosity/permeability relationships, we obtained small-angle neutron scattering (SANS) time and measured changes in the scattering of Marcellus shale samples exposed to solutions supersaturated with respect to barite. Data reduction is ongoing. We have initiated a subcontract with Prof. Susan L. Brantley at Pennsylvania State University, who has performed extensive baseline SANS measurements on unreacted Marcellus shale. Lastly, we have initiated a collaboration with an expert on the organic components of hydraulic fracturing fluid and shales, Prof. Kimberly Carter at UT-Knoxville, who is writing a Joint Directed Research and Development proposal.

Information Shared

A. G. Stack, "Feasibility of In Situ Sequestration of Toxic Metals in Flowback Water from Hydraulic Fracturing," U.S. EPA technical workshop on Wastewater Treatment and Related Modeling, April 18, 2013 (poster and proceedings).

06761

Large-Scale, Out-of-the-Oven Additive Manufacturing

L. Love, V. Kunc, O. Rios, C. Duty

Project Description

The goal of this project is to significantly advance the state of the art in Additive Manufacturing (AM) by developing key technologies to move AM away from a single deposition head operating in an oven towards "out-of-the oven" high-throughput AM work cells. Success will significantly increase the size of parts and enable a CAD-to-Component, not just CAD-to-part, philosophy. Specific challenges include the following:

- Advanced composite polymers capable of low-temperature deposition
- Active localized control of the part's temperature to reduce residual stress
- Coordinated motion and deposition control capable of large-scale (multi-meter) deposition with high-resolution control

The focus of this project will be on the development and deposition of polymers suitable for deposition in the open environment with a robotic platform that has both large volume (> 2 meters) and high resolution (< 2 mm). By the end of this project, we will have developed materials and novel extrusion and heating technologies, produced and characterized test parts, and demonstrated the manufacture of a part that is greater than 2 meters in size.

Mission Relevance

Manufacturing is the production of goods for use or sale using labor and machines. In 2011, the President's Council of Advisors on Science and Technology (PCAST) emphasized the importance of ensuring American leadership the advanced manufacturing. One specific area identified in their report was AM. The focus of this research is to explore the utility of AM at a scale (many meters) and rate (two orders of magnitude faster than the state of the art) that presently does not exist. This project has relevance with the Department of Energy, Department of Commerce, and Department of Defense. The DOE Advanced Manufacturing Office has identified this project as an area for future research. Results of this investigation can enable a new form of manufacturing ideal for commercialization through the Department of Commerce. The ability to manufacture large structures at very high rates without the need for tooling is attractive to the Department of Defense. The Office of Naval Research is interested in supporting the program for enable low-cost tooling for legacy equipment. At the time of this report, both DOE's Advanced Manufacturing Office (AMO) and the Office of Naval Research (ONR) have requested proposals for follow-on research.

Results and Accomplishments

The project has successfully demonstrated the manufacture of large parts (over 2 m) at very high rates (>200 ci/hr) at room temperature. The major breakthrough was the incorporation of carbon fiber into the thermoplastics for deposition. The introduction of the carbon fiber significantly increases the strength and stiffness of the final parts. However, the fibers also increase the thermal conductivity and reduce the net coefficient of thermal expansion. This combination enables the parts to be manufactured at room temperature. The project has demonstrated manufacturing parts using ABS, carbon-fiber-filled ABS, Ultem, carbon-fiber-filled Ultem and PEKK. The ability to manufacture at room temperature eliminates the need for an oven to hold the part's temperature constant (saving energy) while also enabling the integration of other tools into the manufacturing work cell. The team integrated a spindle onto the deposition head and demonstrated in situ post-machining to provide < 0.1 mm accuracy. Sample parts were manufactured and provided to a tooling company who successfully demonstrated an ability to shape sheet metal. Research now is focusing on reduction of porosity and integration of support structures to enable the manufacture of parts with overhanging structures.

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DISTINCTIVE SCIENTIFIC CAPABILITIES

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. Helium-3 gaseous detectors have a number of very attractive features for neutron scattering including a 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 a large active area, single neutron sensitivity and no parallax broadening. Unfortunately their dynamic range and detective quantum efficiency are limited. The low-rate capability of these detectors limits 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 replacing He-3 with 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 is described as follows.

- It is a design tailored to the needs set by the experiments using high-intensity neutron beams provided by the Spallation Neutron Source (SNS) and High Flux Isotope Reactor (HFIR).
- 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.
- The development of this detector technology will reinforce the recognition of ORNL as a leader in neutron detection among the community of users of neutron source facilities.

Results and Accomplishments

Some 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 (1 million counts per second) has been demonstrated.
- The position resolution was measured using a 2 mm mask.
- A background level below 0.1 counts per second was achieved.
- 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 as a converter in a beam monitor, and future steps are focused on increasing the efficiency to above 50%.
- Grant: In collaboration with Nova Scientific, Inc, the project consisting of the high-readout and the microchannel plate (MCP) got a $100,000 award from the DOE Small Business Technology Transfer (STTR) Phase I Program.
- Grant: The DOE STTR awarded Phase II of this project with Nova with $1 million. It will consist of producing a 20 cm × 20 cm high-rate and high-resolution detector.
- Student participant Amanda K. Barnett successfully defended her master's thesis based on work performed as part of this project in May 2013 in the University of Tennessee's Department of Nuclear Engineering.

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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..

Results and Accomplishments

The research supported by this LDRD formulated four key design principles for the design of efficient polymer electrolytes: (1) polymers with frustrated chain packing should be used to decouple ionic conductivity from segmental relaxation; (2) polymers with a high dielectric constant should be used to achieved high free-ion concentration; (3) polymers with low glass transition temperature should be used to increase ionic mobility; and (4) systems with a relatively high salt concentration should be used to increase the ions concentration and lower the energy barrier for ion hopping. We have successfully demonstrated that the ionic transport in many polymer electrolytes can be strongly decoupled from their segmental dynamics, in terms of both temperature dependence and relative transport rate. Our analysis reveals that the ionic transport mechanism in polymers is fundamentally different from that in small molecules and calls for a revision of the current theoretical picture. Several novel polymers developed in this study can be classified as superionic conductors. One of them, PVEC-PVAc/LiTFSI (50 wt%), exhibits higher conductivity than the best data known for PEO: PEO/LiTFSI (45 wt%), which is typically considered as the state of the art of dry polymer electrolytes. The results of this project not only provide a new paradigm for design of highly conductive polymer electrolytes but also create a solid foundation for our competition for the Energy Frontier Research Center (EFRC) on transport phenomena in polymers.

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. Critical 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 Energy Efficiency and Renewable Energy, which is seeking new ways of protecting electrode surfaces and improving the cycle ability 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. This project was rolled into a Basic Energy Sciences renewal proposal and helped secure continued funding on the project as it evolved based on reviewers comments. This project is worth $800K/year to ORNL.

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. We have also studied the passivation of aluminum current collectors as a function of lithium salt. This data revealed the formation of a 3-nm passivation layer comprised of AlF_2H. This composition has not been reported previously and provides insight into the formation of HF in an electrochemical cell. We have also prepared intermetallic anodes and identified the formation of a 3-10-nm thick SEI layer on antimony and tin materials. This is the first evidence for the thickness and composition of an anode SEI layer.

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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, K. Littrell, 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 (OFES) and Nuclear Energy (NE) , 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 the Electric Power Research Institute (EPRI) Long-Term Operation Program in weld repair of irradiated materials. Results on stress effects on helium bubble evolution are also likely to stimulate interest from DOE/OFES. The unique Wide Angle Neutron Detector/School of Nuclear and Allied Science ((WAND/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, and microstructural evolution under conditions far from equilibrium, 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 conditions far from equilibrium. 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, which suggested 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 dissolution of nano-precipitates in aluminum alloys, with the SANS results corroborated by high-resolution transmission elecltron microscopy (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 $2.1 million in research, funding has been received from DOE/NE, DOE/EERE, EPRI, and NRC.

Information Shared

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06026

Optimization of ORNL Neutron Sources to Meet National Mission Needs

P.D. Ferguson, K.W. Herwig, F.X. Gallmeier, J.K. Zhao, B. Riemer, J.L. Robertson, 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 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 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 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. Detailed optimization of the target/moderator geometry has demonstrated that a gain of 2–2.5 can be obtained in neutron beam brightness relative to more conventional designs. While liquid mercury and rotating or stationary solid tungsten are viable target options, tungsten will offer the highest beam brightness. Instrument modeling has shown that neutron scattering techniques that rely on time-averaged flux will perform similarly on either a short- or long-pulse source (within a factor of 2). Alternatively, techniques that rely on peak moderator brightness will perform far better on a short-pulse second target station.

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. Neutronics modeling has demonstrated that a cold H_2 moderator with brightness equivalent to that of the current HB-4 cold source can be achieved. This moderator can illuminate a guide cluster with approximately three times the inlet area of the cold source, supporting at least nine neutron scattering instruments.

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06073

Lignin-Based High-Performance Li-ion Anode Materials Synthesized from Low-Cost Renewable Resources—Nature Provides Enabling Microstructures

O. Rios, K. More, W. Tenhaeff, A. Johs, S. Nagler, D. Keffer, N. McNutt

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 IP and demonstrating exceptional capabilities. Additionally, via the synergistic application of technologies unique to ORNL in advanced processing and characterization, we will control the stabilization and carbonization of lignin to tailor the electrochemical performance of the anode material. A prototypical lignin carbon fiber (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

A key barrier to widespread adoption of electric vehicles is the limited range of currently available models. Overcoming this barrier will require non-incremental improvements in the specific energies and energy densities of battery packs without increasing cost. This LDRD study addresses this problem by demonstrating a novel approach to energy storage that combines low-cost materials and scalable manufacturing methods to yield high-performance electrodes. Lignin is key to this concept; it is the second most abundant naturally occurring biopolymer and on average comprises 18–35% of wood by weight. This low-cost, biomass-derived material was selected as an alternative precursor for the production of free-standing carbon fiber anodes for use in lithium-ion batteries. We report the direct manufacturing of high-capacity carbon/silicon-based composite fiber electrodes that are produced via a flexible low-cost melt processing route to yield low-cost stable silicon particles embedded in electrochemically active and electronically conductive carbon fiber derived from lignin precursor material. In response to DOE's EV everywhere initiative and general goals, we focus this LDRD on a cost-centric approach to battery manufacturing by demonstrating a new technology designed to be compatible with well-established industrial-scale manufacturing methods using only low-cost materials.

Results and Accomplishments

We report the synthesis, processing, and performance of a low-cost monolithic battery electrode produced entirely of natural and renewable resources. This anode material exhibits tunable electrochemical performance suitable for both high,power and high-energy applications. We developed a synthesis method that directly results in electrically interconnected three-dimensional architectures where the carbon framework functions as current collector and lithium insertion material, eliminating the extra mass and expense of inactive materials in conventional designs. Fibrous carbon electrode materials were produced from solvent-extracted lignin using scalable melt processing technology and thermal conversion methods. The resulting free-standing electrodes exhibited electrochemical performance comparable to commercial carbon-based anodes at a fraction of the materials and processing costs. Compositional and electrochemical characterization shows that carbonized lignin has a disordered nano-crystalline microstructure. The carbonized mats cycle reversibly in conventional aprotic organic electrolytes with

coulombic efficiencies of over 99.9%. Moreover, lignin carbon fibers carbonized at 2000°C can cycle reversibly in 1 M $LiPF_6$ in propylene carbonate. We used energy-efficient melt-processing techniques to fabricate a next-generation Si+C architecture using low-cost, industrially scalable materials and process technologies. The combination of high capacity with enhanced electrochemical and chemical stability was achieved by embedding micron-scale silicon particles in binder-free LCF to form composites that are made entirely of active materials having at least semi-coherent grain boundaries, from which three-dimensional monolithic electrode architectures can be made. The precursor for the carbon fiber is lignin. The material is melt-spun, resulting in a very low production cost. Battery tests show a capacity in excess of 2000 mAh/g for 20 cycles and 500 mAh/g for 50 cycles. The Coulomb efficiency of these anodes has been measured to be in excess of 99.5%.

Information Shared

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High Capacity Monolithic Composite Si/Carbon Fiber Electrode Architectures, 2013

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 Energy Research Scientific Computing Center (NERSC), 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 to improve 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.

Results and Accomplishments

1. Neutron scattering measurements:

We have performed measurements of phonons in single-crystalline samples of thermoelectric materials FeSi doped with heavy impurities (Ir, Os), SnTe, and Ge-doped PbTe using both the HB3 and CTAX triple-axis spectrometers at the High Flux Isotope Reactors (HFIR) (IPTS-6448, IPTS-6470) and on the Cold Neutron Chopper (CNCS) and Angular-Range Chopper (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 in SnTe and doped PbTe 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.

In addition, a bcc niobium single-crystal was measured on ARCS in order to obtain a calibration dataset for our modeling methods. The niobium dataset is of very 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 FeSi, SnTe, PbTe, and bcc niobium. As part of this, we did benchmark calculations of several different exchange-correlation functionals. We find the best results with the standard local density approximation. In SnTe, 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 – TO 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 have been performed for both SnTe and PbTe, and the anharmonic components of the interatomic potentials were extracted to calculate the phonon scattering rates (linewidths), as well as the phonon shifts.

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 the dynamical structure factor, 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 used the parallel-optimization package Dakota to optimize parameters in lattice dynamics models to best fit neutron scattering measurements.

The simulation codes developed in this LDRD enable a direct comparison between the calculated and measured four-dimensional S(Q,E), including the instrument resolution function. This tool greatly facilitates the interpretation of scattering intensities measured with time-of-flight neutron spectrometers at the Spallation Neutron Source.

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This LDRD project seeded a new effort to model phonon measurements in ferroelectric oxides, as part of the DOE-funded Center for Accelerating Materials Modeling of SNS data (CAMM).

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 the DOE Office of Basic Energy Science (BES) (either core programs or proposed Energy Storage hub), the Energy Storage Program of the DOE-Energy Efficiency and Renewable Energy (EERE) Office of Vehicle Technologies (OVT), Advanced Research Project Agency-Energy (ARPA-E), and Defense Advanced Research Projects Agency (DARPA).

Mission Relevance

The proposed research, and the strategic partnership with Prof. Braun of the University of Illinois-Urbana 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 OVT. 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 into this important emerging subtopic. In addition to DOE BES and EERE offices, we will be positioned well to approach the Department of Defense (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 an 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. Reversible multi-electron capacity in iron fluoride (FeF_3 and FeF_2) conversion compounds was demonstrated 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 FeF_2 composite electrodes, respectively, for the first few cycles. but the samples showed significant capacity fade and very high hysteresis (> 2V). The capacity retention and hysteresis were significantly improved by incorporating the FeF_3-MLG on a carbon fiber-based 3D architecture. This was 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 1V. 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 a parallel attempt, to facilitate ionic transport across the electrode length scale, we fabricated bicontinuous inverse opal 3D structures in collaboration with Prof. Paul Braun's group. These inverse opal templates are fabricated by etching nickel-deposited silica macrospheres (250–300 nm) followed by electropolishing. 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. To begin with, we tested this particular architecture with a conversion-based anode, Fe_2O_3. Nanoparticles were then electrodeposited on 3D inverse opal electrodes. The electrochemical test results showed much improved capacity retention and rate performance for Fe_2O_3 deposited inverse opals. In order to understand the charge transfer and diffusion mechanism of such conversion compounds, we carried out high-resolution electron microscopy studies on pristine and cycled FeF_3 and Fe_3O_4 electrodes to map various intermediate phases formed as a part of conversion reaction. Our results showed particle coarsening when FeF_3 electrodes are cycled. Towards controlling the molecular architecture, another part of the project was directed towards fluorinating iron oxides to oxyfluorides using a direct fluorination method. Electrode modeling and electrochemical transport simulation studies of conversion based compounds continue.

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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).

(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 Spallation Neutron Source (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 such agencies as 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, e.g., 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 develop a neutron-based biological membranes science program that will not only establish itself as a world-leading biomembranes center but also one that will attract some of the top external scientists as collaborators and users. In the past 30 months, the NBBI has attracted the following people:

- postdoctoral fellow Fred A. Heberle (PhD Cornell University),
- postdoctoral fellow Jianjun Pan (PhD Carnegie-Mellon University) – now professor of physics at the University of South Florida,
- postdoctoral fellow Jonathan Nickels (PhD University of Texas at Austin),
- graduate student Paul Drazba (University of Tennessee) – graduated with an MSc in physics, and
- staff scientist Robert F. Standaert (Energy and Environmental Sciences Directorate [EESD]).

Over that same period of time, NBBI has produced 22 research papers, some of which have been published in DOE-accepted high-impact factor journals (please see information shared). The papers by Heberle et al. (*J. Am. Chem. Soc*. **135,** 6853, 2013) and Marquardt et al. (*J. Am. Chem. Soc*. **135,** 7523, 2013) were highlighted by different American Chemical Society journals in their spotlight section.

At the Joint Institute for Neutron Sciences (JINS), the NBBI in collaboration with the University of Tennessee (M. Dadmun and T. Egami) is continuing to expand the physical characterization and sample preparation capabilities of the labs (A-110, B-107 and B-111). The labs have evolved to the point that external users are using them to prepare neutron-appropriate samples, and characterizing them prior to interrogation by neutrons. The suite of instruments includes differential and isothermal titration calorimetries; time-domain fluorescence; static and dynamic light scattering; Langmuir-Blodgett troughs; densitometry; GC-mass spectrometry; ultra-centrifugation; and zeta potential analyzer with particle sizer.

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06241

High-Energy Rechargeable Magnesium Batteries Based on Nanostructured Materials

S. Dai, 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 Project 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, electrochemical energy storage (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 the continuing interest in development of advanced batteries.

Results and Accomplishments

Good progress was made in the prior year toward the development of a safe magnesium electrolyte, alkoxide magnesium salts, for rechargeable magnesium ion batteries. The alkoxide magnesium salts can be prepared using a variety of alcohol functionalities. These alkoxide magnesium salts are non-pyrophoric and much safer to handle than the Grignard reagents. Three typical magnesium salts, *n*-BuOMgCl, *tert*-BuOMgCl, and $Me_3SiOMgCl$ were synthesized. The alkoxide-based magnesium salts displayed high solubility (up to 2.0 M) in tetrahydrofuran (THF). A maximum ionic conductivity of 1.20 mS/cm was achieved at a salt concentration of 1.2 M. With the addition of $AlCl_3$ the ionic conductivity of the resulting magnesium-aluminum salt is increased as compared to the magnesium salt alone. In addition, upon addition of $AlCl_3$ the electrochemical window of the complexes was also improved. Reversible magnesium deposition and stripping were all observed for the new magnesium-salts-based electrolytes, with and without the addition of $AlCl_3$. Single crystals of *n*-BuOMgCl were grown from the THF solution of $(n\text{-BuOMgCl})_6/AlCl_3$. It is the first time to identify active three coordinated magnesium centers, with a molecular formula of $[Mg_3Cl_3(OC_4H_9)_2\,(THF)_6]^+[(THF)MgCl_3]^-$, as the active species.

In addition to developing a safe electrolyte, Chevrel-phase Mo_6S_8 was also synthesized as a magnesium cathode due to its fast magnesium intercalation/de-intercalation kinetics. The Mo_6S_8 electrode exhibits a reversible discharge capacity of 100 and 130 mAh/g at 20 and 50°C, respectively, with no capacity loss after 50 cycles, indicating that the alkoxide-based magnesium electrolytes can be successfully used in rechargeable magnesium batteries. Furthermore, these new electrolytes also show very good rate performance at 20°C and 50°C. For example, the specific discharge capacity of the cell is as high as 75 and 113 mAh/g under 0.5 C, 56 and 94 mAh/g under 2C at 20°C and 50°C, respectively.

Information Shared

A US patent application entitled "Alkoxide-based magnesium electrolyte compositions for magnesium batteries," filed August 26, 2013, Application No. 13/974,566.

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 second year, research activities were focused on 1) the development of friendly and smart graphical user interfaces for real-time gaze tracking on dual medical-grade monitors and for medical case annotation, 2) development of intelligent algorithms for fusing gaze data and image content to predict the perceptual and cognitive behavior of radiologists viewing medical images, 3) development of individual and group-based predictive models of human error, and 4) dissemination of findings via journal publication and conference proceedings papers. We performed several large-scale IRB-approved studies with 6–11 human observers and 40–100 medical cases to study the stability of our findings across settings (ORNL, University of Tennessee Medical Center, University of Arizona Medical Center), human observers of variable experience levels (novices, radiology residents, experienced radiologists), and medical tasks (lesion detection vs. lesion characterization).

The results of those experiments confirmed that 1) gaze data analytics can capture realiably the visual search pattern, 2) computer vision analytics when combined with gaze analytics can capture cognitive behavior and predict human error, and 3) radiologists of similar expertise *have diverse perceptual and cognitive patterns* when performing medical image interpretation.

The work performed on this project has resulted in four invention disclosures, one 4-year grant application to the National Institutes of Health pending revision ("Human-CAD Collaborative Decision Support in Radiology via Eye-Tracking Analytics," PI: Tourassi), and one CTSA-GHUCCTS-pilot project application pending review ("CAD Support for Optimal Workflow in Radiology", Project Co-PIs: Tourassi and Ratwani). Also, four invention disclosures have resulted from this work: 1) Ref#: 952, with S. Xu and H.-J. Yoon, A Novel Graphical High-Efficacy Modeling of Human Perceptual Similarity Opinions [Elected for patent filing], 2) Ref#: 953, Predicting Diagnostic Error from Visual Gaze Characteristics, 3) Ref#: 954, with S. Xu, Cyber-informatics to Study the Link Between Migration and Environmental Cancer Risk, 4) Ref#: 1156, with S. Xu and H.-J. Yoon, A Cost-Effective, Case-Control Study on the Association between Breast Cancer and Pregnancy through Web Mining.

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06271

New Capabilities for Neutron-Based Biomembrane Research at ORNL

R.F. Standaert, 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 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. Specifically, 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 Basic Energy Sciences (BES) and the Office of Biological and Environmental Research (BER). For BES, it will greatly enhance the capabilities of the SNS user program, and is also 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. This project 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.

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

The broad goal of the project is to develop new capabilities for neutron-based biomembranes research, which involves two main technical thrusts, namely, isotopic labeling and model systems. On both of these fronts, substantial progress has been made, resulting in high-impact publications, advanced model systems that are being deployed in the neutron-scattering user program, and a new approach to studying membrane structure with neutrons that provides the first probe-free means of characterizing membrane domains, or rafts.

Neutrons are keenly sensitive to the difference between normal hydrogen (H, protium) and its heavy isotope (D, deuterium), as reflected in the very different scattering lengths of these two isotopes. To get the most sensitivity and information from scattering experiments, molecules highly enriched in deuterium are required. In the past year, we have introduced several new deuterated molecules for membranes research, including 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) with perdeuterated oleoyl chains and deuterated amyloid beta 1–42 peptide ($A\beta_{1\text{-}42}$).

We have exploited H/D contrast successfully to detect the formation of nanoscopic, phase-separated domains in lipid bilayer vesicles, and have found that the domain size relates to the thickness mismatch between more- and less-ordered phases. Subsequently, we exploited this new method to show that chemically disparate types of phospholipids act via physically related mechanisms to induce domain formation and regulate domain size.

Finally, we have implemented a planar membrane model system, employing lipid bilayers supported on a polyelectrolyte multilayer, for use in neutron liquid reflectometry. Substantial improvements to literature procedures for preparing these systems and analyzing reflectivity data have been made, and studies on the interaction of planar model membranes with medically relevant peptides have been initiated.

Information Shared

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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 the 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

We have developed several solutions to overcome memory limitation when 3D cubic Bspline, comprising the most computationally efficient and scalable representations, is used for one-body orbitals: i) single-precision SIMD specializations; ii) multi-grid methods to partition the simulation cells; and iiii) a PGAS solution to distribute large 3D tricubic B-spline tables across multiple shared memory domains. The data caching method maximizes the overlap of computations and data movement. These allow us to apply

QMC to large-scale condensed matter systems without compromising accuracy and computational efficiency and without introducing basis biases. We have developed an integrated suite of tools to set up, manage, submit, and analyze large collections of calculations involving many dependencies. This suite minimizes the need for human intervention and the time-to-solution, facilitating high-throughput QMC calculations. Finally, new parallel I/O using ADIOS library was developed to support efficient checkpointing at the scale of Titan and fine-grained measurement of many-body properties beyond the total energies. These new capabilities are fully implemented in QMCPACK and have facilitated QMC studies by the Materials Theory group at ORNL and the QMC network supported by the DOE Office of Basic Energy Sciences (BES) predictive theory and modeling program under Materials Genome Initiatives.

We have completed the study of adsorption and diffusion of atomic lithium in graphite and compared the results with density functional theory calculations that include van der Waals interactions. We find that the self-consistent van der Waals functional to be more accurate than other methods and identified the inadequacy of empirical approaches in capturing the charge transfer that is essential in describing the energetics and kinetics of lithium in graphite.

Information Shared

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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 overarching 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. To address this goal, we will focus on two specific objectives. First, can we affect the overpotential for CO_2 reduction catalysis utilizing simple buffers in an aqueous environment? 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 great excess, will provide pseudo-bimolecular reaction conditions. This will allow us to not only simplify this complex problem but also gain 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. Second, from the guiding principles ascertained in the first objective, 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. Furthermore, the goals outlined above fall in line with the DOE's mission and strategic goals of providing energy security in a reliable, clean, and affordable manner.

Mission Relevance

The goals outlined above fall in line with the DOE's mission and strategic goals of providing energy security in a reliable, clean, and affordable manner. The proposed investigations into utilizing CO_2 for fuel generation will impact many areas relevant to the DOE's mission, and successful completion of the outlined goals could have a great impact on fuel generation (energy resources) from waste feedstocks (environmental quality), an area of interest to Basic Energy Sciences and Energy Efficiency and Renewable Energy.

Results and Accomplishments

Great strides have been made in the synthesis of materials and spectroscopic characterization of those materials to meet the goals set at the onset. The intended initial target complex was Re(bpy-$(SO_3H)_2$)$(CO)_3$Cl for homogeneous investigations in an aqueous environment. In addition, starting materials to graft a similar rhenium-based catalyst onto the interior surfaces of mesoporous materials for heterogeneous investigations have been prepared. Copper-catalyzed azide-alkyne cycloaddition was chosen as the preparative method to graft rhenium polypyridyl catalysts to the surface of SBA-15. Solid-state and solution-phase NMR techniques have been used to characterize the azide-modified SBA-15 and alkynyl bipyridine, respectively. In addition, nitrogen adsorption/desorption experiments with subsequent analysis with Brunauer/Emmett/Teller (BET) theory have been utilized to characterize the pores in the various modified SBA-15 silicas.

Lastly, in addition to the internal ORNL collaborations that are developing both in the Chemical Sciences Division and at the Spallation Neutron Source (SNS), 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 the complementary skills of this research group to my own will enhance productivity towards the end goal.

Information Shared

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06361

Toward Scalable Algorithms for Kinetic Equations: A New Hybrid Approach to Capturing Multiscale Phenomena

C. Hauck

Project Description

The goal of this project is to design and implement a hybrid method for the efficient solution of multiscale kinetic equations. It involves an intelligent separation of the equations based on dynamical scales; a closure method for approximating functions using limited data; modern, low-memory, high-order discretization techniques; and implementation on GPUs. The resulting algorithms will be useful for a variety of application specialists, particularly in high-performance computing environments.

Mission Relevance

The Computer Science and Mathematics Division at Oak Ridge National Laboratory is committed to building computational kinetic theory into a signature capability of the Laboratory. Kinetic theory plays a fundamental role in many areas of mathematical physics. Kinetic models are mesoscopic: on one hand, they provide a detailed and accurate description of particle-based systems in regimes where traditional fluid dynamic models are either invalid or simply not available. On the other hand, they can incorporate important features from a molecular- or quantum-level description that cannot be modeled directly because of the prohibitive computational cost. Consequently, kinetic theory is an indispensable tool in the mathematical description of gas dynamics, plasma physics, multiphase flow, and radiative transport—all keys components of current and next-generation energy generation systems. Moreover, in recent years, kinetic theory has emerged as an important analytical tool in other applications of interest to the Department of Energy and Department of Defense, including traffic and network models, computational chemistry, and self-organization of complex systems.

Results and Accomplishments

Our work in FY 2013 includes the following technical accomplishments.

1. New closure methods have been developed which act as a communication layer between equations on different scales.

2. Low-memory spatial discretizations have been designed that capture important asymptotic limits, but with a significant decrease in memory in comparison to current state-of-the-art methods.

3. High-order time integration methods, based on the technique of deferred correction, have been developed in order to increase temporal accuracy.

An implementation of the algorithm that leverages GPU processors for the simulation of fine scales has been completed.

Information Shared

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06362

Probing the Structure-Function Relationship of Protein Kinase A

W.T. Heller, P. Langan, L. Petridis

Project Description

Biological organisms interact with their environment at a cellular level through signaling pathways comprised of dynamic molecular machines, which themselves are comprised of multiple signaling enzymes. Although progress has been made in characterizing the structures of individual components of polyvalent signaling complexes, a major challenge remains to understand interactions between components and how they control function. The overarching goal of this proposal is to exploit neutron scattering capabilities becoming available at the High Flux Isotope Reactor (HFIR) and the Spallation Neutron Source (SNS), in combination with the development of advanced theory and simulation, to provide breakthrough advances in our understanding of the structure and dynamics of these fundamental biological systems by studying a prototypical signaling enzyme, protein kinase A (PKA), in polyvalent signaling complexes. The experimental and theoretical methods developed will be readily applicable to other large, complex systems from biology, bioenergy, and biogeochemistry and will drive the development of technologies that will be included in a BioTechnology Research Center (BTRC) proposal that is being prepared for joint DOE and NIH funding.

Mission Relevance

The proposed work investigating the structure and dynamics of the protein kinase A signaling complexes aims to build models of the protein complexes that provide a full picture of the relationship between their structure and function. Large biological complexes are relevant to bioenergy, where enzymes, such as cellulases, and their complexes, such as the cellulosome, play important roles in the breakdown of biomass into fermentable sugars. The methods and tools developed during the study of protein kinase A will be applicable to the aforementioned systems from bioenergy. Structural biology of proteins and their complexes of key interest in bioremediation will also benefit from the proposed research. Further, structural biologists funded by the National Institutes of Health and the National Science Foundation who employ the neutron and x-ray scattering user facilities sponsored by the DOE will be able to apply the methods and tools developed during the project to their own research. The knowledge gained about the protein kinase A system will benefit the entire biological research community studying protein kinase A.

Scientific and Technical Accomplishments

During FY 2013, the project has made considerable progress. Small-angle neutron scattering (SANS) with contrast variation experiments on two PKA isoform holoenzymes in complex with calcineurin and AKAP79 protein was performed at SNS in March 2013. Analysis of the data indicates that additional modeling is worth pursuing. Several neutron scattering proposals were submitted for the call for proposals at SNS that were awarded time in the August–December cycle of SNS. A proposal submitted to the 2013 Office of Advanced Scientific Computing Research (ASCR) Leadership Computing Challenge call for proposals was awarded 4 million processor hours on the Hopper supercomputer of the National Energy Research Scientific Computing Center (NERSC) between May 7, 2013, and January 13, 2015. Extensive simulations of the PKA catalytic subunit (PKAc) have been performed to complement experiments being performed. Large quantities of hydrogenated PKAc were prepared for crystallography studies and a Neutron Spin Echo (NSE) experiment that was run at SNS in September 2013. Several PKAc complexes were crystallized and their structures solved by x-ray crystallography. Deuterium-labeled PKAc was produced for neutron scattering and crystallography experiments. A jointly DOE-BER/NIH funded Biomedical Neutron Technology Research Center (BNTRC) is being developed for neutron scattering for

structural biology. The Frontiers in Neutron Structural Biology workshop was held at ORNL April 16–18, 2013, to build community support. Susan Taylor, an external member of the project team, participated. Professor Tongye Shen of UT was given a University of Tennessee Joint Directed Research and Development (UT JDRD) award for his proposal "Coarse-Grained Modeling of the Conformational Dynamics of Signaling Protein Complex" to study the PKA system.

Information Shared

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06368

A Novel Uncertainty Quantification Paradigm for Enabling Massively Scalable Predictions of Complex Stochastic Simulations

C. Webster

Project Description

We propose a transformational methodology related to the efficient, accurate, and robust computational determination of statistical quantities of interest, that is, the information used by engineers and decision makers, that are determined from solutions of complex stochastic simulations. Our objective is to effect a transition from current stochastic polynomial approximation techniques, that lack the ability to easily harness powerful high-performance computing architectures, to a truly predictive science. That is, to develop an innovative approach for uncertainty quantification (UQ) that provides quantitative bounds on the applicability of extreme-scale calculations. This remains a fundamental difficulty in most applications that dominate the focus of the DOE mission. Guided by this grand challenge in UQ, we propose a rigorous mathematical procedure for exploiting multicore extreme parallelism by simultaneously propagating numerous realizations of a multidimensional multi-resolution adaptive sparse grid stochastic collocation approach, through both the complex physics and the solver stack in a novel semi-intrusive fashion. This paradigm builds on existing progress in generic programming to selectively couple ensembles of the hierarchical decomposition while enabling advanced recycling and block solver techniques. This massively scalable UQ framework will be made available through the ORNL Toolkit TASMANIAN and will be demonstrated in a stochastic radiation transport calculation using the highly visible Denovo neutronics code.

Mission Relevance

A truly predictive science for most problems of scientific and national interest requires transformational technologies that explain how the uncertainties, ubiquitous in all modeling efforts, affect our predictions and understanding of complex phenomena. Examples include enhancement of reliability of smart energy grids, development of renewable energy technologies, vulnerability analysis of water and power supplies, understanding complex biological networks, climate change estimation, and design and licensing of current and future nuclear energy reactors. These application areas are of critical importance to a number of sponsored programs within the DOE Office of Science, namely Fusion Energy Science (FES), High-Energy Physics (HEP), Basic Energy Research (BER), Basic Energy Sciences (BES) and Nuclear Physics (NP). Moreover, the Applied Mathematics Program at the Office of Advanced Scientific Computing Research (ASCR) is extremely interested in developing the foundations of scalable algorithms for

uncertainty quantification, and the broad scope of the methodologies proposed in this effort directly impact several areas of ASCR, including multi-scale mathematics, advanced UQ, scalable programming models, and extreme-scale solvers.

Results and Accomplishments

Our work in FY 2013 on reducing the computational burden required us to perform rigorous uncertainty quantification (UQ), through the development of novel simultaneous propagation strategies, constructed from an adaptive hierarchical stochastic collocation (SC) method, that exploit greater levels of parallelism provided by emerging many-core architectures. We have completed all the tasks we set out in the proposal, for the first year, and our scientific/technical represent major advancements in mathematical algorithms and analysis, as well as the implementation of new approaches for performing UQ at the extreme scale. In particular, we have develop the following innovative capabilities for extreme-scale UQ.

1. A C++ template-based generic programming approach, that utilizes openMP, for evaluating samples in parallel through a multi-level embedded propagation scheme whereby collections of samples are executed asynchronously and samples within each collection are propagated simultaneously at the node and processor core levels.

2. An advanced multi-level method for alleviating the complexity and accelerating the solutions of both deterministic and stochastic solvers.

3. An implementation of the before-mentioned algorithms in the TASMANIAN, and an initial demonstration through the highly visible radiation transport code Denovo.

This work has dramatically increased our UQ capabilities at ORNL and enabled us to lead a multi-institutional proposal entitled A Mathematical Environment for Quantifying Uncertainty: Integrated aNd Optimized at the eXtreme-scale (EQUINOX). We have also submitted one mathematics paper and are working towards submitting two more computational science papers, related to this effort.

Information Shared

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06380

A Comprehensive Theoretical/Numerical Tool for Electron Transport in Mesoscale Heterostructures

X. Zhang, M. Yoon, A.-P. Li, D. Nicholson, S.T. Pantelides

Project Description

Modeling electron transport in electronic devices using macroscopic equations is a mature industry that generates billions of dollars per year. First-principles, quantum-mechanical modeling of atomic-scale transport has seen significant progress over the past decade. We identify a gap between these two length scales – the mesoscale, where effects described by macroscopic equations are dominant only in nanoscale devices because they depend on some power of a characteristic device length. One such phenomenon is *space charge limited currents* (SCLCs), a central feature of energy-related devices such as light-emitting diodes and organic solar cells, which entail carrier injection. A critical voltage for the onset of injection is proportional to the square of the device length. State-of-the-art commercial modeling tools do not treat such phenomena adequately. In particular, the available theory of SCLCs in the presence of traps either neglects or treats phenomenologically key physical effects such as the interplay between dopants and traps, the Frenkel effect, inter-trap tunneling (relevant at high trap concentrations), etc. Our goal is to develop a set of comprehensive simulation tools for modeling mesoscopic electronic devices that exhibit a strong SCLC effect, in particular quasi-zero-, one-, or two-dimensional structures, based on rigorous physics formulations of the pertinent problems. Such a toolset will provide a flexible foundation to build future energy research programs, for example, battery modeling where charge carriers are ions, and is likely to attract industry interest.

Mission Relevance

Most modern devices, in photovoltaics, batteries, light-emitting diodes, spintronics, etc., employ a combination of semiconductors, insulators, and metals. An especially important challenge for new device applications is the development of renewable energy technologies. High performance in such technologies is often achieved through the design of sophisticated device structures with multiple materials. The limiting factors of performance are usually materials properties related to charge transport. The evolution of technology computer-aided design (TCAD), which combines process, device, and circuit simulation and modeling tools, started with modeling bipolar junction transistors. It has since evolved into a multi-billion dollar industry and has become the foundation of the semiconductor technology. A complete physical model that correctly accounts for all aspects of SCLC phenomena will be an important modeling tool for the emerging nanostructured energy-device industry.

Results and Accomplishments

We have developed the methodology and pertinent computer codes that carry out parameter-free, quantum-mechanical calculations of inelastic scattering of electrons by defects that undergo either depassivation or reconfiguration, resulting in modified defects that cause device degradation. Using both the Born-Oppenheimer or adiabatic approximation (BOA) and the Frank-Condon approximation (FCA), we wrote the transition probability, P, as a product $P = AF$, where A describes the instantaneous electronic excitation in the initial configuration and F describes the phonons that must be emitted when the lattice relaxes, known as the line shape function. For the calculation of the electronic matrix elements we adopted a procedure similar to the "Förster transition" that is used to describe exciton and electron transfer in molecules, and we used the most suitable scheme of the Projector Augmented Wave (PAW) method, which yields the true wave functions while still employing a plane-wave basis. The phonon part of the matrix element can be calculated by employing a Monte Carlo method. We have already coded the

pertinent electronic matrix elements. We are currently testing calculations of cross sections for electron capture by a vacancy in silicon, which can be viewed as a special case of inelastic scattering where the final electron state is a bound state at the defect.

06404

Hybridizing HPC: Modern Cray Architectures for Big Data Problems

J. Horey, M. Shankar, S.R. Sukumar, G.M. Shipman, J.J. Nutaro, R. Gunasekaran

Project Description

We propose to design, build, and evaluate a novel architecture for the storage and analysis of massive datasets using high-performance computing systems from Cray. These massive datasets and the big data problems that are associated with such datasets require the use of large computing facilities (i.e., clusters, parallel storage, etc.). By targeting leadership-class infrastructure, our new big data architecture will be a performant (latency and bandwidth) and scale better than existing state-of-the-art systems. To meet this expectation, we will rewrite and optimize existing big data tools, including Apache Hadoop and Cassandra, to operate over a set of Cray hardware. This hardware will consist of both a Cray XMT-derived machine (the uRiKa platform from YarcData) and existing Cray XT5 clusters (Chester, Arthur) connected to ORNL's Spider file system. To facilitate development, we will engage and collaborate with Cray engineers on this effort. Throughout this process, we will rigorously evaluate our implementation using known benchmarks and real-world analysis derived from our current big data efforts in the Computational Sciences and Engineering Division (CSED).

Mission Relevance

The Department of Energy's (DOE's) Office of Advanced Scientific Computing Research (ASCR) concerns itself with the application of high-performance computing as applied to critical national scientific problems. Although historically focused on modeling and simulation, DOE has recently recognized the need for advanced data analytics. This LDRD proposed to create the necessary tools to conduct such the analytics over a wide variety of scientific and mission-critical datasets. We are taking the first steps to designing, implementing, and benchmarking these tools. Doing so will provide DOE and ORNL with the following benefits.

1. Development of highly capable data analytic routines and software that can be applied to a variety of domains executing in the Oak Ridge Leadership Computing Facility (OLCF) environment.
2. Publications of unique capabilities in leading conferences and journals.
3. Attracting new sponsors that require the use of these unique analytic capabilities.

Results and Accomplishments

For the period ending FY 2013 (and previously FY 2012), our team was able to procure the YarcData uRiKa platform; begin developing basic acceptance tests; organize regular conferences with ORNL's National Center for Computational Sciences (NCCS); and, YarcData/Cray to ensure the platform was fully usable. We have also developed some preliminary software that executes common big data software (i.e., Apache Hadoop) over ORNL's leadership-class computing clusters.

Information Shared

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06408

Hardware/Software Resilience Co-Design Tools for Extreme-scale High-Performance Computing

C. Engelmann, T. Naughton

Project Description

With the deployment of the 10–20 PFlop/s Titan supercomputer and the exascale roadmap targeting 100, 250, and eventually 1,000 PFlop/s, ORNL is at the forefront of scientific capability computing. Resilience, that is, providing efficiency and correctness in the presence of faults, is one of the most important exascale computer science challenges. Several high-performance computing (HPC) resilience technologies have been developed. However, there are currently no tools, methods, and metrics to compare them and to identify the cost/benefit trade-off between the key system design factors: performance, resilience, and power consumption. This proposal focuses on developing an ORNL-branded HPC resilience co-design toolkit with definitions, metrics, and methods to evaluate the cost/benefit trade-off of resilience solutions, identify hardware/software resilience properties, and coordinate interfaces/responsibilities of individual hardware/software components. The primary goal of this project is to position ORNL as DOE's lead institution on HPC resilience co-design, providing the tools and data needed by HPC vendors to decide on future architectures and by DOE to identify research gaps. The secondary goals are to enable direct feedback to ORNL's HPC vendors on emerging resilience threats and to permit ORNL to target corresponding funding on identified research gaps.

Mission Relevance

With the deployment of the 10–20 PFlop/s Titan supercomputer and the exascale roadmap targeting 100, 250, and eventually 1,000 PFlop/s, DOE's Office of Advanced Scientific Computing Research (OASCR) and ORNL are at the forefront of scientific capability computing. Resilience is one of the most important exascale computer science research challenges. Considering the timeline for exascale by 2020, co-design tools for resilience are crucial. The proposed work focuses on developing tools, methods, and metrics to aid HPC hardware/software co-design efforts in mitigating resilience risks for achieving exascale computing capabilities. This proposal benefits OASCR's exascale computer science research program directly by developing expertise and prototype tools for resilience, performance, and power consumption co-design of future-generation supercomputers. This advances DOE's science mission by ensuring correctness and efficiency of these systems.

Results and Accomplishments

The accomplishments are on track with the original milestone schedule. At its core, this work focuses on extending ORNL's Extreme-scale Simulator (xSim), an HPC performance investigation toolkit, with resilience simulation features. To this end, we have developed (1) a simulated MPI process failure injection capability, (2) a simulated MPI process failure detection mechanism with parameterized detection delays, (3) a simulated MPI job failure injection feature, (4) a simulated MPI job failure detection mechanism with parameterized detection delays, (5) a simulated MPI job restart technique, (6) an initial simulated file system interface, (7) a simulated MPI user-level failure mitigation capability, (8) the first component of a simulated soft error injection facility, and (9) an automatic benchmark generation framework. The proposal, "MCREX: Using Monte Carlo Algorithms to Achieve Resiliency and Performance at Scale for Linear and Non-linear Solver Applications," led by Thomas Evans from ORNL was funded under the Resilient Extreme-Scale Solvers program by DOE's OASCR with $300K/year in total for 3 years. The proposal, "Hobbes: OS and Runtime Support for Application Composition," led by Ron Brightwell from Sandia National Laboratories was proposed to OASCR's Exascale Operating and Runtime Systems program with $3,600K/year in total for 3 years. Other program development activities include service on the DOE Technical Council on HPC Resilience and providing input for an expected call for proposals in HPC resilience from OASCR.

Information Shared

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06500

High-Flux Nanoporous Graphene Membranes for the Desalination of Water

S.M. Mahurin, I. Vlassiouk, S. Dai

Project Description

The continued security and economic development of the United States is critically dependent on a sustainable source of clean water because of its role in energy production, industrial growth, and

agriculture. However, a vast majority of the global water supply is either seawater or brackish water, creating significant challenges that will only be exacerbated as demand for freshwater grows. Though relatively mature desalination techniques currently exist, practical and more energy efficient methods are critically needed to meet the demand for freshwater. We propose the development and characterization of an ultrathin graphene membrane for water desalination with enhanced water flux, high selectivity, and improved energy efficiency. This objective encompasses three primary questions. What is role of pore size on the water transport properties through the nanoporous graphene? Can we incorporate functionality into the pore edges to enhance H_2O transport and salt rejection? Can we tune the molecular transport properties by the addition of an applied potential? To address these questions, large area, nanoporous graphene sheets will be synthesized via chemical vapor deposition followed by ion bombardment and selective etching to controllably create the pores. The effect of pore size, added hydrophilic functional groups, and an applied electric potential on the water flux and salt rejection rate will be examined to achieve highly permeable, highly selective desalination membranes. Successful completion of the work will find widespread use in water desalination for industrial and energy generation applications and in other separations applications.

Mission Relevance

The availability of pure water is critical to human life and is further inextricably linked to the secure and sustainable generation of energy since energy production requires a reliable source of water. As such, a source of water is relevant to the mission of the Department of Energy (DOE). More specifically, a recent DOE Office of Basic Energy Sciences (BES) report entitled *Basic Research Needs for Carbon Capture: Beyond 2020* specifically mentions the link between membranes for carbon capture and water desalination. Thus, graphene membranes developed for water desalination will also be of interest to DOE BES for related separations applications. A current call from the Office of Naval Research includes research for advanced materials for water desalination (ORNBAA14-001). We also anticipate interest from the DOE Office of Energy Efficiency and Renewable Energy. The Department of Interior has a program entitled Water Desalination Research and Development Program that is a potential source of follow-on funding.

Results and Accomplishments

We have grown large-area, single-layer graphene sheets by chemical vapor deposition and successfully generated pores in the graphene using both ion bombardment and oxygen plasma etching. The presence of pores in the graphene was verified by both Raman spectroscopy and gas transport measurements. Using graphene on a silicon wafer with a micron-sized hole, we determined that the pristine, freestanding sheet could withstand up to 2 atm of pressure without breaking and there was no gas transport confirming intact graphene. Gas transport was also measured through the porous graphene with values that were in reasonable agreement with reported theoretical values. Further, we have measured both salt transport and water transport through the porous graphene positioned on the silicon wafer with a 5 μm hole. Ion transport was measured using an electric field driving force in a standard transistor geometry, and no salt transport was observed through the porous graphene sheet, indicating that the membrane could completely reject salt ions. Additionally, we have measured water transport through both pristine and porous graphene. The pristine graphene showed no water transport, while the porous graphene showed transport of approximately 3.5 mL H_2O per day. These results are highly promising. Finally, we utilized a porous carbon membrane to initiate our investigation of the effect of an applied potential on the transport of salt. We discovered that a small applied potential could prevent the transport of salt ions through the porous carbon membrane (pore size of 8 nm and thickness of 25 μm), and removal of the potential allowed salt ions to diffuse through the membrane. A manuscript detailing these results has been submitted to *Nature Nanotechnology*.

Information Shared

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06502

Nondestructive Evaluation on Hydrided Zirconium Cladding by In Situ Neutron Scattering and Tomography of Hydrogen

Y. Yan, S. Qian, K. Littrell, G. Bell

Project Description

The goal for this project is to develop a nondestructive in situ neutron scattering method to study the uptake of hydrogen and the formation and distribution of hydride precipitates in commercial light water reactor (LWR) zirconium alloy fuel cladding while charging the clad with hydrogen. This will provide a nondestructive method to measure the total hydrogen content and hydride distribution in used nuclear fuel cladding. Samples of fresh zirconium alloy (Zircaloy-4) clad used in commercial LWRs will be exposed to hydrogen to produce hydrided test articles. Neutron scattering will be used to study the structure and composition of the hydrided samples and determine the amount and distribution of hydrogen in the samples. Following the nondestructive evaluation, the samples will be destructively analyzed using standard techniques to examine the microstructure and hydride morphology for direct comparison with the results from neutron scattering. An in situ neutron scattering and tomography setup will then be developed in a neutron scattering beam line to study the hydrogen distribution change when charging the clad. The final goal is to develop neutron scattering beam line capabilities to perform nondestructive evaluation on irradiated Zircaloy-4 cladding in the future.

Mission Relevance

The recent delay by DOE and the US Nuclear Regulatory Commission (NRC) in licensing a geologic repository at Yucca Mountain Nevada will likely result in used nuclear fuel being stored at independent spent fuel storage installation sites for a very long time after reactor discharge. Therefore the NRC must reevaluate its basis for confidence in the US government's ability to safely store used nuclear fuel for an indefinite period of time, which could have direct implications for the continued operation of all US nuclear power plants. For mechanical properties testing of used fuel, it is highly desirable to select samples having well understood hydrogen content before conducting the experimental work. This proposed project is focused on developing in situ neutron scattering and tomography techniques for nondestructive evaluation of hydrided zirconium cladding, which will enable better selection of samples having the prescribed hydride content for regulatory performance testing.

Results and Accomplishments

1) Hydrided pure zirconium and Zircaloy cladding samples were successfully produced by a gaseous method under stress-free conditions with a well-controlled hydrogen concentration (±25 ppm to the target hydrogen concentration), ranging from 70 to 1100 wppm.

2) Metallographic examinations were performed on hydrided Zircaloy-4 samples, which showed uniform distribution of circumferential hydrides across the cladding wall. It was observed that the hydride density increases as the hydrogen concentration in the sample increases.

3) The hydrogen content of the hydrided specimens was directly measured using the vacuum hot extraction method, by which the samples with desired hydrogen concentration were selected for the small-angle neutron scattering study in the High Flux Isotope Reactor (HFIR).

4) Nondestructive evaluation of hydrided zirconium cladding has been successfully achieved by neutron scattering at HFIR. Hydrogen concentration was obtained by scaling the number with a factor, which is determined by calibration process with VHE method. This scale factor can be used for future tests with unknown hydrogen concentration samples, thus providing a nondestructive method for absolute hydrogen concentration determination.

5) Evaluation of neutron beam attenuation was performed through lead blocks. This test provides information that will guide fabrication of a lead chamber for shielding irradiated cladding to be used in neutron beam lines in the future.

6) There are several growing programmatic opportunities in the areas of hydrogen charging and embrittlement study. The principal investigator was invited to attend the 2012 Electric Power Research Institute Used Fuel-High Level Waste Extended Storage Collaboration Program Meeting and the 2013 International High-Level Radioactive Waste Management Conference.

Information Shared

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06521

Synthesis and Characterization of Novel Two-Dimensional Mesoscale Organic Nanomembranes

K. Xiao, K. Hong, M. Yoon, Y. Ma, J. Browning, D. Geohegan

Project Description

The overarching goal of this proposal is to chemically synthesize and characterize the unique properties of novel two-dimensional (2D) mesoscale semiconducting organic nanomembranes (ONMs), which are just now emerging worldwide as rivals to graphene. Like graphene, the ultrathin 2D morphology of single-crystalline ONMs offers tremendous opportunities in basic science and technology, yet these nanomembranes can be *chemically synthesized*, opening the door to a wider range of applications for their unusual electronic, thermoelectric, optoelectronic, photonic, and magnetic behaviors, unavailable with bulk and nanoscale materials. In this project, we propose to develop novel methods to synthesize 2D ONMs such as graphdiyne and polymeric metal-phthalocyanines with precise dimensions, building upon our established strength in the synthesis of graphene, organic nanowires, and inorganic NMs. Our

approach to understand and develop unique 2D ONMs integrates team expertise in the molecular design, modeling, and chemical synthesis of 2D organic mesoscale materials, and the development of optoelectronic and neutron scattering characterization techniques. The specific aims of the proposed research will address this challenging issue by coordinating our studies in the following areas: (1) the design and controlled synthesis of 2D ONMs using chemical approaches; (2) characterization of 2D ONMs at multi-length and timescales through STEM, neutron/x-ray scattering, and ultrafast laser spectroscopy; (3) understanding the collective (optoelectronic, electronic, and magnetic) behaviors across a wide range of 2D ONMs lengths. The success of this project will position ORNL's leadership for the forthcoming BES initiatives in meso-scale science.

Mission Relevance

The intense interest in graphene worldwide has been generated by its incredible potential to transform the electronics and nanotechnology landscape, with vast economic potential. Chemically synthesizable analogues of graphene, such as graphdiyne and polymeric organic nanomembranes, are just now emerging and have great processing advantages, and ORNL is uniquely poised to take advantage of the opportunity to capitalize on the organic synthesis, neutron scattering, nanoscience, electron microscopy, and computing strengths required to take a lead in what is sure to become a highly competitive field in the near future. This proposal is to integrate the molecular design, chemical synthesis, and multiscale characterization of 2D organic nanomembranes with guidance from theoretical modeling and simulation to understand the collective (optoelectronic, electronic and magnetic) behaviors of 2D ONMs. The information obtained in this project will help the design and synthesis of 2D mesoscale organic graphene analogues and surely initiate new programs in this emerging area to utilize the innumerable and multifunctional properties of these materials, such as optoelectronic, sensing, power generating.

Results and Accomplishments

The first year of this program we focused on the synthesis of two-dimensional organic nanomembranes.

We first studied the growth characteristics of CuPc monomer on graphene through the combined X-ray scattering and diffraction, STM in combination with first-principles calculations. The nucleation, orientation and packing of CuPc molecules in films on graphene show a fundamentally different behavior compared to the films grown on silicon substrate. The CuPc molecules in the first two layers nucleate as islands and finally form a continuous film by edge growth. The CuPc molecules formed a closely packed structure on graphene with a face-to-face columnar growth that maintained the face-on orientation throughout the growth process. We further observed that the CuPc molecules at high temperature are more preferentially grown on monolayer graphene than multilayer graphene, even at high coverage, because of charge transfer between them. Therefore, graphene is an effective template to confine the CuPc monomers in a face-on orientation for the synthesis of 2D CuPc polymer.

The CuPc polymeric 2D NMs were synthesized through template-guided metal-directed assembly method. The functional monomer tertracarbonitrile benzene (TCNB) with –CN side groups was coevaporated with copper at controlled stoichiometry on the substrate to form the polymer sheet. The effect of the stoichiometry, evaporation rate, and different substrates on the growth of polymeric CuPc was studied. We found that the substrate is important to confine the reaction in two dimensions. The polymeric CuPc forms a monodomain phase over the graphene, and the size of the CuPc polymer sheet is limited by the graphene grain size. Therefore, the atomically flat single-crystalline graphene surfaces can serve as templates to confine polymerization reactions epitaxially in 2D. The demonstrated synthesis approach is promising for controlling synthesis of organic 2D materials desired for emerging 2D opto-electronics and energy applications.

Information Shared

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06528

Advanced Modeling and Simulation to Support High-Performance Research Reactor Conversions to Low Enriched Uranium

G. Davidson, P. Jain, J. Peterson, D. Chandler, S. Johnson, T. Pandya, B. Mervin

Project Description

The Research and Test Reactors program has been working to convert research and test reactors that use highly enriched uranium (HEU) to low enriched uranium (LEU) as a means to reduce the availability of weapons-usable material. The program has converted all of the US domestic research reactors that can be successfully converted to LEU using existing qualified fuels. However, there are six high-performance research reactors (HPRRs) for which higher fuel densities are required to support conversion without loss of performance. The primary objective of this project is to demonstrate that advanced modeling and simulation can bring significant new capabilities to support the conversion of HPRRs to LEU, thereby accelerating reactor conversions while ensuring that performance and safety are maintained. An additional key outcome of the application to the High Flux Isotope Reactor (HFIR) is that Oak Ridge National Laboratory (ORNL) will have a much-improved capability for modeling HFIR that will support isotope production, materials irradiation, and upgrade analyses.

Mission Relevance

In the United States there are six HPRRs for which higher fuel densities are required to support conversion without loss of performance. Under the National Nuclear Security Administration Global Threat Reduction Initiative (GTRI), the Reduced Enrichment for Research and Test Reactors program has been working to convert research and test reactors that use HEU to LEU as a means to reduce the availability of weapons-usable material. The simulation approach currently used by the GTRI program for analysis of HFIR uses continuous energy (CE) Monte Carlo with homogenized materials in the fuel region and without automatic thermohydraulics coupling. Plate-resolved modeling is currently under investigation, but the current tools lack the ability to scale to leadership-class machines, requiring excessive run times. We propose to replace this set of tools with a single integrated code system capable of high-fidelity transport with no spatial homogenization on massively parallel architectures with integrated isotopic depletion and thermohydraulics coupling. This will result in improved modeling capabilities to support LEU conversion, isotope production, and other missions.

Results and Accomplishments

Our accomplishments this year include integration of the CE physics library SCEMPP into the Shift Monte Carlo code. Previously, Shift only supported limited multigroup physics but has now integrated a fully featured CE physics package. This package supports coupled neutron-photon collision physics. Shift also now supports both fixed-source and k-eigenvalue modes and has been validated against CE KENO and MCNP on several benchmark calculations with excellent results. Support for MCNP models has been

developed, as well as initial support for CAD geometry. A new parallel ray-tracer for hybrid methods has been implemented. Additionally, we redesigned the Shift tally system to support energy-binned, cell union, and reaction rate tallies, with an extensible polymorphic interface. Shift supports advanced hybrid methods and a fully featured implementation of the CADIS method, and an initial implementation of FW-CADIS has been completed.

A depletion package coupling ORIGEN to Shift has also been developed, enabling coupled transport-depletion calculations. Coupled transport-depletion simulations have been performed on pincells and two-dimensional pincell arrays and will be featured in an upcoming journal article. The depletion capability is currently being optimized and validated for analysis of HFIR.

Single plate-channel COMSOL models of both inner and outer HFIR fuel elements for thermohydraulic analysis have been designed and tested. Mesh refinement studies of the thermohydraulic models have been performed and compared to the legacy code SSHTC with excellent agreement. The models are being extended to multiple plates and channels. Efficiency and scalability studies of the various COMSOL solvers are also under way.

Together, these capabilities will enable high-fidelity, high-performance simulations of HFIR.

Information Shared

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B. T. Mervin, "Integration of ORIGEN Depletion Capabilities into Exnihilo (Rev. 1)," RNSD-TN-13-003 (2013).
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06552

Meso-scale Liquid Confinement Systems for Enhanced Bioseparations and Bioconversion Strategies

V. Urban, H. O'Neill, D. Hayes, P. Langan, S.V. Pingali

Project Description

The project builds new capabilities and captures world leadership for neutron scattering analysis of fluid meso-structures that take inspiration from the functionality of biological organelles. We will advance understanding of these complex architectures by studying related man-made systems: bicontinuous

microemulsions (BMEs). BMEs are less complex and not as highly organized as organelles, but they share important characteristics, such as high interface area, compartmentalization, and continuous channels for fluid transport. As such, BMEs have potential in many technological areas such as drug production and catalysis. Small-angle neutron scattering has a unique ability to probe these structures in situ, and in response to changes in relevant parameters, for example solute concentrations. This project will develop and supply experimental capabilities that allow refined studies of BMEs that are not currently available anywhere; it further focuses on carefully selected questions that will demonstrate advancement of our understanding of BMEs and by extension fluid membrane systems in general. Finally, our selection of membrane proteins incorporated into BMEs will focus on functionality, thus emulating nature's approach of meso-scale "factories." The project will deliver new neutron scattering capabilities, publications in high impact journals, data for future proposals, and interdisciplinary postdoctoral training.

Mission Relevance

This proposal aligns neutron scattering capabilities at SNS and HFIR with bioenergy missions at BioEnergy Science Center (BESC) and other bioenergy research centers such as the Photosynthetic Antenna Research Center (EFRC). The work will position ORNL to effectively compete in any growth opportunities in this area led by DOE. The new capabilities generated in this proposal will provide opportunities for neutron scattering research that are not available elsewhere and will therefore contribute to sustaining the international leadership of the ORNL neutron scattering facilities. Studies of integral membrane protein structure remain a grand challenge and have a high potential for attracting funding from NIH. Bicontinous systems may prove to be efficient bio-reactors for enzymatic production of drugs, with high interest to NIH. Future collaborations between ORNL and the University of Tennessee, Knoxville (UTK) researchers will train students in neutron scattering techniques and contribute to the sustained growth of the neutron user community at ORNL.

Results and Accomplishments

Scientific/Technical: We hired Dr. Ran Ye as a postdoctoral research associate in March of 2013 to support the effort of synthesis, characterization, and neutron scattering investigations of bicontinous microemulsion systems. We conceptualized and developed a four-port flow-cell optimized for small-angle neutron scattering studies and found an external vendor that has manufactured and delivered these sample cells to our custom design. Surfactant CK-2,13 has been synthesized with a small ethoxylate polar group. The membrane proteins/peptides bacteriorhodopsin and mellitin have been obtained. We successfully competed for neutron beam time and carried out small-angle scattering experiments on the CG-3 Bio-SANS instrument (Integrated Proposal Tracking System numbers: IPTS 9726 and IPTS 9445) in May and October of 2013. The results demonstrated that membrane proteins can influence synthetic surfactants in a bicontinuous microemulsion to adopt architectures that are commensurate with the lipid bilayer thickness that normally accommodates such proteins in their natural biological environment.
Program Development: The three-phase micoemulsion approach with bicontinous middle phase for studying membrane proteins is one important component in a proposed integrated approach of developing new sample environments and SANS techniques to provide new tools that further our understanding of biological structures. Implementation of these techniques has been included in a Biological Technology Research Center proposal that is being prepared for joint submission to NIH and DOE-BER.

Information Shared

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06565

Towards a Resilient and Scalable Infrastructure for Big Data

B.W. Settlemyer, M.J. Brim, D.A. Dillow, T.R. Jones, S. Oral, F. Wang

Project Description

The goal of this project is to research the techniques necessary to establish a path toward branding ORNL as the leader in hosting Big Data for simulation science and emerging cloud workloads. We propose the initial research required to design and evaluate the scalable object storage infrastructure issues present in any Big Data system – resiliency and performance of I/O at scale:

1. new asynchronous storage programming models and advanced storage scheduling schemes that improve scalability and performance, provide quality of service guarantees, and support both scientific analysis techniques and modern loosely coupled analysis codes;

2. new data location and replication schemes that ensure data access is mapped to devices that perform the target workloads with high performance while also duplicating important data to durable media; and

3. an evaluation of techniques for constructing hierarchical storage systems composed of multiple media types including magnetic disk, tape, and Flash and evaluating candidate architectures with diverse Big Data workloads.

Mission Relevance

The research supported by this LDRD has been successful in establishing the path toward ORNL's leadership in hosting Big Data for simulation science and cloud workloads. This research effort is squarely aimed at improving the software infrastructure used by ORNL's Compute and Data Environment for Science (CADES). Our efforts are focused on improving I/O scalability, performance repeatability, and resiliency. We believe that this effort will lead to at least two specific improvements in the design of center-wide storage systems:

1. the ability to simultaneously support a mix of I/O jobs that have divergent I/O requirements (e.g., check-pointing and large data analysis), and

2. the infrastructure support to leverage emerging commercial data analysis techniques on data sets generated by open science applications.

Spider, the existing center-wide file system deployed at ORNL's National Center for Computational Sciences (NCCS), is not well suited to simultaneously service compute jobs that have diverse I/O requirements. In particular, analysis jobs that perform intensive read operations have the capability to generate substantial interference for large scientific simulations performing checkpoints (i.e., file writes). Essentially, parallel file systems are client driven, and thus clients must coordinate their access to avoid generating I/O interference. Our system allows clients to reserve time with a storage systems I/O

scheduler that eliminates interference, and thus allows I/O intensive jobs to run without generating the type of interference patterns that reduce overall storage medium throughput.

A second important artifact of this research is the opportunity to leverage the big-data techniques available in commercial data systems. Traditional HPC storage systems have focused on using enterprise hardware to achieve reliability and performance, which has resulted in much smaller scale storage systems than commercial storage infrastructure. Commercial storage systems typically integrate more disks than HPC storage systems and use replication to achieve both fault tolerance and performance. By providing support for intelligent data replication we can both improve storage system availability and accelerate data analysis jobs providing multiple copies of the data to improve locality and parallelism in data access.

Results and Accomplishments

Leveraging the QoS ideas developed in this research effort, we participated in a proposal for the DOE funding call Big Data-Aware Terabits Networking (LAB-13-883). The proposal, entitled "Technologies and Tools for Synthesis of Source-to-Sink High-Performance Flows," requested $350,000/year for 3 years to ORNL (total budget for all participants is $800,000/year). Nageswara Rao leads this proposal; however, significant portions of the storage QoS research ideas in the proposal were developed as part of this LDRD effort.

Our project has been invited to send a white paper to DOE Program Manager Lucy Nowell describing the challenges we have identified in simultaneously executing large-scale simulation/check-pointing jobs and big data analysis jobs. In particular, she indicated interest in learning more about the limitations of existing systems and how we could overcome these challenges going forward.

Additionally, a DOE Office of Advanced Scientific Computing Research program announcement for Big Data research is planned for this summer. We have prioritized the collection of pilot data for use in the preparation of a proposal to continue the development of our Scalable, On-demand Object Storage System.

Information Shared

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M. J. Brim, *Asynchronous Object Storage for Scientific and Commercial Big Data*, ORNL/TM-2013/372, Oak Ridge National Laboratory, Oak Ridge, TN, 2013.

F. Wang, *Ceph Parallel File System Evaluation Report*, ORNL/TM-2013/151, Oak Ridge National Laboratory, Oak Ridge, TN, 2013.

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 can also 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 are 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 Egami, Chang-Smith, Nagler, and others, Broholm developed and taught a graduate course on neutron scattering in hard condensed-matter physics. The course was co-taught by six professors. Lectures covering a full range of the subject were given online and remain accessible.

Neutron scattering experiments were conducted on materials with emergent magnetic phenomena. These include $Pr_2Zr_2O_7$ which may realize magnetic monopoles with quantum spin dynamics. The Angular-Range Chopper Spectrometer (ARCS) at the SNS was used to determine the crystal field scheme. A paper was published in *Nature Communication*, and a number of prominent talks were given to describe the results.

Powder diffraction experiments were conducted on the POWGEN instrument to determine the magnetic structure of a novel layered magnetic, $Sr_2F_2Fe_2OS_2$, related to iron superconductivity. Published in *PRB*,

the corresponding paper shows how the excellent resolution of POWGEN contributes to resolving complex magnetic structures.

A method was developed to determine the magnetic contribution to the superconducting condensation energy from normalized inelastic neutron scattering data. It was applied to $FeTe_{1-x}Se_x$ data acquired with ARCS at SNS and MACS at NIST. The spatial extent of changes in the magnetic exchange energy was shown to coincide with the superconducting coherence length.

We have examined a material that appears to be a topological insulator as a result of electron interactions. Methods for single-crystal synthesis have been developed, and a recent experiment on the SEQUOIA spectrometer provided evidence for a unique emergent quasi-particle that may be a signature of the topological insulator.

Information Shared

K. Kimura, S. Nakatsuji, J.-J. Wen, C. Broholm, M. B. Stone, E. Nishibori, and H. Sawa, "Quantum fluctuations in spin-ice-like Pr2Zr2O7," *Nature Communications* **4**, 1934 (2013).

L. L. Zhao, S.Wu, J. K. Wang, C. Broholm, and E. Morosan, "Quasi-two-dimensional noncollinear magnetism in the Mott insulator $Sr_2F_2Fe_2OS_2$," *Phys. Rev. B* **87**, 020406 (2013).

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. No instruments are capable of measuring spillover routinely. We will modify an existing instrument to measure spillover between well-defined metal surfaces as a function of temperature and time. We hypothesize that the activation energy for spillover processes is related to the enthalpies of adsorption on the two surfaces, and to the activation energies for diffusion on the two surfaces. We will study spillover of CO molecules between metal surfaces, which will enable the rational design of a spillover catalyst for CO_2 splitting, facilitating the use of CO_2 as a renewable feedstock in fuel production. This application fits into DOE's long-term goals. The fundamental insights gained about the factors governing spillover from our studies will enable more accurate microkinetic simulations for heterogeneous catalysis in general, which is also a goal for DOE.

Mission Relevance

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

An existing apparatus was modified for the detection of spillover via addition of a molecular beam and line-of-sight mass spectrometer. Concept designs and then 3D designs were made based upon calculations of the flux and angular distribution of the molecular beam and background gas molecules, depending on a variety of parameters in the instrument design (e.g., aperture sizes and pumping speeds). Changes were made to the designs of previous researchers in the field to achieve the precision required. Due to various delays in manufacturing, equipment failures, and parts delievered not meeting expectations, experiments have not been performed though the molecular beam has been tested and is working: this achievement has provided us with a world-class instrument. A linux virtual machine was successfully installed on Windows, and a specialized kinetic Mont Carlo simulation software package called "kmos" was installed and used to run spillover simulations. Quantitative data was produced reflecting the effects of configurational entropy on spillover. By construction of this instrument, more accurate experimental measurements of surface kinetics can be performed in future work, and the new simulation software will enable accurate analysis of kinetics and mechanisms for multistep heterogeneous catalysis processes. Possible applications include studies on reforming of organic compounds, emissions control, and CO_2 reduction.

Information Shared

A. Savara, "Standard States for Adsorption on Solid Surfaces: 2D Gases, Surface Liquids, and Langmuir Adsorbates, *J. Phys. Chem. C* **117**, 15710–15715 (2013).
A. Savara, Invention Disclosure for the Molecular Beam Apparatus, Invention ID 2850.
A. Savara, "Experiments and Simulations for Elucidating Spillover: The Diffusion of Molecules across Surface Interfaces," 246th ACS National Meeting, Indianapolis, IN, September 8, 2013.
A. Savara, "Elucidating & Developing Spillover Catalysis: A New Paradigm for Predictive Catalysis," SECS 12th Annual Fall Symposium, Asheville, NC, September 29, 2013.

06587

Experimental Studies and Theoretical Modeling of the Spin Dynamics in a Multiferroic Material

G. Ehlers, R. Fishman

Project Description

Understanding the fundamental magnetic interactions, at the atomic/molecular level, in multiferroic systems is the key to unlocking their potential for technological applications. Neutron scattering is the microscopic probe of choice, but the experimental work also needs to be combined with detailed theoretical modeling and computational analyses of the data. We have hired a postdoctoral researcher to join our team and take on all experimental and theoretical work that we are planning in this context for a particular system, nickel vanadium oxide ($Ni_3V_2O_8$). This material is far from being well understood: not even the *k*-vector of the magnetically ordered state at low temperature has been unambiguously determined. At least six different phases have been identified so far in the temperature/magnetic field phase diagram. We expect the work to be mostly theoretical and computer code development, although participation in future scattering experiments will also be necessary. Thus, this project ties together different areas of competence at ORNL: the neutron-scattering and computational facilities, as well as theoretical expertise for the modeling of complex systems.

Mission Relevance

Several reports by the national academies and committees convened by the US Department of Energy attest to the importance of quantum materials in future directions for condensed matter research (see for example, National Research Council CMMP 2010 Solid State Science Committee, *Condensed Matter and Materials Physics: The Science of the World Around Us*, National Academies Press, 2007. ISBN-10 0-309-10969-8). This project will lead to a basic understanding of a classic model multiferroic system, $Ni_3V_2O_8$. In multiferroics, the magnetization can be controlled with an electric field, and the electric polarization can be controlled with a magnetic field. Such coupling provides the opportunity to design a new class of multifunctional materials with vast technological potential.

Results and Accomplishments

A team member (postdoctoral level) was hired for the project and started at the end of calendar year 2012. Twelve months into the project, we have now gained complete understanding of the computational approach to calculate the spin wave energies and intensities and of the computer code previously used. We have done calculations for two multiferroic systems, $Ni_3V_2O_8$ and $YFeO_3$, for which data had been taken at the Spallation Neutron Source during the last 2 years. Agreement between model calculations and data is already good but can be further improved. One scientific paper about one of the systems ($Ni_3V_2O_8$) has been published, showing some of our results. This paper documents significant progress (over previous work by other groups) that we have reached in the fundamental understanding of this compound. For the first time, the correct ground state has been determined in neutron scattering experiments. This state is characterized by antiferromagnetic order with an incommensurate propagation vector along the crystallographic c direction. Furthermore, for the first time we have published on the spin wave spectrum and described it quantitatively with a model Hamiltonian that contains local exchange, anisotropy, and biquadratic coupling energies. A second paper (on $YFeO_3$) has been submitted and is now with the referees. We have started developing new code that makes the first important step towards project completion - setting up the matrix elements for the calculation is desired to be independent of the particular details (site symmetry and occupation, size of the unit cell, number of magnetic atoms, choices for interactions between them, etc) of any given system. Previously the code itself needed to be adjusted for each new system that was studied - we want to get away from this inconvenient limitation. During the next six months we expect to accomplish this. We are now able to compute the scattering function from a model setting as it is measured (i. e., including instrumental resolution) in a format that allows for direct fitting to real time-of-flight scattering data.

Information Shared

G. Ehlers, A. A. Podlesnyak, S. E. Hahn, R. S. Fishman, O. Zaharko, M. Frontzek, M. Kenzelmann, A. V. Pushkarev, S. V. Shiryaev, and S. Barilo, "Incommensurability and spin dynamics in the low-temperature phases of $Ni_3V_2O_8$," *PRB* **87**, 214418 (2013).

06717

NEMO Code Enhancement for Vector Sensor Towed Array Signal Processing

C.W. Kotas

Project Description

With the emergence of ever stealthier underwater targets, there is a continuing need to develop innovative approaches for near-real-time remote detection, classification, localization, and tracking. The complexity of calculations required to perform these tasks increases dramatically with the rapidly growing sophistication of the required algorithms, as well as with the capabilities of the deployed sensor arrays. This results in processing power requirements that cannot readily be met with conventional computing hardware and software. To take advantage of modern high-performance computing processors, current sequential algorithms need to be examined and reworked to expose sections where parallelization is possible. The Center for Engineering Science Advanced Research (CESAR) at the Oak Ridge National Laboratory (ORNL) has previous experience in adapting array signal processing codes for the Office of Naval Research (ONR) for parallel computation on an NVIDIA Tesla C2050 (Fermi architecture chip). Building on this experience, this project will demonstrate the additional utility of NVIDIA's Kepler architecture chips and Intel's MIC architecture chips in solving complex array signal processing problems.

Mission Relevance

In keeping with ORNL's mission to develop capabilities for global security, the project aims to demonstrate the benefits of deploying leading-edge, complex signal processing methodologies on emerging, massively parallel processors such as NVIDIA's Kepler processors, as well as on devices using Intel's new MIC architecture, using underwater array signal processing as a test case. The projected benefits include more advanced signal processing, which will allow the Navy to improve detection of stealthy underwater targets, at a reasonable cost using off-the-shelf components.

Results and Accomplishments

This project has supported my work to parallelize algorithms for undersea signal processing, including beamforming algorithms for sensor arrays that are part of the NEMO code base that is being developed for the Navy. The algorithms are being verified on graphical processors (i.e., GPUs) including NVIDIA's Tesla and Kepler processors. Future implementations will include Intel's MIC processor as well. The ultimate goal of this work is to support a real-time processing system for arrays of sensor data, including the vector sensor towed arrays and hull-mounted arrays used by the Navy.

The research conducted through this project has direct applications to the work done at the National Reconnaissance Office and the Department of Defense. In FY 2013, this work supported two proposals. The first proposal to NRO focused on parallelizing additional algorithms including an FFT without corner turning and a fast inversion of certain types of matrices. The second proposal to NAVSEA dealt with parallelizing algorithms used in conformal hull mounted sensor arrays.

Information Shared

n/a

06741

Exploration of Superconductivity in Non-Layered Three-Dimensional (3D) Materials for Potential High-Field Applications

A. Safa-Sefat, D. Parker, C. Cantoni

Project Description

This research tests the hypothesis that superconductivity can be induced in materials with simple non-layered three-dimensional (3D) structures; if the hypothesis is correct, more powerful, compact, and cost-competitive generators may be the result. This study involves the design of 3D superconductors, from a proposed list of binary 3*d* transition-metal pnictides or chalcogenides by the means of chemical substitutions and electronic dopings, using first-principles calculations and chemical intuition. To be economically viable, the design of generators requires superconducting wires to operate, first, with critical current-densities (J_C) higher than 10^5 A/cm^2; second, at superconducting temperatures above 30 K in order to use a closed-cycle refrigerator for cooling; third, in magnetic fields above 5 Tesla; and fourth, nearly independently of crystal orientation. Anisotropy leads to low J_C values under high magnetic fields (with magnesium diboride), and very high processing costs (with cuprates). Our investigation into isotropic 3D superconductors may revolutionize high-field applications.

Mission Relevance

This project will contribute to the understanding of high-temperature superconductivity through theory-guided synthesis and physical characterization of new materials. This proposal leads the path to new, practical superconducting wires for use in high-field, efficient, and environmentally friendly generators, for example for use in compact, high-power wind turbines, which would ultimately enhance the nation's energy security and reduce carbon emissions.

Results and Accomplishments

This project was approved for funding recently (~ June 2013); hence, not much science has been done on this LDRD project yet. In FY 2013, a few large and key items were bought (e.g., a glove box), a few theoretical calculations were done, and a few material syntheses were tried. This project has enabled the hiring of a postdoctoral fellow to intensely work on this project; this individual should begin work at the Lab in the next month.

Information Shared

One manuscript is currently being written, entitled "Filamentary superconductivity at T_C = 12 K in a Mo-As-O phase."

06743

Computational Design of Soft Matter Materials

R. Kumar

Project Description

The overarching goal of this proposal is a concerted and integrated computational effort to address the challenges in developing new/improved soft materials with robust morphologies while simultaneously

taking advantage of experimental efforts in precision synthesis and state-of-the-art characterization methods enabled by new soft matter electron microscopies and neutron scattering science. Toward this end, the PI will develop a leading research program in computational soft matter science focusing on field theoretic (FT) methods, and the development and implementation of new algorithms to take advantage of leadership and emergent computing architectures and data analytics. This program will act as a synergistic interface between the Computing and Computational Sciences, the Physical Sciences, and the Neutron Sciences Directorates at the Oak Ridge National Laboratory (ORNL). The project will further develop these methods to become a key part of the ORNL materials simulation portfolio, complementing, supporting, and extending existing methods and resources.

Mission Relevance

The PI will develop a leading research program in computational soft matter science focusing on FT methods, and the development and implementation of new algorithms to take advantage of leadership and emergent computing architectures and data analytics. The proposed work will directly address goals in the DOE BES Materials Genome Initiative.

Results and Accomplishments

Over this funding period, we have used field theoretical methods for the study of thin films of di-block copolymer melts, where one block is polydisperse in chain lengths while the other is monodisperse. Computing neutron reflectivity profiles and directly comparing them with experiments confirm the theoretical predictions for structure in these thin films. Validation of theoretical predictions provides a firm support to the use of coarse-grained models for studying polymeric systems, in general. We are in the process of applying the same methodology to more complex polymeric systems.

Information Shared

R. Kumar, B. S. Lokitz, S. W. Sides, B. G. Sumpter, W. Heller, J. F. Ankner, J. Browning, and S. M. Kilbey, "Thin films of lamellar forming polydisperse di-block copolymers," in preparation, 2013.

06745

Expanding ORNL Neutron Capabilities by Increasing Spatial Resolution at the High Flux Isotope Reactor CG-1D Neutron Imaging Prototype Beam Line and Co-registering Imaging and Diffraction Data

H. Bilheux, B. Bailey, K. An, J. Bilheux, L. Santodonato, D. Selby

Project Description

The focus of this LDRD proposal is to address the needs identified by the research community within DOE Basic Energy Sciences (BES) and Energy Efficiency and Renewable Energy (EERE) programs by developing and demonstrating state-of-the-art combined neutron computed tomography and diffraction-based residual strain mapping techniques for complex engineered systems. Within this project we will improve spatial resolution at the CG-1D neutron imaging facility located at the High Flux Isotope Reactor (HFIR). We will develop algorithms to spatially co-register neutron imaging and diffraction-based strain maps of individual objects. We will demonstrate the value of these combined results through analysis and publication of results on imaging and diffraction friendly calibration samples. Successful completion of this LDRD project will improve the spatial resolution of the current ORNL neutron imaging facility, provide new capabilities for integrating imaging data with neutron residual strain measurements, and

demonstrate the value of the combined imaging/strain measurement capability proposed for the VENUS instrument at the Spallation Neutron Source.

Mission Relevance

The industrial and academic neutron user communities have expressed the need to increase spatial resolution in the fields of additive manufacturing, energy storage (i.e., high-resolution mapping of battery porosity and constituent deposits), plant physiology (i.e, observation of thin roots and rhizosphere), biology (i.e., improve assessment edges of tumors), and transportation technology (e.g., diesel injection nozzle channels). The proposed research directly addresses these needs and demonstrates the value of new approaches to imaging for potential users and research sponsors.

One advantage of higher resolution imaging is that the structural information obtained through computed tomography can be used to determine optimum gauge volume selection for subsequent residual strain mapping of complex structures on the HB-2B or VULCAN instruments. Moreover, surface texture information obtained using neutron-computed tomography may be used as input to computational modeling tools to better understand systems in operation (e.g., the affect of surface texture on flow circulation in additive-manufactured turbine blades).

Results and Accomplishments

Spatial resolution at an imaging beamline is driven by the L/D ratio (where L is the distance between the defining aperture and the detector where the image is formed and D is the size of the aperture) and the detector pixel size. High spatial resolution (below 25 microns) can be achieved by increasing L/D and/or reducing the detector pixel size, which is the strategy followed for this project:

1. L/D increase: engineering design, safety review, and fabrication of a new aperture/diffuser system allowing several L/D ratios (from 400 to 2000) is being installed in January 2014. As a comparison, the current capability offers an L/D of approximately 480 with a spatial resolution close to 50 μm. The choice of diffusers was based on preliminary measurements using both C powder and Al2O3 nanoparticles, both of which forward scatter cold neutrons and thus limit loss of flux from a "4-π" scatterer.

2. Detector pixel size reduction: a new micro-channel plate (MCP) detector with a pixel size of 10 μm × 10 μm, a neutron detection efficiency of 70% in the cold neutron range, high count rate capability ($> 5 \times 10^6$ n/cm^2/s) is being developed in collaboration with the University of California, Berkeley. Preliminary measurements at CG-1D are planned in January 2014.

To respond to an increasing need for fast dynamical measurements, that is, high flux and low spatial resolution measurements (i.e., L/D ~ 400), helium-filled flight tubes were installed (January 2013), enabling a factor ~ 4 increase in flux (from 1 to 4.4×10^6 n/cm^2/s). In May 2013, the use of an aperture of 1.2 cm in diameter (previously 0.8 cm) yielded an increase to 7.2×10^6 n/cm^2/s with an unchanged spatial resolution of 50 microns (against the detector). Silicon windows were also installed to reduce gamma background and improve signal-to-noise ratio, a parameter hindering fast dynamical measurements.

Finally, calibration samples made of two metals (copper/steel and aluminum/steel), one of which being compressed into the other, were made to prototype the dual-modality (diffraction and imaging) capability. The samples were measured at both CG-1D and VULCAN in August 2013. Computerized tomography and analysis of the diffraction data are ongoing.

Information Shared

None.

06762

Materials under Extreme Conditions: Ion Beam Irradiation

Y. Zhang, C. Fontana

Project Description

Largely because of a recent multi-million dollar investment by the University of Tennessee (UT) in accelerator equipment and facilities refurbishment, we are on the verge of completing a world-class UT/ORNL ion beam facility that will incorporate state-of-the art technology and materials diagnostic tools for probing radiation effects on materials. The key remaining step is to (1) develop and complete assembly of an advanced single ion detection telescope and (2) perform some scoping ion irradiation and materials characterization studies to demonstrate the versatility and precision of the new capabilities in the ion beam facility. This proposed project would primarily be used to provide funding for a postdoc to complete the ion beam facility and lead the transition to efficient operations.

Mission Relevance

Knowledge of materials response to energy deposition and advanced materials for radiation detectors has a wide impact on DOE, the US Department of Defense, US Department of Homeland Security (DHS), and National Institutes of Health (NIH) missions, including nuclear technology, national security, proliferation detection, treaty verification, international and domestic safeguards, crisis managements, unconventional warfare, medical diagnostics, and fundamental research, as well as environment and process characterization, etc. The proposed work, if successful, will have direct value throughout the NA-22 (National Nuclear Security Administration for nonproliferation research & development) and DTRA (Defense Threat Reduction Agency) organizations. The fundamental science associated with single particle response in materials and scintillation physics has broader impact in DOE, DHS, and NIH mission areas, which could serve as a base for funding from Nuclear Energy (NE), Basic Energy Sciences, Fusion Energy Sciences, Biological and Environmental Research, DHS, or NIH.

Results and Accomplishments

Largely because of a recent multi-million dollar investment by ORNL and UT in accelerator equipment and facilities refurbishment, we are on the verge of completing a world-class UT-ORNL ion beam facility that will incorporate state-of-the art technology and materials diagnostic tools for probing radiation effects on materials. The key steps for this LDRD are to (1) develop and complete assembly of an advanced single ion detection telescope and (2) perform some ion irradiation and materials characterization studies to demonstrate the versatility and precision of this new capability in the ion beam facility. This is a new project started this summer. We have, in the past few months, designed and constructed a customized telescope. With advanced microchannel plates (MCPs) and electronics, the telescope will allow ions to be detected one at a time with 300 picosecond timing resolution and a controllable rate from a few ions per second to tens of thousands per second. We are current waiting for the MCPs that are scheduled to be delivered in 1 month. We have tested some of the electronics using pulse generators and will finish assembly of the telescope. The ion beam facility will be a key element in the ORNL/UT fission and fusion materials portfolio that synergistically complements our world-class

neutron irradiation (the High Flux Isotope Reactor and proposed Spallation Neutron Source Fusion Material Irradiation Test Facility) and post-irradiation materials examination capabilities.

Information Shared

No publication due to the short time of the project.

06901

Laser-Based Diagnostics for Characterizing Materials Exposed to a Plasma Environment

T. Biewer, J. Caughman, R. Goulding, K. Leonard, J. Lore, M. Martin, R. Martin, J. Rapp, G. Shaw, B. Wirth

Project Description

This proposal is a direct response to one of the key priorities of the 2014 LDRD call for the development of new experimental approaches for the testing of materials subjected to plasma environments of a fusion reactor. This will be accomplished by implementing laser-based diagnostic techniques, which will be used to characterize the plasma environment and to probe the material surface during and/or following plasma exposure. The plasma will be produced by the proto-MPEX (Materials-Plasma Exposure eXperiment) device at ORNL in the Fusion and Materials for Nuclear Systems (FMNS) Division. A Nd:YAG (neodymium-doped yttrium aluminum garnet) laser will be installed on proto-MPEX to enable Thomson scattering (TS) measurements of the plasma parameters, particularly in the region adjacent to a material target. The same laser will be used to in situ probe the material target, via laser-induced ablation/breakdown/desorption spectroscopy (LIAS/LIBS/LIDS), as appropriate, to characterize the effects of plasma exposure. Material targets can be further characterized ex situ by surface techniques available in the Biosciences and Materials Science and Technology divisions that are available for both nuclear (radioactive) and nonnuclear materials studies. Measured material surface effects (erosion/redeposition, thin film formation, morphology changes, etc.) will be compared with computational modeling predictions of materials surface response to plasma exposure, predominately using molecular dynamics simulations. These diagnostic techniques are directly transferrable to future plasma-material interaction (PMI) machines proposed for Oak Ridge National Laboratory (ORNL), e.g. MPEX and FNSF (Fusion Nuclear Science Facility) as well as ITER (International Tokamak Experimental Reactor), and will serve to establish ORNL as a place capable of performing world-leading PMI research.

Mission Relevance

This project is directly relevant to the mission of the US Department of Energy (DOE), specifically the Office of Fusion Energy Science (OFES). Fusion energy is arguably the most promising energy source for the future. One of the most important issues to be solved in progressing to a commercial fusion reactor is the identification of plasma facing materials compatible with the hostile environment of a future fusion reactor. The Fusion Energy Science Advisory Committee (FESAC) subcommittee, chaired by Steve Zinkle, identified the need for new linear plasma devices to address the plasma material interface of fusion reactors in the medium term. Within the ORNL strategy, a new device is planned called MPEX, which will help to advance plasma-facing components from technical readiness level (TRL) 3 to TRL4 as well as aspects of TRL5 and 6 (end of lifetime studies). An essential part of this MPEX device is a novel plasma source. This source system is being developed and will be tested in the devices PHIX (Physics

Integration eXperiment) and later expanded into PHISX (Prototype High Intensity Source Experiment), also known as proto-MPEX. This LDRD aims to be a key component in the ORNL strategy, using the capabilities of the PHIX and PHISX devices, leading up to MPEX, to develop at ORNL diagnostic techniques and capabilities that can be used in situ to study materials exposed to a plasma environment.

Results and Accomplishments

The proposed period of award for this LDRD project includes FY 2014 and FY 2015. Because of the availability of unspent FY 2013 funds, a strategic decision was made by ORNL management to award partial funding for this LDRD in the last 2 months of FY 2013. This FY 2013 funding was specifically targeted at the purchase of the high-power Nd:YAG laser, which is the key enabling hardware of this LDRD. The laser was a long-lead-time item, which was successfully delivered to the ORNL site before the end of the FY 2013 budget year. Because this Nd:YAG is a "Class IV" laser, precautions are necessary to allow for safe operation. These procedural and engineering safeguards are being developed currently. In particular, a dedicated laboratory space near to the PHISX device for the Nd:YAG laser, and other associated diagnostic hardware, has been identified and re-appropriated. The Nd:YAG laser is being housed in this area while research safety summaries (RSS) and specific work plans are being established.

In addition to the procurement of the laser hardware, the other key activity (in the 2 months of FY 2013 that this LDRD was funded) was to secure the staffing arrangements necessary for the project to be successful. A subcontract was established between the ORNL Fusion and Materials for Nuclear Systems Division and the University of Tennessee-Knoxville (UTK) for the support of collaborative research. In particular, through the Bredesen Center for Interdisciplinary Graduate Research and Education (CIRE), a UTK graduate student has begun working on this LDRD project, in partial fulfillment of the requirements for her PhD program. Guinevere Shaw's CIRE appointment will continue to be funded through this LDRD for the next 2 years.

This LDRD has only recently been established, and all of the project milestones are scheduled for FY 2014 and FY 2015. However, the procurement of the laser and the establishment of the staffing agreements are both critical events that are necessary for the success of the project. Work is continuing, and results will be reported at the American Physical Society Division of Plasma Physics Conference and at the High Temperature Plasma Diagnostics Topical Conference next year.

Information Shared

None.

06917

To the Nation's Health: Computational National Healthcare Model for Value-Based-Purchasing Cost Projections

M. Shankar, G. Tourassi, J. Schryver, J. Nutaro, M. Leuze, E. Uberbacher, G. Kora, G. Weigand, G. Thakur

Project Description

A fundamental shift in national healthcare from fee-for-service (FFS) to value-based-purchasing (VBP) will take place over this and the next decade. The Patient Protection and Affordable Care Act (ACA) promises a sea-change in cost-control and quality improvement by shifting incentives and payments to

"value" and "quality," instead of paying for physician visits. Addressing the dynamics of this change, we construct a large-scale high-fidelity model for the constituent actors in the United States healthcare ecosystem. The model will support scenario-driven and prospective investigations of cost and quality outcomes regionally and nationally, and allow us to anticipate and respond to the challenges of VBP. The large-scale computational model is necessary to illuminate the system behaviors and unintended consequences of the complex rule-based and highly discontinuous nature of the interactions among key actors ("beneficiaries" – care recipients; "providers" – physicians, hospitals, etc.; and, billions annually of FFS "claims/encounters"). By creating non-Protected-Health-Information emulated claim data sets and by introducing linking techniques to Electronic Health Record data, we are uniquely positioned to create a first-in-the-nation computational model of healthcare actors and data. Our model forces the creation of an intertwined large-scale data-and-compute programming harness. By directing this model at the questions of cost projections and VBP, we create a valuable resource for tackling a leading national question of our time.

Mission Relevance

While it is well known that the proportion of the national gross domestic product (about 18%), the national budget (about 20%), and a great part of the deficit going forward are due to healthcare expenditures, it is less widely known that very little large-scale systematic modeling is done to understand the cost drivers before policies and procedures are put into law. We aim to take the first critical steps to address this shortcoming. Our acknowledged ability today to create and execute large-scale models in simulation and to analyze the data for explicit and latent behaviors situates us well to create and advance a national healthcare model that runs on our large-scale computational platforms. Such a model must be configurable and extensible because the high-performance computing system architecture itself is rapidly changing, with a single system lifetime of only 3–4 years. The combined source data, computation data, and output data trajectories require analysis at multiple scales and with a large scenario-driven parameter space.

Results and Accomplishments

1(a) An agent-based model was constructed for an Accountable Care Organization (ACO) including providers, beneficiaries, and sample interventions.

An important differentiating aspect of the ORNL agent-based model is that it was constructed taking into account aging of the population, as well as published data on demographic distributions of disease prevalence. These differentiators help project into the future expected costs and outcome measures.

1(b) An agent-based model was constructed for a joint replacement intervention.

Impact: The models constructed so far are the first agent-based healthcare entity models of ACOs that are important constructs in the new ACA legislation. The simulations that have been created also include a browser user interface that allows end users to modify input parameters and run what-if simulations on system behavior. These models will be a baseline for extending them to scalable simulations that realistically emulate the potential costs and outcomes of new healthcare policy guidelines and regulations emerging from the ACA.

Information Shared

Y. Park, M. Shankar, B. Park, and J. Ghosh, "Graph Databases for Large-Scale Healthcare Systems: A Proposal for Efficient Data Management and Service," Proceedings of IEEE Workshop on Graph Data Management: Techniques and Applications (GDM 2014), accepted.

GLOBAL SECURITY SCIENCE AND TECHNOLOGY

06041

Fully Virtualized Computational Energy Infrastructure Model for Improved Cyber Resilience

T. Kuruganti

Project Description

Multiple interdependent energy foundations, comprising energy generation, transmission, and end use, serve as a critical infrastructure facility for ORNL. These energy 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 typically 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 various interdependent installations and usage to analyze the whole-campus resilience to degradation in the performance of infrastructure due to cyber attacks. We propose to develop a network- and computer-centric infrastructure modeling and simulation tool that facilitates simultaneous simulation of multiple energy foundations and associated control systems. A detailed sensitivity analysis will be performed to understand the fidelity required to capture the behavior of the energy infrastructure at a level suitable for characterizing risks posed by cyber attacks. The end result will be a simulation framework to comprehensively analyze the resiliency of the ORNL campus that can be scaled to include regional- and national-level infrastructure modeling.

Results and Accomplishments

The major technical goals in the project proposal are achieved with specific accomplishments that include (1) a risk-based resilience analysis method for developing secure control systems. We completed proof-of-concept demonstration for a supercomputing chiller system, and demonstration for ORNL Electric Distribution is currently in progress, (2) a method for model-based optimization of investment strategies for protecting critical infrastructure against cybersecurity threats, and (3) a method for vulnerability identification using state transition diagrams to identify forbidden states that can pose a threat to the system.

The protection of physical infrastructure from attacks on its computing and communication components is addressed only in part by what are typically thought of as cyber-security controls: strong passwords, process white-lists, encrypted data, authentication of a message's source, and similar security controls. These defensive measures reduce the likelihood that the computing and communication components will be breached, but do not enable a system to operate in spite of that breach. When these security controls fail, it is necessary to detect the breach, understand its intent and purpose, formulate a plan for response,

and then act on that plan to mitigate the consequences of the attack. This must be done in a time commensurate with the dynamics of the physical system to prevent unwanted physical effects.

Most work on cyber-security emphasizes methods and technology for prevention, detection, or mitigation. We focus on how the effectiveness of each and the dynamics of the physical system together 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 (and, therefore, cost) of a security system and the likelihood of an undesired outcome.

Investments in the cyber-security of critical infrastructure must balance preventing intrusion, detecting a cyber-attack, and mitigating the attacker's physical effects on computer controlled equipment. For this purpose, we developed a method for making optimal investment decisions that balance these aspects of a cyber-defense. The proposed method accounts for the physical process that is being controlled and the relative cost and performance of technologies for prevention, detection, and mitigation.

We are adapting methods from Failure Modes and Effects Analysis (FMEA), which is commonly used in reliability engineering, for the identification of cyber-vulnerabilities (and the risks assumed by their presence) in the design and implementation of cyber-physical systems. Our FMEA method for cyber-security analysis generates two artifacts. First, it creates Markov models of the cyber-physical system, which can be integrated with models of its physical dynamics to assess risk. Second, it creates a list of failure modes and their consequences that are the source of risk, which may be mitigated to reduce the system's vulnerability, improve its resilience or reliability, or any combination of these based on a threat vs. opportunity cost function.

We have engaged in proposal development and program development activities, which include:
(1) Initiated discussions with DOE Office of Electricity (OE) to utilize the LDRD and develop projects with program manager Dr. Carol Hawk for potential investments in the LDRD area through the Annual Operating Plan process, (2) the LDRD team is developing collaborations with Software Engineering Institute (SEI), UtiliSec, and other partners for the upcoming DOE OE laboratory-led and industry-led call for proposals in cybersecurity for critical infrastructure along with understanding of future needs for secure control system designs for critical infrastructure, (3) the team had initial discussions with researchers from NIST who were interested in our simulation capabilities of cyber-physical systems. The goal is to develop relationships for a joint NIST-DOE OE funding of future work, (4) the team participated in authoring a proposal for DOE OE to develop a testbed for cybersecurity analysis of advanced metering infrastructure for smart grid, (5) the team is in discussions with PNNL and OE on developing program plans for future advanced modeling and simulation technology for smart grid applications, (6) the team is in discussions with ORNL Power and Energy Systems researchers and Global Security Directorate personnel to develop a synergistic Experimental and Simulation testbed for cybersecurity research in critical infrastructure.

Information Shared

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J. Nutaro, G. Allgood, T. Kuruganti, and D. Highfill, "Using simulation to engineer cybersecurity requirements," in Proceedings of the Eighth Annual Cyber Security and Information Intelligence Research Workshop (CSIIRW '13), Oak Ridge, TN, January 8–10, 2013.

I. Patterson, J. Nutaro, G. Allgood, T. Kuruganti, and D. Fugate, "Optimizing investments in cyber-security for critical infrastructure," in Proceedings of the Eighth Annual Cyber Security and Information Intelligence Research Workshop (CSIIRW '13), Oak Ridge, TN, January 8–10, 2013.
J. Nutaro, G. Allgood, and T. Kuruganti, "Towards using simulation to achieve built-in security," submitted to the *Journal of Computers & Security.*
J. Dong, X. Ma, S. M. Djouadi, H. Li, and T. Kuruganti, "Real-Time Prediction of Power System Frequency in FNET: A State Space Approach," Proceedings of IEEE SmartGridComm, Vancouver, Canada, 2013.

06055

Automated Software Tools for Engineering Quantum Computers (ASTEQC)

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

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. To address this problem we developed a blueprint for a software toolkit for the design, programming, and analysis of application-specific quantum information systems (QIS). In particular, we (1) developed a schema of user-level concepts for modeling hybrid classical-quantum dynamical systems; (2) developed a mathematical/logical formalism to impart precise meaning to user-level modeling concepts in support of simulation and analysis; and (3) implemented part of the schema in SysML, an existing general-purpose modeling language.

Mission Relevance

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

Results and Accomplishments

Development of a Modeling Schema. We developed a novel approach to the design of QIS based on the principles of model-based design (MBD). Our approach was informed by existing MBD frameworks in conjunction with several original insights regarding the applicability of existing MBD to QIS: (i) The prevailing systems modeling paradigm, in which a system consists of communicating encapsulated components, is ill-suited to account for quantum entanglement; (ii) QIS performance metrics are inherently probabilistic; (iii) a QIS modeling framework must be very general due to the diversity of physical architectures under development for QIS; (iv) simulation of QIS is not scalable, but analytical methods are scalable in some cases. We developed an object-oriented, strongly typed modeling schema similar to that underlying *Modelica*, but more compatible with quantum mechanics. In our schema, a system is defined hierarchically in terms of typed components, each of which may specify structure and/or dynamics. (Our choice to treat dynamical behaviors as composable modules—similar to mixins or traits—is a notable example of a choice motivated by quantum mechanics, wherein entangling interactions are fundamentally shared and cannot be ascribed to individual physical structures.) Components can be composed both spatially and/or temporally. Design requirements and operational constraints are expressed as logical predicates on model elements. A type system based on a rigorous notion of abstraction allows the system to be described and analyzed at varying levels of abstraction and

from multiple perspectives. We have identified three primary levels of abstraction (algorithmic, computational, and physical) and the kinds of design inputs needed at each level.

Development of a Mathematical Formalism. We developed a mathematical/logical formalism providing rigorous semantics to QIS models in support of both simulation and formal analysis. One part of this formalism is the notion and theory of a quantum-analog-digital (QuAD) system, which may be seen as an extension of piecewise deterministic Markov processes to the quantum realm. 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. The formalism provides mathematical definition to modeling concepts such as sequential and parallel composition, projection, simulation, equivalence, and abstraction/ refinement. A second part of our formalism is a low-level programming language for expressing QuAD systems. Finally, we investigated several dynamical systems logics, including quantum Hoare logic, differential dynamic logic, and interval temporal logic (ITL), as candidates for behavior specification languages.

Implementation in SysML. To exercise our modeling schema, we expressed it in SysML and applied it to the design of a quantum random number generator. SysML is an open-standard general-purpose modeling language for systems engineering applications. We created a new class hierarchy for quantum signals and quantum processes and incorporated instances of such classes in structure diagrams and activity diagrams. While this exercise illustrated many aspects of our schema, we found that SysML was not entirely suitable as a platform for our envisioned modeling framework. Many SysML modeling concepts lack clear, mathematically rigorous semantics. Furthermore, SysML's set of modeling concepts is (for us) overly rich and not uniformly applicable in quantum mechanical contexts. The modeling language *Modelica*, which is also well known and supported in industry, is conceptually much more similar to our modeling schema and appears to be a more promising platform for implementation.

Information Shared

In preparation.

06068

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

M. Shankar, J. Beaver, C. Briere, S. Chinthavali, A. Dimitrovski, S. Fernandez, B. Jewell, J. Nutaro, V. Protopopescu, A. Ramanathan, R. Sukumar, Z. Li

Project Description

Using real data obtained from the field over the past 3 years, we constructed a data-driven threat radar for the electric grid. Our threat radar takes into account distribution outages, transmission outages, and incipient cyber vulnerabilities. Signals of cyber incursions along threat vectors applicable to electric grid Supervisory Control and Data Acquisition (SCADA) systems with tracked behaviors in the electric grid are combined. The detections are first enabled at a fine-grained resolution within a facility – a local cyber-to-SCADA impacts model. These are coupled with regionally detected behaviors – distribution and transmission outages, which may suggest an evolving attack. Our capability is distinguished by using a one-of-a-kind grid awareness dataset available only at ORNL. By also representing the grid topology as a graph, a large-scale and high-speed cyber/grid infrastructure analytics is performed 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 (SC), 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. The vital first step is taken 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.

1(b) Cyber threat scenario catalog and case-study for Hurricane Irene – Additionally, SCADA descriptions are cataloged for substation resources across the utility sector.

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

2(b) The full end-to-end prototype Grid Threat Radar (GTR) software was developed to perform preliminary correlation of Cyber and SCADA incursions. This prototype is being commissioned for testing at potential sponsor facilities.

Information Shared

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J. Nutaro, V. Protopopescu, Z. Li, A. Dimitrovski, and M. Shankar, *Potential Cyber-attacks on Power Systems through Load Manipulation*, ORNL/TM-2013/589, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2013.

C. Briere, A. Ramanathan, S. Chinthavali, R. Sukumar, and M. Shankar, *Correlation Patterns in Grid Outage Data*, ORNL/TM-2013/588, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 2013.

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 but 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. Since *B. thuringiensis* chinensis CT-43 contains plasmids that *B. thuringiensis* ATCC 10792 does not, we will be able to use the already acquired data to analyze changes caused be plasmids or other genetic modifications.

Punita Mange, who is a first year graduate student in the UT-ORNL Genome, Science and Technology Program, presented a poster at the summer BESC meeting and won the best poster award (see publication #1 below).

Information Shared

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06384

Distributed Enterprise-Level cyber-PHysical Intelligence (DELPHI)

M.A. Buckner, J.M. Beaver, E. Farquhar, I.B. Snyder, A.D. Dimitrovski

Project Description

The electric grid is arguably the most critical of our nation's infrastructures because all other sectors depend upon electricity for operation of essential services. Cyber threats to energy delivery systems (EDS) are real and increasingly innovative, complex, and sophisticated. Flaws in system components, communication methods, and common operating systems make modern EDS vulnerable to cyber infiltration and sabotage, and dependence on GPS timing for grid-phase synchronization makes GPS spoofing or jamming attacks a serious concern. Our vision is to develop the science and technology required to detect both cyber and cyber-physical attacks to EDS in real time. Distributed Enterprise-Level cyber-PHysical Intelligence (DELPHI) will provide persistent enterprise-level situational awareness of the grid, detecting and identifying attacks as they occur. DELPHI will leverage ORNL's unique capabilities in advanced behavior-based network intrusion detection technologies, intelligent energy motoring and delivery systems, industrial control system (ICS) security, and learning-from-signals. A proof-of-concept capability will be demonstrated using ORNL's state-of-the-art energy delivery infrastructure and smart metering test facilities. Successful completion of this project will establish ORNL as a leader in this field and serve as a key component in an extreme cyber test bed.

Mission Relevance

A key mission of the Department of Energy's (DOE) Office of Electricity Delivery and Energy Reliability (OE) is to enhance the reliability and resilience of the nation's energy infrastructure. Consequently, cyber security of EDS is critical for protecting the energy infrastructure and the integral functions that it serves. In today's connected environment we must assume our nation's energy delivery system is always under attack and that at any moment some part could become compromised. This necessitates an approach to securing our nation's critical infrastructure that addresses both cyber and cyber-physical threats at all stages of the EDS (generation, transmission, distribution) and at all times. This LDRD addresses this concern by developing the capabilities to provide real-time situational awareness of the grid by sensing potential threats whether from cyber or cyber-physical attacks.

Results and Accomplishments

A threat assessment was conducted across multiple databases, and multiple media access control (MAC) layer-2 command and control (C2) attack scenarios were identified. A software framework was developed with models to simulate network intrusion and malware insertion attacks.

The Critical Infrastructure Protection Center at Mississippi State University (CIPC/MSU) provided data from their ICS/SCADA (supervisory control and data acquisition) test bed. A machine-learning-based network intrusion detection sensor (NIDS) was developed using this data.

KillerBee is a tool set for exploiting ZigBee and 802.15.4 networks. The Air Force Institute of Technology (AFIT) made contributions to the code base, which was used to demonstrate attacks on a ZigBee network. Progress was made on detecting and preventing these attacks using physical layer-1 (PHY) radio-frequency distinct native attribute (RF-DNA) fingerprints. Signals were collected for multiple ZigBee devices, and initial fingerprints were developed.

Phasor measurement unit (PMU) attacks based on GPS spoofing were demonstrated using the University of Texas GPS Spoofing Test Battery (TEXBAT).

Simple load swing attack models were developed.

Detection of Stuxnet-like attacks on a programmable logic controller (PLC) based on RF-DNA was explored. Signals were collected, and initial RF-DNA fingerprints were developed.

Briefings on our research were made to National Instruments Energy Sector Leadership, Joint Interagency Task Force South, Mississippi State University Faculty, Yokogawa Electric Corporation, Power Fingerprinting, LLC, AFRICOM, Clemson University Faculty, and Lockheed-Martin Cooperation.

Seven related publications have been submitted or are in process.

Information Shared

C. K. Dubenhorfer, B. W. Ramsey, and M. A. Temple, "An RF-DNA Verification Process for ZigBee Networks." submitted to MILCOM 12.

B. W. Ramsey, M. A. Temple, and B. E. Mullins, "PHY Foundation for Multi-Factor ZigBee Node Authentication," submitted to GlobeCom12.

B. W. Ramsey, M. A. Temple, B. E. Mullins, and M. A. Buckner, "ZigBee PHY-Based Device ID Verification: Security Enhancement for Industrial Control and Building Automation Systems," in draft.

B. W. Ramsey, M. A. Temple, and B. E. Mullins, "PHY-Based Multi-Factor Authentication for Critical Infrastructure WPANs," submitted to IEEE Journal on Selected Areas in Communications, Special Issue on Signal Processing Techniques for Wireless Physical Layer Security.

B. W. Ramsey and B. E. Mullins, "Defensive Rekeying Strategies for PHY-Monitored Critical Infrastructure LR-WPANS," submitted to the Seventh Annual IFIP WG 11.10 International Conference on Critical Infrastructure Protection.

J. M. Beaver and M. A. Buckner, "An evaluation of machine learning methods to discriminate malicious SCADA communications," targeting an expected ACM CCS (http://www.sigsac.org/ccs/CCS2013/index.html) workshop on AI for Security, AISEC '13.

S. J. Stone and M. A. Temple, "Detecting Anomalous SCADA Operation Using RF-Based Hilbert Transform Responses with a Correlation-Based Verification Process," submitted to IFIP CIP 2013.

06420

Detecting Network Malicious Behaviors at Scale

J.M. Beaver, C.T. Symons, R.E. Gillen, M. Disney, K. Kerr

Project Description

Modern enterprise networks support thousands of nodes and terabytes of data per day. Most existing network intrusion detection systems (NIDS), designed to identify suspicious elements in network streams, are extremely limited because they require manual encoding and only operate on known attacks. Recent works at ORNL and elsewhere have explored intrusion detection via machine learning that discriminates malicious behaviors without using human-coded signatures, but these techniques have been demonstrated only on small-scale networks. Their efficacy in large-scale environments, comprised of tens of thousands of nodes, is an open problem.

We propose to develop a currently nonexistent capability to detect malicious behaviors at scale. To this end, we will develop new dimension reduction and parallelization techniques that will enable behavior-

based NIDS to operate at the speed and scale of modern networks, and also optimize their performance as discriminators of malicious traffic. Our work will include evaluation in existing operational environments such as the Pacific Command and ORNL. In addition, we will evaluate their potential as predictors of future attack behaviors in order to "tip the boundary" of defense. This project will demonstrate behavior-based NIDS in large-scale heterogeneous computing environments, and will result in a capability to operate/evaluate these systems at scale.

Mission Relevance

Despite several years of research investment, behavior-based NIDS are not used in modern Computer Network Defense (CND) systems. Although there are many advantages, including minimizing the reliance on human analysis, adaptation to local network environments, and the zero day detection of attack variants, enterprises do not employ these systems because they have not been sufficiently validated in large-scale networks, in terms of both capability to manage the speed, scale, and heterogeneity of data and their accuracy in detecting attacks.

This project focuses on answering the scalability and performance questions associated with behavior-based NIDS operating in enterprise networks. We will develop methods to scale these algorithms such that they reliably detect malicious traffic in real time on networks that are the size and complexity of large military and commercial entities (800 nodes and Gigabit bandwidth). This will result in a unique national capability that will position ORNL as a leader in network intrusion detection work.

Results and Accomplishments

Scaling Execution Performance. We developed and implemented a prototype parallelized architecture for processing network data streams, extracting feature sets from the raw network data, and applying machine learning algorithms to discriminate malicious traffic. The architecture focuses on parallelizing independent feature extraction/addition tasks, and then the independent classifiers that make the decisions based on the trained machine learning model. The prototype implementation was evaluated to comfortably process a 400 Mb/s live network data stream, which approaches the 500 Mb/s goal for the initial year of this work.

Scaling the Learning Algorithms. We evaluated multiple learning algorithms in the network intrusion detection domain and determined that graph-based semi-supervised methods were the optimum fit due to their ability to intrinsically accommodate small amounts of labeled information by leveraging large amounts of unlabeled information. We addressed the constraints of operational training time and execution time by incorporating (1) Multi-dimensional Spectral Hashing (MDSH) to speed graph construction time and improve training time by 100×, and (2) a linear Laplacian regularized least-squares method to improve classification time by 10× while maintaining generalization performance.

Operational Evaluation. We deployed the scaled behavior-based NIDS prototype as a research/development sensor on the ORNL Visitor's Network. We ran controlled network attacks against intentionally positioned vulnerable hosts to acquire both training and test data in a live network environment. The deployed prototype was able to process in real time the visitor network data stream, and our evaluations demonstrated an ability to detect 97% of the levied attacks with a false positive rate of 0.179%.

Information Shared

C. T. Symons and J. M. Beaver, "Nonparametric semi-supervised learning for network intrusion detection: combining performance improvements with realistic in-situ training," in *Proceedings of the 5th ACM Workshop on Artificial Intelligence and Security,* Raleigh, NC, October 2012.

J. M. Beaver, C. T. Symons, and R. E. Gillen, "A learning system for discriminating variants of malicious network traffic," in *Proceedings of the 8th Cyber Security and Information Intelligence Research Workshop (CSIIRW8),* Oak Ridge, TN, USA, January 2013.

06427

Interactive Analysis of High-Throughput, Unstructured Information Streams

C.A. Steed, J.R. Goodall, R.M. Patton, T.E. Potok, C.T. Symons

Project Description

With more than 140 million active users, each day Twitter produces about 340 million posts (called *tweets*), which are limited to 140 characters.[1] Such social media systems are credited with escalating social protest during the so-called "Arab Spring" revolution of 2011—an event that blindsided the global community. Virtual communities form rapidly in these online systems, and they occasionally foster violence and unrest that is conveyed in the users' language. Techniques for analyzing broad trends over these networks or reconstructing conversations within small groups have been demonstrated in recent years, but state-of-the-art tools are inadequate at supporting near real-time analysis of these high-throughput streams of unstructured information.

We propose the development of an adaptive system to discover and interactively explore these virtual networks, as well as detect sentiment, highlight change, and discover spatio-temporal patterns within the network movements. For example, connecting public tweets with the hashtags **#syriarevolution** and **#OpSyria** forms a grim picture of life in Syria today and the global connections that are sympathetic or antagonistic to the Syrian Government. By discovering these communities and detecting sentiment such as fear or anger, we will be able to understand and forecast the reaction of virtual communities to a given situation, especially when traditional media reports are limited due to hostile or disastrous circumstances.[2] This form of predictive insight will provide the United States with a strategic advantage in anticipating and responding to complex, "intelligence hard" problem sets such as the "Arab Spring."

Mission Relevance

The copious information streams from social media and similar online feeds represent a largely untapped resource of collective wisdom for monitoring global events, exploring trends for cause and effect, and predicting future events. The rising value of these platforms is apparent as we see journalists increasingly turning to social media and other online sources of user content to track the importance of events and find sources of expertise. These streams are generally characterized by sources that produce large and rapidly changing content in the form of unstructured information. These dynamic technologies are rapidly transforming public discourse and setting trends and agendas in domains such as politics, technology, and environment. Effectively investigating such resources requires the ability to grasp the pulse of the network of information and drill-down to increasingly detailed perspectives in near real time. The goal of such analysis is to reveal keys connections, associations, and anomalies by harnessing a visual analytics approach that combines the strengths of humans (rapid visual pattern recognition, background knowledge, intuition) with the computational power of machines.

[1] Twitter Blog. *Twitter Turns Six*. http://blog.twitter.com/2012/03/twitter-turns-six.html
[2] USA Today. "CIA's 'Vengeful Librarians' Monitor Twitter, Facebook Posts." http://www.usatoday.com/news/washington/story/2011-11-04/cia-facebook-twitter/51069030/1

Results and Accomplishments

We have made excellent progress toward the achievement of our objectives for developing a unique collection of modules that bridge visualization and data mining to support dynamic exploration of streaming text. These modules support sentiment analysis, detecting change and key associations and automatically highlighting spatio-temporal patterns in the network. We have received very favorable feedback on our progress from potential funding agencies, Global Security Directorate (GSD) collaborators, and peer research institutions. In the remainder of this section, we will summarize our accomplishments and our future plans for the main components of our work.

Stream Data Management: Efficient management of streaming textual information is crucial to any interactive analysis and visualization objectives. Our system is capable of continuously monitoring and archiving streams from multiple platforms in a variety of database formats to support interactive processing.

Stream Data Analytics: Given our objective of highlighting significant trends and events from textual streams, it is imperative that we develop a highly efficient library of analytical tools that are specifically optimized for streaming textual information. These analytics will operate directly with our data management system and augment our interactive visualizations described in the next section. Our system performs sentiment analysis, graph discovery, efficient stream processing, and topic monitoring.

Interactive Visualization and Analysis: We have developed a highly interactive visual analytics framework, called Matisse, for analyzing the streaming content. At the end of year 2, Matisse will support full spectrum analysis in both a near real-time and forensics mode with novel interactive visual analytics techniques. Our system is intended to support exploratory analysis as well as global situational awareness well suited to watch floor operations for cyber and social media listening centers. We offer stand-alone and web-based applications with connections to out-stream data analytics. We also provide novel interaction techniques for visual data analysis.

Information Shared

R. Patton, C. A. Steed, and C. Stahl, "Visualizing Community Resilience Metrics from Twitter Data," The 2nd Workshop on Social Media Visualization, July 2013.

R. M. Patton, C. A. Steed, C.G. Stahl, and J. N. Treadwell, "Observing Community Resiliency in Social Media," The 13th International Conference on Computational Science and Applications (ICCSA 2013), June 2013.

C. A. Steed, T. E. Potok, R. M. Patton, J. R. Goodall, C. Maness, and J. Senter, "Interactive Visual Analysis of High Throughput Text Streams," The 2nd Interactive Visual Text Analytics Workshop, October 2012.

C. A. Steed, T. E. Potok, P. Bogen, C. Symons, and R. Patton, "An Interactive Visual Analysis Method for Dynamic Exploration of Streaming Textual Information," invention disclosure, Docket Number 201303076.

06463

Development, Testing, and Evaluation of Resilient Control Techniques for Cyber-Defense of Real-Time Control Systems

A. Melin, E. Ferragut, J. Laska, S. Djouadi, R. Kisner, D. Fugate

Project Description

Resilient control capabilities will increase the survivability of critical industrial processes during a cyber-attack. Resiliency to intentional malicious acts is an emerging field of research with great industry interest. Fundamental research is needed to gain an understanding of attack detection methods, process-specific sensitivities, risk susceptibility, the effect of detection time latency, and attack mitigation techniques. Recent discussions with manufacturers of industrial control systems (ICSs) have identified interest in the creation of a set of tools to create reduced-order models applicable to real-time resilient control. These tools will have broad commercial applicability. The development of these tools requires mathematical generalizations of attack vectors and system models. We therefore propose to develop a strategic number of generalized, widely applicable models of critical industrial processes and analytical models of attack vectors. These models will be used to develop new theoretical techniques by expanding existing work in control system design and analysis to create reduced-order models that can be applied to commercial ICSs. This research is complementary to ongoing research at ORNL on attack detection and mitigation techniques for the Jaguar chiller system being performed by Nutaro et al. By developing tools from an analytical standpoint, we believe that a set of universally applicable techniques can be created to increase the resiliency of real-time control systems under cyber attack.

Mission Relevance

This research is aligned with reliable energy delivery, which is the primary mission of the DOE Office of Electricity Delivery and Energy Reliability (OE). The Department of Homeland Security (DHS) Cyber Security Division's Control System Security Program is focused on reducing the ICS risks within and across all critical infrastructures. The project establishes a capability essential for sustainable cyber-security improvements in reliability and resiliency of critical infrastructure. Specifically, understanding how to survive the next-generation Stuxnet attack will make this capability both timely and novel. With funding from DOE, DHS, and the Department of Defense, this effort can continue by assessing the resilience of and understanding the impact of new smart devices on the existing energy infrastructure. The capability will also be of interest to industry, particularly in chemical processing, energy generation, transmission, and critical industrial/facility loads.

Results and Accomplishments

The focus of the project investigators over the previous year has been the development of a solid theoretical foundation from which to understand the application and limitation of current control theory to adequately deal with the problem of cyber-attack detection and mitigation in real-time control systems. This foundation was developed for the most widely used class of linear controllers, known as linear quadratic controllers, which includes the ubiquitous proportional, integral, derivative controllers. For these systems, an attack classification based on the attack energy was developed. This classification includes all potential attack signals with the exception of denial-of-service (DoS) attacks.

The investigators showed that the attack's signal energy and frequency content are directly related to the impact the attack has on the physical dynamics. Signals with high frequency (e.g., random variation of a sensor signal) or finite energy have limited effect on the physical dynamics, while constant (infinite

energy) and low-frequency attacks have the most effect. They also showed that the detectability of attacks is related to their energy content.

DoS attacks present a different theoretical problem. These attacks were analyzed using a graph-theoretic approach and metric, and a corresponding polynomial time algorithm was developed for determining a priori the resiliency of a system to DoS attacks. This algorithm also yields the lowest-cost method for maximizing system resiliency through intelligent sensor and actuator redundancy and use. The investigators also identified fundamental problems with attack mitigation, potential mathematical tools for solving these problems, and the theoretical extensions of these mathematical tools required to apply them.

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06481

Improved Metagenomic Analysis with Confidence Quantification for Biosurveillance of Novel and Man-made Threats

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Project Description

Genetically engineered and naturally occurring, novel pathogens are currently blind spots of biosurveillance. Such threats confound or defeat standard biosurveillance techniques based on PCR and immunological assays. This challenge can be addressed by using a metagenomics approach, in which all microorganisms in a field sample are directly sequenced together. The genome of a pathogen, even if it is altered by natural recombination or genetic engineering, can be computationally reconstructed and identified from background microorganisms. The pathogen's genome provides information on its full malicious capability, evolutionary origin, and genetic manipulation history. Although next-generation sequencing technologies are ready for biosurveillance deployment, the informatics needed to extract information from the vast amount of sequencing data still requires significant improvements in terms of detection accuracy, analysis speed, and information content. The objective of this proposal is to develop an integrated informatics solution for applying metagenomics to accurately detect novel or man-made pathogens and comprehensively characterize their genetic capabilities in a short turnaround time. The key technical innovation of the proposed work is the construction of probabilistic error models of next-generation sequencing data and the quantification of statistical confidence in threat detection and

characterization. The proposed informatics solution will be systematically tested and evaluated for different biosurveillance scenarios using real-world and simulated metagenomic data.

Mission Relevance

The proposed project leverages a number of strong ORNL capabilities, including environmental microbiology, large-scale data mining, and high-performance computing. We believe the proposed work will attract follow-up funding from the Department of Homeland Security (DHS) and the Department of Defense (DoD) Defense Threat Reduction Agency (DTRA) to push the prototype system into production. The Joint Project Manager Transformational Medical Technologies (JPM-TMT) program in DOD is created to "protect the Warfighters from emerging, genetically altered and unknown biological threats." These research programs are expected to be expanded and integrated with the development of a "national biosurveillance strategy." Application of metagenomics to environmental microbiology supports DOE missions in carbon cycling and environmental remediation. Development of the proposed algorithms will position ORNL to pursue future computational biology funding opportunities from DOE Office of Biological and Environmental Research and Office of Advanced Scientific Computing Research. The National Institutes of Health (NIH) provides funding opportunities for metagenomics in the context of human microbiota, infectious diseases, and epidemiology.

Results and Accomplishments

A prototype assembler has been developed for assembling metagenomic reads using the overlap-layout-consensus strategy. It included the following steps. First, an overlap graph was built from input reads. An efficient algorithm based on a hash table was developed to calculate the overlap between every pair of reads using a reasonable amount of memory. In the overlap graph, reads with significant overlaps were connected by edges. Second, the overlap graph was simplified to remove redundant transitive edges and spurious edges. Third, the simplified overlap graph was converted to a unitig graph. The vertices in the unitig graph represent different directions for connecting adjacent unitigs. Fourth, flow analysis was used to find the optimum coverage depth of every unitig in the unitig graph. The optimum flows in the unitig graph indicated assembly paths in the unitig graph. Contiguous genomic sequences, or contigs, can be reconstructed from the assembly paths. Currently the prototype algorithm is under evaluation using simulated data. We also developed a genomic typing algorithm to detect and reconstruct genomes using reference genomes. All reads were aligned with reference genomes. We scaled up the alignment computation to the Kraken supercomputer. The probability of obtaining a read from a genome was calculated based on the number of mismatches between their alignment. The new genomic typing algorithm used maximum likelihood estimation to calculate the relative abundance of each reference genome in the metagenomic sample. The genomic typing algorithm showed excellent performance on a simulated dataset consisting of 1% *E. coli* O157:H7 EC4115, 3% *E. coli* O157:H7 EC4024, 9% *E. coli* K12 DH1, 27% *E. fergusonii* UMN026, and 60% *S. enterica enterica* sv Paratyphi A. We were able to accurately detect and quantify these five genomes from a list of 2000 genomes. We were able to distinguish the two low-abundance pathogenic *E. coli* O157:H7 strains from others.

Information Shared

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06512

Automated Computation of Microchip Behavior

M. Pleszkoch, S. Prowell, J. Black, D. Lepro, R. Willems, K. Sayre, N. McFarlane

Project Description

The Hyperion Protocol is an existing, proven technology for automatically extracting the functional behavior of software directly from the machine code level. It has found many applications, from malware analysis to software assurance. This project seeks to extend and apply the Hyperion Protocol technology to address the analysis of reverse-engineered microchip schematics, thereby closing a gap in the chain of trust required to achieve certifiably secure computing systems. A Hyperion Protocol-based approach for analyzing microchip schematics would be a novel and profound departure from current methods, which typically rely on data structures such as Binary Decision Diagrams that provide uniform, universal representations of Boolean logic functions. In contrast to these methods, the Hyperion Protocol makes use of customized abstractions (called Behavior Specification Units or BSUs), and corresponding recognizers (called Semantic Reduction Theorems or SRTs), to express the entire behavior of a system in a compact and understandable form (called Conditional, Concurrent Assignments or CCAs) that seamlessly scales up through higher levels of abstraction. Once customized libraries of BSUs and SRTs can be developed for existing microchip design archetypes, the Hyperion Protocol system will be able to apply those libraries to analyze reverse-engineered microchip schematics, either verifying desired behavior or identifying undesired behavior such as malicious trap doors.

Mission Relevance

The assurance of microchips used in critical government, military, and private industry applications is vital to the national interest. The primary use of the proposed technology, for the verification of microchips procured from an untrusted supply chain and the detection of intentionally malicious microchip behavior, ties directly to this goal.

Results and Accomplishments

We have developed a mathematical model for hardware circuit component behavior that is directly amenable to analysis using the Hyperion Protocol concepts. The model applies to all MOSFET transistor-based digital logic, whether NMOS, PMOS, or CMOS, and has several novel features. First, it defines a unified method for describing the behavior of both transistor-level logic and gate-level logic, as well as a mixture of both types within the same schematic. Second, it provides a general method for identifying logic gates of any construction from precisely defined mathematical concepts within the model. Third, it allows the combination of the behavior of lower-level circuit components into the higher-level behavior of a larger component or even the overall circuit.

As automated tool support for this hardware mathematical model was being developed and refined, the research was redirected to find a different domain within the field of hardware circuit design where there is an identifiable present need for automated analysis support. The remainder of the project term was spent pursuing this goal, and a potential government sponsor for this work has been found. Additionally, attempts are under way to extend the mathematical model beyond the initial domain of digital logic implemented with MOSFET transistors.

07043

Operationally Focused Active Learning in Cyber-Security

J. Laska

Project Description

There has been increasing motivation to automate the online updating of cyber security classification models and implement an operationally relevant interactive feedback loop with domain expert operators to ensure the usefulness and relevance of security tools. Active Learning is the term for the collection of machine learning techniques that query the user for data labels concerning the process of updating the supervised models. Cyber security analysis is a natural application of active learning. Cyber security traffic models need to be updated to incorporate information from zero day attacks as they occur, but the process for acquiring accurate and timely labeled data in cyber security is expensive. Analysts must be trained and multiple competing attack vectors must be investigated simultaneously. Standard supervised learning approaches fail to account for the cost of acquiring the labels of the data as active learning can. State-of-the-art applications of active learning in cyber security make the operationally inappropriate assumption that user feedback is both instantaneous and correct. We propose strengthening the operational relevance of active learning by updating the state of the art by relaxing these assumptions, thereby strengthening security.

Mission Relevance

The operational cyber security environment cannot support the costs in time and resources of labeling all data without suffering from a misallocation of resources that leads to a delay of analysis and a weakened defense. The querying framework of active learning has been shown to minimize the amount of labeled data required to reach the same level of model generalization accuracy. A need exists to address the operational concerns associated with the cost of acquiring timely, labeled data that is needed to train supervised machine learning algorithms. This project proposes to modify current state-of-the-art active learning strategies to better ensure that operational and implementation concerns are addressed for cyber-security.

Results and Accomplishments

Previous work has assumed that the most efficient querying strategy for an active learning task under imperfect feedback is to choose the agent with the highest probability of providing the correct answer. We have developed cost models of querying that expand the expressiveness of models while including the previous state of the art as special case. These cost-based models can be used to demonstrate the appropriateness of the underlying model assumptions. Furthermore, we have implemented competitors and demonstrated in the scenario of Support Vector Machines that our cost models methods achieve equivalent accuracy in a classification test while decreasing time until completion. The development of operationally useful cost models must incorporate both the cost of scoring a data point with an imperfect algorithmic model and the cost of a difficult data point with a model. As such we transformed publically available datasets to be amenable to human-in-the-loop active learning tasks with the objective to determine to what extent the most "expensive" data points, from the algorithms perspective, overlap with the data points that are difficult for humans. From a programmatic perspective, we assessed the fitness of the active learning component of current SITU implementation for deployment and participated in developing an active learning SITU proposal.

Information Shared

Interpreting cascade style algorithms as active learning with imperfect oracles (in prep).

SCIENTIFIC DISCOVERY AND INNOVATION

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 the DOE Office of Biomass Program, US Department of Defense, and the Advanced Research Project Agency–Energy. 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 a 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

Previously, we had shown that aqueous ethanol (5-100%) can be converted to hydrocarbon blend-stock at 350°C and atmospheric pressure without the need of external hydrogen. The blend-stock was a mixture of paraffins, iso-paraffins, olefins, naphthalenes, and aromatics. The performance of an engine running on this blend-stock was identical to that running on certification gasoline. Preliminary techno-economic analysis showed that the resulting blend-stock has the potential to meet the DOE Office of Energy Efficiency and Renewable Energy alternative fuel selling price target of $3.0/gal.

We showed that the established mechanism involving ethanol dehydration and ethylene upgrading is incorrect. Our results also showed that ethanol conversion to hydrocarbons occurs via a hydrocarbon pool-type mechanism.

We demonstrated that the catalyst is durable by carrying out accelerated aging. The carbon deposits build up on the catalyst after a reproducible time-frame (depending on the space velocity), and carbon removal protocols lead to complete recovery of catalyst performance. The durability tests were repeated employing distilled fermentation streams, and it was found that impurities have no impact on catalyst or product distribution.

We also modified the catalyst to eliminate benzene from the product stream, which is regulated by the US Environmental Protection Agency to be less than 0.68% in transportation fuel.

In FY 2013, the technology moved towards commercialization and was offered for licensing, which is ongoing.

Information Shared

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05641

Advanced Bioprocessing for Sustainable Biorefinery Technology Development

A.P. Borole, D. Pelletier, J. Mielenz, J. Elkins, 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 carbon monoxide (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 Project Agency–Energy (which recently had a solicitation for breakthrough concepts of this nature), DOE–US Department of Agriculture Biomass R&D Initiative (which is now seeking innovative integrated projects), the Office of Energy Efficiency and Renewable Energy, as well as chemical companies like DuPont that are moving into the fuels market (DuPont Danisco Cellulosic Ethanol LLC Joint Venture). The results will be a drop-in fuel that meets the current infrastructure and vehicle requirements in this country.

Results and Accomplishments

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

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

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

Milestone status: Month 24. (a) Demonstrated expression of biosynthetic pathway in *R. rubrum*
(b) Completed assessment of CO conversion in the BER.

Information Shared

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05685

Modeling Long-Term Population Resettlement under Climate Change Scenarios

B. Bhaduri, D. White, 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 the 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 US Department of Defense and the United States Agency for International Development because of the potential applications of the research with respect to identifying vulnerable populations and communities that could be adversely affected by climate change in the decades ahead, prompting humanitarian and/or security crises to which US agencies might 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 using scientific knowledge from close to 200 research articles on the 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 the 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. Using 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. An independent methodological peer review of the project's output to date was also conducted during summer 2013. A subject matter expert in climate-induced migration first reviewed the literature base and ended up adding a substantial number of new references to bring it in line with the current state of knowledge, then constructively critiqued the conceptual model to highlight areas that still require improvement before large-scale development and deployment of the associated software.

Information Shared

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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, and contemporary models often simulate carbon 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. We created an improved mechanistic model of cycling organic carbon (OC) in soils. We hypothesize that attachment at the interface with soil minerals will determine the bioavailability of OC to microbes and thereby exert control over soil OC turnover. The relationship between attachment and stabilization for common OC compounds was determined in batch sorption and long-term incubation experiments using a global suite of soils. The mechanisms of attachment were determined using a coupled application of neutron reflectometry and molecular dynamics simulation. The turnover of the OC compounds as they cycle through measurable soil pools was modeled via enzyme-facilitated microbial degradation. The model framework was developed and validated using published data, followed by testing using our coupled sorption and degradation measurements on global soils. The ultimate outcome was a validated, realistic, globally relevant soil carbon 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 carbon 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 carbon, and in using molecular-scale techniques to study interfacial processes between contaminants, soils, and aquifer materials. We 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. Additionally, 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 BER and many other areas.

Results and Accomplishments

Our new model can mechanistically represent the turnover of major OC compounds in soils. We determined relationships between attachment and stabilization for aromatics, fatty acids, sugars, and starch using batch sorption and long-term incubation experiments to artic, tropical, and temperate soils. Adsorption of the different OC compounds decreased bioavailability, and we observed progression of the dissolved, sorbed, and biomass pools over 1 year coincident with CO_2 respiration. Consumption was rapid, but we also found extensive ^{14}C residence times. We investigated mechanisms of OC stabilization on pure minerals using a novel, coupled application of neutron reflectometry (NR) and molecular dynamics (MD) simulation. Experiments at the Spallation Neutron Source (SNS) using OC-mineral systems prepared at the Center for Nanophase Materials Sciences (CNMS) identified stacked layers of OC on mineral surfaces with internal arrangements dictated by chemical character. Finally, we created a mechanistic microbial model of enzymatic degradation of soil OC using steady-state and dynamic analyses to consider the activities of extracellular enzymes. We found that when carbon use efficiency was allowed to fluctuate with temperature, substantial differences are observed compared to a constant carbon use efficiency. Changes in microbial biomass and enzyme production were predicted to 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 carbon cycling model to use measureable pools of soil carbon, and to explicitly consider microbial dormancy, 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, S.D. Wullschleger, T.J. Tschaplinski, H. Yin, A. Borland

Project Description

As an emerging biofuel crop, *Agave* has high cellulose and sugar contents, along with high biomass yield. It is one of the most water-use efficient plants in the world because of its crassulacean acid metabolism (CAM). The goal of this project is to establish CAM expertise at ORNL and characterize genes regulating CAM. CAM has four phases by which it assimilates CO_2 from the atmosphere and incorporates that carbon into biomolecules: 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 over the middle of the day; and phase IV, direct CO_2 fixation by Rubisco with limited stomatal opening in the late afternoon. Two-dimensional aspects (time course and developmental difference 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 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* 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 basic 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 in the original proposal. Our physiological studies and metabolomics analyses provided evidence supporting our hypothesis that the CAM expression is induced developmentally in *Agave*, with the CAM expressed in the mature leaves but not in the young leaves. Our network analysis identified co-expression modules associated with CAM dynamics. We identified CAM gene modules involved in carboxylation, decarboxylation, and stomatal movement, providing new insight into the molecular mechanism underlying CAM photosynthesis. We made striking discoveries regarding the role of the circadian clock and photosynthetic electron transport (PET) in regulating the CAM pathway. We found that a circadian clock gene family, the CCA1/LHY/RVE family, diverged into two functional categories: one category showing C_3 expression pattern (i.e., with peak expression in the morning) and the other showing the CAM expression pattern (i.e., with peak expression in the middle of the night). Our comparative genomics analysis revealed that CAM-related genes were over-represented in CAM plant-specific genes and that heat shock proteins Hsp90 and Hsp70 were significantly expanded in CAM species as compared with non-CAM species. This project has generated $14 million in follow-on funding through a successful DOE BER biodesign project, has fostered the development of a CAM research community through organizing an international CAM symposium funded by New Phytologist, has contributed to four published manuscripts, and has developed the ORNL expertise to successfully extend CAM to ORNL bioenergy research.

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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 predicting long-term radionuclide mobility and associated electron donor (i.e., bioavailable carbonaceous materials) turnover. Further, the microbial reduction of ubiquitous ferric iron produces ferrous iron, which reacts with nitrite to form the potent greenhouse gas nitrous oxide (N_2O). In essence, metal, carbon, and nitrogen cycles are interconnected, and a better understanding of the microbes controlling metal speciation and associated carbon and nitrogen fluxes is needed. The proposed work will advance scientific understanding towards DOE mission goals by i) obtaining relevant metal-respiring bacterial isolates from contaminated DOE sites, ii) performing comparative analyses of metal-reducing bacteria to determine differences in reduction rates, mechanisms, and growth yields, iii) identifying biomarkers to measure the presence and activity of relevant bacteria, and iv) eluciating the microbiology controlling metal oxidation/reduction and mobility near oxic-anoxic transition zones. 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 metals, including radionuclides, and associated carbon and nitrogen fluxes (e.g., CO_2 and N_2O emissions).

Mission Relevance

Controlling and predicting the fate and the mobility of DOE-relevant contaminants in subsurface environments is a major challenge. Knowledge of the microbial processes that affect contaminant transformation is crucial for predicting contaminant flux and longevity, and, if necessary, implement cost-effective corrective solutions. Microbes mediating the reduction of oxidized metal species require reducing equivalents, which stem directly or indirectly (e.g., in the form of hydrogen) from organic materials. Further, the chemodenitrification process (i.e., the abiotic reduction of nitrite to N_2O by ferrous iron) links metal reduction to N_2O emissions, indicating that the fate of metals, including radionulcides, can only be understood if systems information is generated that integrates research in carbon, nitrogen, and metal cycling. The study of microbial metal cycling and associated carbon fluxes (e.g., CO_2 emissions) is a focal area in the DOE Biological and Environmental Research (BER) portfolio, and this project anticipates future funding from DOE BER to apply systems biology approaches for studying carbon and nitrogen cycling in soil and subsurface environments.

Results and Accomplishments

Significant accomplishments have been made in several project-related areas. (i) A collaborative effort with the University of Illinois demonstrated that uranium isotopes can be accurately measured with high-resolution multiple collector inductively coupled plasma source mass spectrometry (HR-MC-ICPMS). Using the isolates obtained in years 1 and 2 of the preformance period, we measured the magnitudes of isotopic fractionation for $^{238}U/^{235}U$, and demonstrated a relationship between bacterial U(VI) reduction rates and isotopic fractionation. Further, the isotope measurements suggested that mechanistically distinct microbial processes contribute to U(VI) reduction. (ii) Together with ORNL collaborator Dr. Bob Hettich, a global proteomics approach applied to the metal-reducing isolates identified biomarker proteins for different redox processes. The environmental proteomics pipeline was applied to ORNL groundwater impacted with nitrate and uranium, and demonstrated the utility of this approach as a microbial activity

monitroing tool. (iii) A combined computational/experimental study revealed that a novel group of "atypical" NosZ are abundant in soils and sediments and contribute to the reduction of the greenhouse gas N_2O to benign dinitrogen gas. This was a relevant finding because N_2O is produced via chemodenitrifcation in ferric iron-rich soils and sediments impacted with nitrate (e.g., the ORNL subsurface). (iv) Microbial nitrate reduction directly and indirectly affects metal and carbon cycling, and our efforts elucidated the environmental factors that control nitrate reduction to ammonium or to gaseous products including N_2O. (v) A continuous-flow column system has been constructed and is used to reveal the types of metal-reducing microbes relevant for metal, carbon, and nitrogen cycling in oxic-anoxic transition zones. The efforts conducted under this LDRD project generated new information about the microbiology and the environmental conditions that control contaminant fate and associated greenhouse gas emissions.

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06008

Novel Covalent Organic Frameworks with Tailored Carbon Capture Functionality

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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; and 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, may 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 Basic Energy Science 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 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 increasing interest in the development of the next generation materials from nano to mesoscale, and carbon capture is one of the potential applications for these materials.

Results and Accomplishments

Work continued on the hydrazone-linked COFs with pores functionalized with ethyleneoxide (EO) units. A total of six COFs with different pore sizes and various numbers of EO units (from 0 to 5) have been synthesized, and their crystallinity was confirmed by powder X-ray diffraction (PXRD). However, nitrogen sorption isotherms showed no accessible pores for any of these materials. Nevertheless, some of them displayed modest to moderate CO_2 adsorption capacities, with maximum observed values of 3 wt% and 14 wt% at 1 bar and 10 bar, respectively. The measured CO_2/N_2 selectivity in this series varied between 18 and 47. No simple correlation between these CO_2 sorption parameters and the number of EO units could be found.

Another series of imine-linked COFs functionalized with EO units has been synthesized. PXRD measurements indicated these COFs are highly crystalline. Unlike the hydrazone-linked series, the imine-linked COFs were highly porous, with a measured surface area as high as 2400 m^2/g, and CO_2 capacity up to 6.7 wt% and 35 wt% at 1 bar and 10 bar, respectively. This represents the highest reported CO_2

capacity for a COF material. However, its CO_2/N_2 selectivity of 16 is relatively modest. Thus, it remains difficult to achieve both high CO_2 capacity and CO_2/N_2 selectivity in a framework material.

Information Shared

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06060

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

M. Ashfaq, S.-C. Kao, A.A. Oubeidillah, D. Touma, R. Mei, V.G. Anantharaj, S.M. Absar, B. Naz

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. Because of their policy relevance, 8-10 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 is 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 ultrahigh 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 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 the US 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 US Global Change Research Program.

Results and Accomplishments

This project provides a framework for downscaling future climate projections to ultrahigh-resolution that is relevant for policy making. There are three main components of this framework. In first part, we provide the detailed analysis of the CMIP5 GCMs regarding their ability in the simulation of key processes that govern climate variability at varying temporal and spatial scales and their responses to increase in greenhouse forcing. In the second part, we dynamically downscale GCMs using two regional models (RegCM4 and WRF) at 18 km horizontal grid spacing. At the end of this project, we have finished more than 12 of these downscaling experiments. In the third part, we have developed a new calibrated version of Variable Infiltration Capacity hydrological model that can run at 4 km over the conterminous United States. We have started using our dynamically downscaled data to provide 4 km hydrological projections over the conterminous United States. This effort so far generated two three peer-reviewed publications in Nature Climate Change, Journal of Geophysical Research-Atmospheres and Hydrology and Earth System Sciences. First manuscript describes the projections of snow-dependent hydrological extremes in multi-model ensemble of GCMs from CMIP5. 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 manuscript describing near-term hydrological changes in the western United States is in. Our results show that increase in greenhouse forcing result 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. Third manuscript describes the hydrological modeling database and framework that we developed over the conterminous United States. We anticipate that through this hydrologic parameter dataset, the repeated effort of fundamental data processing can be lessened, so that research efforts can be emphasized on the more challenging climate change impact assessment.

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, five- and six-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 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 to the DOE Energy Efficiency and Renewable Energy (EERE), and 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 previously designed a metabolic pathway to allow *E. coli* to grow on a model compound that can be derived from lignin, but plasmid-based gene expression proved toxic. Upon stably integrating these genes into the *E. coli* chromosome, growth improved. We synthesized the isobutanol production pathway on plasmids for expression in the above strain to create an organism capable of producing isobutanol from lignin derivatives. We also created a metabolic model of this modified *E. coli* strain. When mutations are

introduced into this model, it predicts that the model compound can be converted to liquid fuels at high yield. Further metabolic engineering, in part guided by the model, will increase liquid fuel yield from lignin derivatives. The demonstration that lignin can be biologically converted to liquid fuels could fundamentally alter the biofuels industry by increasing fuel yield from plant biomass and decreasing the toxicity of phenolic compounds.

We made several advances in the function prediction algorithm: (a) integrated Needleman–Wunsch global alignment into our process; (b) tested scaling up PCN algorithm to include fungi and plants (pushing number of database entries to 12M); (c) explored hypothetical predictions in other bacteria, showing that over 98% of the hypothetical genes in all considered bacteria are linked into PCN network, and therefore have at least a tentative range of the function assigned to them. We have also put a special effort into the development of the computational approaches to the verification of the obtained annotation through the usage of the genome context.

Information Shared

Two invention disclosures submitted.

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 to (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's 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

The work of this project has resulted in the addition of significant new model capabilities to PFLOTRAN. We have greatly enhanced the unstructured grid capabilities of the code, enabling accurate representation of subsurface features in permafrost regions, allowing detailed representation of complex drainage basin topography, and avoiding disconnectedness between adjacent 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 (with a modification to account for freezing of surface water) 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 biogeochemistry and have verified its correctness in a series of benchmark problems. All of these capabilities are being exercised in simulations of permafrost hydrology at NGEE-Arctic field sites in the Barrow Environmental Observatory on the North Slope of Alaska.

Information Shared

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06232

Integrative Signaling Modules Guiding Plants 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 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 the USDA National Institute of Food and Agriculture Plant Sciences Program and of the 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 the RACK1-WNK8 complex regulates sugar sensing and is involved in abscisic acid (ABA, a key plant stress hormone) responses.

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 critical components of many of DoD's 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 2013 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.

The C++ implementation of the before-mentioned algorithms is 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 generated $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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06428

Structural Biology of Metabolic and Signaling Pathways in Plants

H. O'Neill, U. Kalluri, W. Heller, L. Coates, L. Petridis, J. Smith

Project Description

The overarching goal of this proposal is to initiate a new structural biology program focused on investigating the metabolic pathways of plants by uniting our demonstrated expertise in molecular biology, biochemistry, plant biology, neutron scattering, and high-performance computing to establish a new core strength at ORNL. We propose to study a single vital plant process, cell wall synthesis. This pathway is selected based on ORNL's established reputation in plant systems biology, and in particular its contributions to understanding the cell wall synthesis, with the aim to further augment ORNL's leadership and competiveness in the area of biomass-based biofuels. Specifically, we will focus on cellulose synthase, the major multi-subunit protein complex involved in cellulose biosynthesis, for which there is little structural information because of its inherent complexity. We will develop the first structural model of CESA, a component of cellulose synthase, based on analysis of its individual domains– using molecular biology, neutron scattering, X-ray crystallography, and computer simulation techniques – to gain insight into the mechanism of cellulose biosynthesis in plants. The technological advances that will result from the proposed work will jump-start a new plant structural biology program at ORNL. The success of this project will also aid in initiating a new area of research that will focus on the development of synthetic biology approaches for biofuel and biopolymer synthesis.

Mission Relevance

This interdisciplinary project will bring together expertise in plant biology and biochemistry, neutron scattering, crystallography, and high-performance computing. Successes within the proposed LDRD effort are expected to (a) lead to fundamental knowledge discovery in the field of cellulose biosynthesis in plants, (b) generate high-impact publications, (c) position ORNL in a uniquely advantageous position to compete for new or renewal funding for biological science programs, and (d) help elevate the relevance and prominence of the SNS/HFIR user program. Relevant sources of follow-on funding include the Biosystems Design and Plant Feedstock genomics FOAs at the DOE Office of Biological and Environmental Research (BER), Early Career Award at DOE Office of Science, Advanced Research Project Agency-Energy (ARPA-E), and Energy Efficiency and Renewable Energy (EERE) FOAs on improvement in biomass productivity. In addition, the complementary nature of the skill sets of the team members and the tool kit of experimental techniques developed during the project will also grow other programs related to research into membrane-driven processes that are currently of interest to the National Institutes of Health.

Results and Accomplishments

In this fiscal year we establishd a protein expression and purification pipeline. To date we have designed and tested 10 constructs that span the three major domains of the CESA proteins. Expression experiments were performed with each construct in five different vectors at two temperatures to determine the optimal conditions for protein expression. The pipeline has been optimized to determine the conditions for expression and purification of any construct in 11 days starting from amplification of a DNA fragment. A small-angle neutron scattering (SANS) study of N-terminal domain of CESA3 was performed. A Guinier fit to the scattering profile of the monomeric protein indicates that the radius of gyration of the protein is ~69 Angstroms. The lack of a peak in the high Q region of the Kratky plot is indicative of a disordered protein. In contrast, the multimeric form of the protein has a helical conformation. Currently, efforts are directed at determining the factors important in the formation of the multimer. We have optimized the SASSENA algorithm required to reproduce experimental SANS profiles. The surrounding solvent was explicitly modeled and included in the scattering computation rather than modeling the solvent implicitly as constant background. Future theoretical scattering profiles from the CESA computational models will include realistic modeling of the molecular environment with their respective deuteration state, to achieve as close agreement with the experimental scattering profiles as possible. A major part of our program development activity this year was to initiate collaborations with university faculty. We were awarded two ORAU high-performance grants led by university faculty to carry out computational analysis of CESA. In addition, a University of Tennessee Knoxville Joint Directed Research and Development (UTK JDRD) grant was awarded to contribute to the development of approaches for advanced labeling techniques of proteins. Finally, a faculty researcher and student were awarded an ORAU Historically Black Colleges and Universities/Mintority Education Institutions (HBCU/MEI) summer faculty grant to contribute to protein expression and purification efforts.

Information Shared

None.

06436

Developing Grazing Incident Small-Angle Neutron Scattering for Studying the Interplay between Amyloid-beta Peptide and Cholesterol in Lipid Bilayers

S. Qian, W. Heller, V. Urban, H. O'Neill

Project Description

Grazing Incident Small-Angle Neutron Scattering (GISANS) is a versatile technique for characterizing nanoscale structures and correlations at surfaces, buried interfaces, and in thin films. GISANS combines features from small-angle scattering and diffused reflectivity to provide mesoscopic length scale structural information on thin film materials and is ideally suited to the study of protein-lipid membrane interactions. We are developing GISANS on the Bio-SANS instrument at ORNL to study the interaction between amyloid-beta peptide (Aβ) and cholesterol in lipid bilayers. Aβ is regarded as a factor in the development of Alzheimer's disease (AD), the most common form of dementia. Accumulating evidence points to the positive association between cholesterol and AD, but a molecular-level interaction between cholesterol and Aβ has not been established. GISANS, when combined with selective deuteration and contrast matching, will provide new, unique insight into this important problem. This research will not only advance the understanding of the interplay of Aβ and cholesterol at the molecular level but will also

implement an important new tool for materials research at ORNL by extending the capabilities of its world-leading neutron scattering instruments.

Mission Relevance

This research proposes to develop GISANS on the Bio-SANS instrument at ORNL and use it to study the interaction between amyloid-beta (Aβ) peptide and cholesterol in lipid bilayers. GISANS, combined with selective deuteration and contrast variation technique, is a powerful tool to characterize nano- to meso-scale structures and correlations at material surfaces, buried interfaces, and in thin films. The implementation of GISANS will not only benefit biological study of membrane-protein interaction and other soft matter thin films but will also provide new capabilities for DOE mission-critical materials research. This work will have a broad impact on membrane protein research community as it demonstrates a new capability to study membrane protein structure in a membrane environment. The work will form the basis of a program studying disease and energy-related membrane proteins in lipid membranes and will position ORNL to attract additional funding from the NIH and DOE.

Results and Accomplishments

A goniometer sample stage with three axes (x, z, rotation) to hold a film-like sample in a GISANS geometry was commissioned on the Bio-SANS instrument in July 2013. The goniometer interfaces with a chamber connected to a relative humidity generator (an RH-200 by L&C Co.) that provides a suitable sample environment for studying biomembrane films. A beam time proposal entitled "Study of Interplay between amyloid beta-peptide and cholesterol in bilayer" was awarded 3 days on the Bio-SANS during the 2013B cycle. Studies of the secondary structure of the Abeta(1-40) peptide by circular dichroism (CD) spectroscopy showed how the peptide conformation changes with time in response to different lipid compositions, providing guidance for SANS and GISANS sample preparation. Data reduction routines for the GISANS data have been developed. Data analysis for the vesicle solution scattering was implemented and applied to data from another lipid peptide system that has guided additional development of more advanced modeling methods for investigating the interaction of Abeta(1-40) with cholesterol-containing vesicles. Dr. Andy Sarles (UTK) was awarded JDRD funding to support collaboration with this project for his proposal entitled "Single channel recordings and GISANS of amyloid-beta peptides in fully hydrated, unilamellar lipid bilayers." A jointly DOE-BER/NIH-funded Biomedical Neutron Technology Research Center is being proposed for neutron scattering for structural biology. GISANS development is included in one of core projects. The Frontiers in Neutron Structural Biology workshop was held at ORNL April 16–18, 2013, to build community support for the proposal.

Information Shared

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06442

Lignin Fractionation and Purification with Nanoporous Inorganic Membranes for High-Strength Structural Carbon Fiber and Value-Added Co-Products

R.R. Bhave, J. Messman

Project Description

We propose to develop a novel cost-effective approach utilizing precisely tuned nanoporous membranes for lignin fractionation and purification to remove low molecular (LMW) materials to substantially increase the quality of the high molecular weight (HMW) lignin fraction essential for high-strength structural carbon fiber. The current state of the art, such as the LignoBoost and ethanol-based Organosolv processes, both developed for the pulp and paper industry, are unsuitable for fractionating lignin into discrete fractions in a continuous operation and result in lignin-rich residues combined with hemicellulose which must be removed separately by acid treatment and/or precipitation.

A single-step membrane-based simultaneous fractionation and purification (with diafiltration) process is proposed for efficient isolation of lignin of desired molecular weight fractions from a variety of renewable feedstocks such as hybrid poplar, switchgrass, and mixed hardwoods. We propose to develop and evaluate high-permeability nanoporous membranes in the 1 to 5 nm pore diameter (<10,000 mol.wt. cut-off) functionalized to maximize throughput and minimize fouling. This process will result in two valuable streams: purified HMW lignin fraction and LMW by-products including cellulosics and phenolics. It is hypothesized that LMW fractions of lignin will be useful in adhesive formulations and activated glassy carbon applications, whereas HMW residues of lignin can be converted into structural carbon. The proposed work will support the ongoing ORNL program on carbon fiber development, which has identified the critical need to substantially improve the quality of lignin used for structural carbon fiber production.

Mission Relevance

Separations is one of the key focus areas of DOE Energy Efficiency and Renewable Energy (EERE)/Advanced Manufacturing Office (AMO). Our novel research initiative in the development of high-strength carbon fiber for structural and non-structural applications using membranes can deliver competitive performance compared to the current state of the art. We anticipate significant benefits to the DOE-EERE/AMO program and the Carbon Fiber Technology Facility resulting from this research that focuses on isolation of HMU lignin for composite carbon fiber products.

Results and Accomplishments

In FY 2013, we evaluated six lignin feedstocks that included both softwood and hardwood varieties. These were Mascoma, Lignol, Greenwood Resources hybrid poplar, Kruger low ash, FP Innovations (FPI) and Domtar. We established that lignin can be effectively separated to remove the LMW fraction to isolate HMW lignin using nanoporous inorganic membranes. These tests were conducted on samples containing up to 10 wt.% lignin that were prepared in dimethyl acetamide (DMAC), a typical industrial solvent, as well as 2 wt.% NaOH. The membrane separation process involved concentration and diafiltration to selectively remove LMW lignin while retaining the HMW fraction. A systematic study was performed to determine optimal pore size and molecular weight cutoff using several membranes from 3 to 50 nm pore diameter. Membrane separation tests with DMAC as the solvent were performed at 60–65˚C and 4–5 bar transmembrane pressure (TMP). The separation tests using aqueous NaOH were performed at temperatures in the range of 75–85˚C and TMP of 5–6 bar, similar to conditions in the Kraft

lignin process widely used in the pulp and paper industry. The concentration of HMW fraction in the permeate was more than an order of magnitude lower when compared to the concentration in the feed sample. These results clearly demonstrated that HMW materials were selectively isolated in the retentate and LMW materials were preferentially transported into the permeate. These purified HMW materials serve as the base material to produce carbon fiber and to evaluate structural and mechanical properties.

We have also performed quantitative determination of lignin polydispersity index (PDI). The HMW lignin isolated with membrane showed a PDI value substantially lower (2.56) compared to the starting feed material (9.33). In the presence of agglomeration, however, the PDI was found to be about 7. Lower PDI of HMW lignin may have a beneficial impact on the mechanical properties (i.e., higher modulus) of lignin-based carbon fiber.

The enriched concentrate containing HMW lignin was dried and then used to spin precursor fibers. Preliminary carbon fiber preparation and evaluation indicate excellent fiber spinnability characteristics. The glass transition temperature (T_g) of HMW FPI lignin isolated from aqueous NaOH was >200˚C, which is very desirable for stabilization prior to carbonization of precursor fiber. The T_g of the HMW lignin prepared from DMAC was however substantially lower. This may be attributed to the greater tendency for agglomeration in aprotic solvents such as DMAC compared to a high-ionic-strength caustic solution.

For experiments with FPI and Domtar lignin in aqueous NaOH, the flux averaged 45–55 liters/hr-m^2 at a pressure of about 60–75 psi (4–5 bar) using 5–30 nm membranes. However, the flux values for FPI and Domtar lignin solubilized in DMAC were substantially lower in the range of 20–25 liters/hr-m^2 using 5–30 nm membranes. This may be due to pore fouling with a larger percentage of LMW lignin resulting from agglomeration. This also leads to much broader MWD and polydispersity. The tubular membranes tested to date performed well without excessive plugging or fouling and were fully regenerated by flowing through pure solvent (DMAC or aqueous NaOH) to remove all lignin from the membrane surface and support structure.

Information Shared

There are no publications for FY 2013.

06450

Stochastic Parameterization of the Influence of Subgrid-Scale Land Heterogeneity on Convection in a Climate Model

D. Ricciuto, S. Mahajan, R. Archibald, J. Mao, X. Shi, C. Yang, R. Langan

Project Description

Extreme precipitation events have high impact, but are currently poorly modeled. Land-atmosphere coupling often plays a major role in determining the intensity and duration of these events. The purpose of this project is to develop a parameterization to simulate sub-grid-scale influences of landscape features and develop time-dependent forcing flux probability distribution functions (PDF) to influence convection in the Community Atmosphere Model. The parameterization is based on a multiscale and multiphysics code and incorporates state-of-the-art adaptive stochastic collocation techniques to select model PDFs. The stochastic term represents the effects of subgrid variability in land-atmosphere energy fluxes. The initial focus is improving modeled precipitation distributions at intensively observed sites (model

gridcells) where land-atmosphere coupling is strong and covering a wide range of terrestrial ecosystem types. This method will also allow for the uncertainty quantification (UQ) of key model outputs. After the model is refined, it will be tested in the global, fully coupled framework of the Community Earth System Model (CESM).

Mission Relevance

This proposal supports ORNL and DOE missions to advance understanding in the climate system. Improving the performance of climate models is a key mission in particular of the DOE Office of Biological and Environmental Research (BER) and is a primary driver for research funding. One key outcome of this project is a highly efficient single-column land-atmosphere testbed for earth system models that will facilitate the testing of new model code. The proposal also supports the mission of the Laboratory in developing large user facilities. Specifically, this proposal supports the mission to develop leadership-class computers by defining and exploring technically challenging scientific directions that can only be addressed on leadership-class computers.

Results and Accomplishments

A method for incorporating stochasticity in land-atmosphere coupling was developed and implemented in the Community Earth System Model (CESM). Specifically, the stochastic term represents sub-grid variability in the contribution of energy fluxes from the Community Land Model (CLM) to the single-column atmosphere model (SCM) from different plant functional types (PFTs). Initial results have shown that including the stochastic term improves the modeled distribution of precipitation compared to observations at the Atmospheric Radiation Measurement site in Oklahoma (ARM-SGP), especially for extreme events. We have also conducted preliminary experiments with a low-resolution version of the global CESM (2.8×2.8 degrees) for 5 years with two stochastic approaches. This was made possible by using a flexible framework adaptable from the SCM to the global model. Initial analyses of the simulations generally reveal results comparable to those of the SCM.

Input data files and code infrastructure were developed to support running ensembles of the coupled CLM-SCM system for any land gridcell in the Community Earth System Model (CESM). Several sites around the globe with different PFT distributions are being tested. In addition, a methodology for calibration is being developed that will inform parameters controlling the PDF of the stochastic term. We have presented this research at various venues and are working to incorporate further development of these methods into a new DOE BER multilab SFA for Earth System modeling. Multi-component UQ and integration are of key importance to this proposal.

Information Shared

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06472

High-Voltage Electrode Development for a Neutron Electric Dipole Moment Experiment at the SNS

V. Cianciolo, M. Dadmun, F. Meyer, H.M. Meyer III

Project Description

An experiment (nEDM@SNS) has been proposed to measure the neutron electric dipole moment with unprecedented precision at the Spallation Neutron Source (SNS). nEDM@SNS is a very high priority for the US Nuclear Physics community due to its potential to shed light on the mechanism responsible for producing matter in the aftermath of the Big Bang.

One significant outstanding technical issue is the need to develop a high-voltage electrode meeting several unique and challenging materials requirements. We propose to carry out a set of systematic studies to evaluate two possible electrode fabrication techniques: 1) forming carbon nanoparticle / polymer solutions and painting the electrode surface and 2) using ion implantation techniques to deposit a metallic layer immediately under the surface of the acrylic surface. We will characterize properties of small samples versus appropriate fabrication parameters. Techniques used to produce promising samples will be used to fabricate small three-dimensional electrodes that will be subjected to large electric fields at cryogenic temperatures.

Successful completion of this proposed research will significantly increase the chances for nEDM@SNS approval, with the associated construction effort, long-term programmatic effort, and a high degree of visibility for ORNL and the SNS on a high-priority 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

Robust carbon-acrylic composite coatings satisfying resistivity requirements have been obtained. Variations in coating performance vs. control parameters (nanoparticle size, solvent, application technique) have been obtained and used to optimize the coating to reach the target requirements: 50 kV/cm has been obtained.

Variations in electrode performance vs. control parameters (fluence and incident energy) have been obtained for tungsten implantation. Reasonable robustness and resistivity in the desired range have been obtained.

Information Shared

M.E. Bannister, H. Hijazi, H. M. Meyer III, V. Cianciolo, and F.W. Meyer, "Surface-conductivity enhancement of PMMA by keV-energy metal-ion implantation," 2013 EMRS Spring Meeting, Strasbourg, France, Symposium on Ion Beam Applications Proceedings, Nuclear Instruments in Physics Research B (to be published).

06508

Quantum State Stabilization for Unbiased Random Number Generation

R. Pooser, P. Evans, T. Humble, N. Paul

Project Description

Controlling quantum systems is an essential component of quantum information technologies. Here we propose to implement a new means of quantum control termed quantum state stabilization (QSS). QSS performs nondestructive diagnostics and applies closed-loop feedback control upon a quantum system to ensure its stabilization to a desired state. This is a departure from the current norm of open-loop quantum control widely used today. As an illustration of this new methodology, we will apply QSS to demonstrate a self-correcting quantum random number generator (QRNG). QRNGs represent a very important class of quantum information technologies that supports a variety of cryptographic and communication applications. By locking onto a desired bias-free quantum state, the output state of the QRNG can be tuned to ensure that the source always outputs numbers with maximal entropy (i.e., minimal predictability). Our proposal is the first design, development, and implementation of the QSS methodology, and the resulting ability to stabilize quantum states will represent a significant advance in quantum information science and quantum device engineering. The QSS implementation of a self-correcting QRNG will also result in a first-of-its-kind, bias-free device that offers a radical departure from previously known random number generators.

Mission Relevance

Quantum state stabilization (QSS) will benefit DOE in several key ways. QSS will make several quantum information protocols more tractable by exerting quantum control automatically in closed-loop form. In particular, DOE is interested in quantum simulation, and QSS would enable automatic quantum control over large-scale systems for this purpose. As a direct result of this project, a self-correcting quantum random number generator would be of great interest not only to DOE but also to the National Security Agency (NSA), and any other agency interested in cryptography and authentication. A trustworthy true random number generator that detects and removes its own bias would be the first device of its kind.

Results and Accomplishments

Our year one milestones were 100% completed by the end of FY 2013, and we foresee no major obstacles to continuing towards the second-year goals. The milestones we accomplished are as follows:
1) developed a theory of quantum state stabilization (QSS); 2) developed an algorithmically defined design technique for quantum information technology devices; 3) applied the theory of milestones 1 and 2 to the design of a self-correcting quantum random number generator; 4) developed and built a new weak measurement device that allows us to measure the polarization statistics of an ensemble of photons; 5) built a new quantum random number generator using tapered amplifiers, which is extensible for the application of QSS via weak measurement and feedback. We also developed a new bias detection technique that uses Bayesian hypothesis updating to validate assumptions about the quantum state, and we have developed a new binning technique which uses the QRNG's bias to whiten its own distribution. We published several conference papers and presentations, noted below. We are currently writing two publications on the subject of the combined theoretical and experimental aspects of QSS as applied to QRNGs and on novel binning and bias detection techniques.

Information Shared

T. S. Humble, R. C. Pooser, and K. A. Britt, "Quantum Statistical Testing of a QRNG Algorithm," Proc. IEEE Photonics Society Topical Meeting Series, 149 – 150, 2013.

R. C. Pooser, P. G. Evans, T. S. Humble, W. P. Grice, and B. P. Williams, "Self Correcting Quantum Random Number Generators using Tapered Amplifiers," Proc. IEEE Photonics Society Topical Meeting Series, 147 – 148, 2013.

R. C. Pooser, P. G. Evans, T. S. Humble, W. P. Grice, and B. P. Williams, "Self Correcting Quantum Random Number Generators using Tapered Amplifiers." Quantum Information and Measurement, 2013 http://dx.doi.org/10.1364/QIM.2013.W6.37.

R. C. Pooser, T. S. Humble, P. G. Evans, W. P. Grice, and B. P. Williams, "An algorithmically defined QRNG." Third international conference on quantum cryptography, 2013 (poster: http://2013.qcrypt.net/).

06509

Single-Crystal and Single-Crystal-Like Graphene in Large Areas for Electronic and Energy Applications

A. Goyal, L. Heatherly, I. Vlassiouk, A. Belianinov, A. Baddorf

Project Description

Graphene is one of the strongest, lightest, and most conductive materials known and hence has the potential to revolutionize the world with new "carbon-based electronics." A new class of high-speed transistors and integrated circuits that consume less energy than conventional silicon electronics could potentially be realized if large sheets of single-crystal graphene can be grown. Graphene-based transistors can operate at higher frequency because of the faster speed at which electrons in graphene move compared to silicon. Then there are graphene applications in practically every energy-related application including batteries, photovoltaics, grid technologies, building technologies, bio-devices, etc. It is the promise of such applications that resulted in the 2010 Nobel Prize. Grain boundaries (GBs) have detrimental effects on electronic, thermal, and mechanical properties of graphene, including reduced electronic mobility, lower thermal conductivity, and reduced ultimate mechanical strength. For electronic applications, mobilities are of greatest concern. It is believed that large-area, single-crystal graphene or very large-grain, single-crystal-like graphene would revolutionize the field of flexible electronics. Scientists worldwide have been trying to achieve this holy grail of fabricating such large-area, single-crystal graphene films. While heteroepitaxy of graphene has been demonstrated in small areas on select surfaces, large-area substrates amenable to graphene heteroepitaxy are so far not available. This project precisely addresses this challenge via innovative materials science and engineering followed by development of advanced manufacturing processes for realizing large-area, single-crystal, or single-crystal-like metallic substrates with (111) crystallographic orientation using thermo-mechanical processing and with suitable surfaces for hetereoepitaxial growth of graphene. This would eventually result in a scalable process for fabrication of large-area, single-crystal, or single-crystal-like graphene sheets. Experimental analysis will be conducted to understand fundamental material issues followed by development of innovative solutions towards realizing metallic substrates with single-crystal or single-crystal-like (111) crystallographic orientation. Success in the project will establish unique expertise in this important area of large-area, single-crystal, or very large-grain, single-crystal-like graphene at ORNL and lead to multiple opportunities for follow-on funding and technology transfer.

Mission Relevance

Success in the project could attract major R&D investments to the Laboratory because ORNL could apply the fabricated large-area, single-crystal graphene to all kinds of devices including transistors, batteries, solar cells, etc. The applications of high-quality, single-crystal graphene are too many to list.

Success in the project is expected to attract funding from DOE's EERE (Advanced Manufacturing), DOE-BES, ARPA-E, NASA, DARPA, ONR, and AFSOR programs. A specific, ongoing DARPA program of interest is The Carbon Electronics for RF Applications (CERA) program on wafer-scale graphene synthesis approaches for ultrahigh-speed, low-power graphene field effect transistors for RF/millimeter-wave circuits from the Microsystems Technology Office. If we are successful in this LDRD project, it will stand a very good chance of obtaining funding from this DARPA program and other programs focused on electronic and energy applications of graphene.

We fully expect to create new intellectual property and a patent portfolio related to the fabrication of large-area, single-crystal, or single-crystal-like graphene, based on the results obtained in this project. Hence, in addition to research funding, success in the project is also expected to lead to follow-on funding from the LDRD Technology Innovation Initiative at ORNL, followed by potential private equity investment for a potential new entity spun from the Laboratory. Also, the possibility of funds via licensing opportunities and new partnerships is a possible outcome.

Results and Accomplishments

There were three main tasks in the proposal: (1) investigation into fabrication of large-area (111) textured substrates via epitaxy on lower-symmetry surfaces; (2) investigation into fabrication of large-area (111) textured substrates via solid state, secondary recrystallization; and (3) studies on the growth of heteroepitaxial graphene on (111) textured surfaces. The near-term technical goals of the project were (a) evidence of FCC (111) or hexagonal close-packed (HCP) (0001) oriented surfaces on cubic surfaces with lower symmetry or broken symmetry and/or evidence of successful seeding and growth of FCC (111) seed crystal orientation into cube-oriented substrate and (b) evidence for heteroepitaxial growth of graphene on appropriately oriented single-crystal and/or single-crystal-like surfaces. The project goals were very *high risk* as no reports of (111) textured, large-area surfaces exist in the literature and there were no reports of graphene epitaxy via atmospheric-pressure chemical vapor deposition (APCVD). Nevertheless, significant technical progress has been made, and both near-term objectives were met. Details on substrate fabrication and heteroepitaxial graphene growth are discussed as follows.

(1) Large-area (111) textured substrates via epitaxy on lower-symmetry surfaces

a. Fabrication of substrates with broken symmetry

This was accomplished by performing studies of controlled secondary recrystallization on fully, cube-textured, {100}<100> oriented copper substrates. The goal was to isolate a single, secondary recrystallized grain of copper using purely high-rate, solid-state recrystallization and converting the entire cube-textured, polycrystalline substrate into a highly mis-oriented or miscut grain. All annealing experiments to form the cube-textured copper were done in a high-temperature, roll-to-roll system. Briefly, oxygen-free copper was heavily deformed successively to a deformation greater than 99%. The sample was then annealed at around 900°C to form a very sharp, single-orientation, {100}<100>, cube texture. Four broad (111) poles are expected for a single-orientation cube texture. The breadth of the peaks revealed a mosaic or full-width-half-maximum (FWHM) of ~ 5° in all directions. The sample was tapered down prior to undergoing secondary recrystallization. In the tapered region, a single, off-cube, or rotated cube grain was nucleated via the process of secondary recrystallization by heating above the secondary recrystallization temperature and then propagated by moving the sample along the length using

the roll-to-roll system above. By this process, a single grain was extended into the entire 2-cm-long length (1-cm-wide sample), with the grain having a reduced or broken cube symmetry since the grain was rotated 18° off the cube orientation.

We conducted studies with BCC materials with a goal to form (110) oriented substrates that have a lower symmetry than a cube-oriented, {100}<100> oriented substrates, by going from a four-fold to a two-fold symmetry surface. The pole figures obtained show an ideal (110) texture. Upon these {110}<100> oriented iron substrates, we deposited heteroepitaxial FCC copper films. As expected, FCC copper on BCC, (110) surface leads to the desired (111) orientation. The copper (111) pole figure shows the characteristic three-fold symmetry of the (111) oriented planes grown heteroepitaxially on the (110) surface of iron. So now we have both a oriented copper (111) surface as well as an oriented iron (110) surface on which we can grow graphene directly. Growth of graphene on copper is well studied. Growth on iron surfaces is expected to be similar to growth on nickel surfaces, and similar graphene growth conditions as used for nickel are expected to work.

(2) Copper (111) textured substrates via solid state, secondary recrystallization

For this objective, all sub-tasks have been done except the last – (a) fabrication of cube-oriented copper, (b) preparation of (111) single-crystal seeds with a polished surface, (c) development of attachment procedures of seed crystal on to cube-textured copper foil, and (d) optimization of thermal processing conditions to nucleate a secondary recrystallized (111) orientation in the copper foil via high-rate, solid-state grain growth. The first three points have been fully completed, and experiments continue to be done to develop the right thermal processing conditions to result in seeding. Initial results look very promising.

(3) Evidence for heteroepitaxial growth of graphene on appropriately oriented single-crystal and/or single-crystal-like surfaces

Experiments were conducted using both atmospheric-pressure chemical vapor deposition (APCVD) and low-pressure chemical vapor deposition (LPCVD). For APCVD, the procedure was heating the samples for 30 min at 1000°C under the 500 sccm flow of 2.5% hydrogen in argon. Graphene was grown by introducing 40 ppm of methane, keeping the total flow equal to 500 sccm. After 90 min of synthesis, methane was turned off and the furnace was cooled to the room temperature. Several kinds of samples with (111) and (110) orientation were used. The first involved development of copper (111) and (110) surfaces via heteroepitaxial growth on YSZ (111) or (110) substrates. Experiments were done to develop conditions which result in a single copper orientation. Graphene films were grown on these heterepitaxial copper films on YSZ substrates as well as on copper single crystals. On both the (110) and the (111) surfaces, heteroepitaxial alignment was obtained as determined by low-energy electron diffraction (LEED) patterns. From copper surfaces exposed to air, no LEED patterns are observed. The observed LEED pattern is a collective pattern from the graphene grains on the copper (111) sample. The LEED pattern shows the six spots expected from graphene. This data unequivocally establishes evidence for heteroepitaxial graphene growth. Please note that this project offers the *only* possibility reported thus far for fabrication of large-area, single-crystal or single-crystal-like graphene.

Information Shared

None to report so far.

06544

Understanding and Controlling the Nanoscale to Mesoscale Evolution of Structure and Function in Electroactive Molecules during Thin Film Formation

S. Smith, B. Sumpter, D. Geohegan, G. Smith, K. Hong, K. Xiao, V. Lauter, J. Browning, C. Do, I. Ivanov

Project Description

The overarching goal of this proposal is to study the dynamics of structural evolution of model electroactive molecules from single chain (solution) to thin films using neutron scattering, optoelectronic characterization, and theoretical modeling. It has been demonstrated that the optoelectronic properties and morphology of optoelectronic materials are dictated by their MW, chain conformation, and processing solvents. Critical information about their dynamical and structural evolution from dilute solution to thin film assembly is still elusive. The focus of this project is to develop a fundamental understanding of how the structure, ranging from nano-, to meso-, and to macroscale, of optoelectronic materials is correlated to their properties and how this structure-property relationship is impacted by the time-dependent processing conditions. Our approach combines MD simulations and a SCF theoretical approach with carefully designed ex situ and in situ experiments to determine the structures and dynamics of a series of well-defined model electroactive molecules (P3HT and bithiophene derivatives) in various environments. This project provides key guidelines to control of the dynamics and structures of optoelectronic materials during solution processing. This proposal complements current ongoing R&D efforts in optoelectronic active polymers.

Mission Relevance

This proposal complements current ongoing R&D effort in optoelectronic active polymers. The success of this project will strengthen ORNL's leadership in neutron science, material synthesis, characterization, and computational science, and position ORNL strongly for the forthcoming Office of Basic Energy Sciences (BES) initiatives in meso-scale science.

The project will lay out a foundation for new neutron experiments with active incorporation of computer simulation and statistical modeling. The Center for Nanophase Materials Sciences (CNMS) and the Spallation Neutron Source (SNS) collaborative effort is foreseen as enabling tool for the experiment.

Results and Accomplishments

Optical and structural properties of poly (3-butyl-thiophene) (P3BT) aggregates were studied in solutions and films cast from an aggregate-inducing binary solvent. The electronic spectra of the aggregates were correlated with the photoluminescence spectra and Raman scattering signatures. The results were modeled using statistical techniques such PCA and MCR and others were modeled to identify the most probable molecular orientation during thermochromic conformational transformations and aggregations in solutions.

Information Shared

J.-M. Y. Carrillo, R. Kumar, M. Goswami, B. G. Sumpter, and W. M. Brown, "Coarse-Grained Molecular Dynamics Simulations of Thermal Annealing of P3HT:PCBM Blends for Organic Photovoltaic Applications," *Phys. Chem. Chem. Phys.* **15**, 17873–17882 (2013), DOI: 10.1039/C3CP53271B.

M. G. Stanford, D. Hu, J. K. Keum, J. Zhu, K. Hong, B. Hu, B. G. Sumpter, S. Smith, and I. N. Ivanov, "Correlation of Structure and Optical Signatures of Poly(3-butylthiophene) Nanofiber Aggregates in Binary Solvents and Thin Films," in preparation.
Z. Zhu, P. Bonnesen, B. Sumpter, K. Hong, C. Do, and I. Ivanov, "Thermodynamics and Structure-Functional changes in Thermo-Chromic Polythiophene Brushes in Solution," in preparation.

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, B. Radhakrishnan

Project Description

A recent breakthrough by ORNL researchers was the discovery 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 for 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 April of 2012. Highlights of the project in the past year include designing, fabricating, and testing the melting and solidification test apparatus. The environmental chamber and testing apparatus allow us to heat materials beyond their melting points (approximately 1773 K or 1,500°C) in an inert environment, while being magnetized by a superconducting (SC) solenoid magnet at 4.2 K. Due to problems with the vertical magnet, we have been able to perform experiments in the 9 Tesla, horizontal SC magnet at ORNL and verify that we can produce single-crystal or highly

textured materials using facilities at ORNL. We have also designed and fabricated a differential scanning calorimeter system (DSC) that can be integrated in the test apparatus and precisely characterize shifts in the phase diagram due to application of magnetic field. Our project includes a parallel effort to create a mathematical model for theoretical analysis and exploration of the phenomena behind material solidification under high magnetic field, and we report the results of these simulations and analysis. We have filed two invention disclosures on the method and apparatus for this project, and we are preparing a second invention disclosure on the high-magnetic-field DSC system.

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. Manuscripts are being prepared regarding the Monte Carlo simulations. Intellectual property is being prepared regarding the DSC system and publications will follow.

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 project 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 involves 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 is on 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 have sufficiently low radioactivity to enable safe target production and handling.

Mission Relevance

Success in this work will invigorate DOE's 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 relevant to the recovery of ^{251}Cf material included the following items. (1) Approximately 160 sources currently in the californium storage pool in Building 7930 were evaluated to determine which sources provided the best option for enriched ^{251}Cf recovery. Seventeen ^{251}Cf sources were identified and removed from the storage pool. (2) A tool (small jeweler's lathe) was obtained and modified for cutting open the californium capsules. The modifications addressed the safety concerns regarding potential ignition of zirconium filings. (3) The lathe was used to remove the outer capsule of the selected zirconium-encapsulated californium sources, and the inner capsules were cut in half and acid leached to remove the californium and curium material. The leach solution contained 15.8 mg total californium (5.7 mg ^{251}Cf, 7.6 mg ^{249}Cf, 2.5 mg ^{250}Cf, and 0.007 mg ^{252}Cf). (4) Chemical separation and

purification, with 0.25 *M* AHIB (α-hydroxyisobuteric acid) at pH 4.2 and 4.6, were performed with excellent recovery, and the californium fraction was concentrated by cation exchange. A fraction containing 100 mg of valuable ^{248}Cm was also recovered.

Work completed relevant to the development of electrodeposition method for titanium target production included the following items. (1) An electrodeposition technique using isobutyl alcohol was developed. The electrodeposition procedure, including the use of high-voltage equipment, was reviewed, and Research Safety Summaries (RSS), Radiation Work Permits (RWP), and Unreviewed Safety Question Determinations (USQD) were completed. (2) An electrodeposition unit for the curved rectangular titanium foil sectors that are to be used to assemble an accelerator target wheel was designed and fabricated. A technique for mounting thin titanium foil onto the electrodepostion sector frame was developed. (3) Multiple tests of the electrodeposition procedure were conducted using 1.2 mg natural samarium with ^{153}Sm tracer as a surrogate for californium. Optimum parameters and techniques (0.3 mA/cm^2, 250 volts, Teflon-coated aluminum frames, magnetic stirrer, and 4-hour deposition time) resulted in desired deposition levels of 350 μg/cm^2. Relatively uniform deposition was confirmed by radiographic imaging techniques.

Work completed relevant to shipping of the completed ^{251}Cf foils included the following items. (1) Shipping holders were designed for the final titanium foil sectors that will provide protection from damage for the sectors and radiation shielding for personnel handling the target sectors. (2) Possible shipping methods were evaluated, including the use of a Type B container. (3) Researchers from the Joint Institute for Nuclear Research, Dubna, Russia, were consulted concerning the assembly of the titanium foil sectors onto the target wheel and the related dose levels.

Information Shared

None for FY 2013.

06736

Pulsed Magnetic Fields for Neutron Measurements

G.E. Granroth, M. Matsuda, J. Carmichael

Project Description

Magnetic fields provide a unique capability to tune states in novel systems such as quantum magnets, multiferroics, metal-organics, and novel superconductors. Recent reports, commissioned by DOE and the National Research Council (NRC), highlight needed resources for such studies. The NRC report emphasizes that the Spallation Neutron Source (SNS), if combined with fields in excess of 25 T, would provide "a world-leading capability" for studying material response. Recent SNS experiments provided evidence for different phases up to 30 T by diffraction on samples in pulsed magnetic fields. However critical research and development work is required to take this technique beyond a demonstration test experiment to a versatile scientific capability for Neutron Sciences Directorate (NScD) scientists and users. Completing this goal will be accomplished through science-based use of the pulsed magnet that will be facilitated by a postdoctoral fellow. Already the science driving the demonstration experiment identified key tasks for this proposal. First the background from the coils of the pulsed magnet imposes limitations on possible samples. To reduce background and, consequently, expand the capability we will need to develop the ability to wind our own coils. Second, the scientific impact of a pulsed magnet for NScD would be greatly enhanced by extension of this technique to multiple instruments at SNS,

including NOMAD, SANS, SNAP, HYSPEC, Corelli, or TOPAZ. Completing these tasks will develop technical skills and familiarity with high fields and pulsed fields at ORNL and will position NScD to pursue higher field projects in the future.

Mission Relevance

Our plan is to expand the use of pulsed high magnetic fields for neutron scattering enabling measurements at unprecedented fields. The effectiveness of these devices has been demonstrated in a prototypical manner. Improved shielding and expanded availability of this technique will make this a routine way of investigating novel behavior in many materials. Successful completion of work on pulsed magnets will expand our expertise with high magnetic field measurements, positioning us to pursue future higher field projects.

Results and Accomplishments

We have accomplished all of the major goals of this LDRD project for fiscal year 2013. The major goals for the FY were to get people and materials in place for FY 2014. Specifically we hired Jooseop Lee as a postdoc (start date October 7, 2013) to work on experiments to further the development of the technique. G. Matt Rucker, along with Justin Carmichael and Masaaki Matsuda, visited Professor Nojiri's laboratory at Tohoku University, where they learned the details of winding these specialized high field coils. We purchased the materials for coil winding, including the coil winder and tensioner. All the devices are assembled, and the technician G. Matt Rucker wound a practice coil to test some technique. A mockup coil with off-the-shelf copper wire is ready to be wound. The specialized high-strength CuAg wire for making the coils is on order and will be delivered this fall ready for a first wind of an ORNL coil in the spring. Boron nitride shielding pieces are on order and will be machined to produce reduced background configurations for a December 2013 experiment. A design for an integrated safety system is complete.

07041

Rapid and Highly Fieldable Viral Diagnostics

T. McKnight, N. Ericson, D. Hensley, J. Parks

Project Description

This project investigated a potential new approach for rapid, reagentless, and thereby highly fieldable, diagnostics for determination of active viral infection of a large subset of priority pathogens impacting human and livestock health. Technology is based on delivery and rapid expression of bioreporting DNA constructs in isolated white blood cells (derived from a fingerprick of blood). Rapid response is dependent upon the presence and activity of specific viral replication complexes within leukocyte populations. Initial proof-of-principle experiments targeted Dengue Fever Virus, which impacts over 40% of the world population and infects upwards to 100 million people each year.

Mission Relevance

Development of an innovative platform that provides rapid and fieldable diagnostics of active viral infection will enable accelerated response to threats to national and global security including direct threats to human health and threats to our livestock and associated food supply chains. This supports the Department of Energy's mission of improving quality of life through innovations in science and technology, and the Laboratory's mission to "Deliver scientific discoveries and technical breakthroughs

that will accelerate the development and deployment of solutions for…global security, and in doing so create economic opportunity for the nation."

Results and Accomplishments

With support of facility safety personnel, a BSL-2 laboratory was authorized to work with infectious Dengue virus (DenV).

A DNA-launched viral replicon has been constructed comprising green fluorescent protein (GFP) flanked by viral sequences from DenV-2. Impalefection-mediated delivery and expression of this construct provides measurable GFP signal in DenV receptive cell lines within 2 hr of delivery.

Cell lines acutely infected with DenV-2 NGC have been demonstrated to exhibit measurably higher levels of virally amplified replicon signal (GFP) versus a non-amplified control signal within 6 hr of viral infection, providing proof of principle of this approach.

Fieldability of the approach has been demonstrated at the proof-of-principle level using commercially available size exclusion filters for cellular enrichment and as a substrate for impalefection-mediated delivery of the bioreporting DNA construct.

RNA sequence alignments of various serotypes and substrains of DenV have been performed to demonstrate the potential of this approach for determining serotype and substrain of DenV infections.

Information Shared

U.S. Patent Application Filed, "Rapid and Highly Fieldable Viral Diagnostic", Application No. 61/791,923.

Non-disclosure agreements have been put in place with a number of potential domestic and international interests including both commercial and state-sponsored entities.

07042

Algorithm Resilience with Respect to Hardware Error

M. Stoyanov

Project Description

We propose a new analytic approach for improving algorithm resilience with respect to silent errors encountered in modern extreme-scale computers. Our objective is to extend the current framework of numerical analysis by removing the assumption that all arithmetic operations can be computed accurately within machine precision. We introduce the concept of "hardware error" added to our numerical approximations by potentially unreliable hardware. Using rigorous analysis, we develop new algorithms that minimize the propagation of hardware error and therefore guarantee convergence even when faults are encountered. Furthermore, our approach results in optimal cost with respect to the overhead associated with the resilience, thus minimizing computational cost and retaining the same convergence rate as their non-resilient counterparts. We focus our attention on iterative linear solvers and non-linear Newton iteration since they are associated with the bulk of the computations in most common problems; however, our framework extends to other methods.

Mission Relevance

High-Performance Computing is an essential part the DOE science mission, and within the next decade supercomputers are expected to transition from the current multi-petascale power to the exascale. However, the increase of computational throughput has also led to a decrease in reliability, and software resilience has been recognized as one of the critical challenges on the path to exascale machines. Our work will enable the development of the next-generation extreme-scale resilient numerical solvers that will yield reliable results even if executed on unreliable hardware.

Results and Accomplishments

We established the mathematical foundations of a new framework for numerical analysis that is free form, the assumption that numerical operations can be always performed reliably. In our most recent report, we provide a rigorous definition of both "hardware error"' (i.e., error introduced into the computations by faulty hardware) and convergence with respect to the hardware error. We demonstrate how the classical fixed point iteration is not convergent when executed on unreliable hardware; however, the algorithm can be extended to a fully resilient one. Using an already established technique of selective reliability, we split the algorithm into "safe" and "fast" modes, where computations in safe mode are considered reliable and expensive, while computations in fast mode are considered cheap but potentially unreliable. We use several accept/reject criteria that control the hardware error so that faults resulting in discrepancy with large magnitude are rejected, while small faults are handled by the natural self-correcting properties of the method. We derive a stability condition with respect to the hardware faults, and we prove that if the condition is satisfied (i.e., the rate of faults does not exceed a given threshold), then the algorithm is guaranteed to converge. In addition, our analysis is agnostic with respect to the specific hardware configuration (i.e., CPU or GPU or RAM); we only consider the rate of faults, that is, the probability that an iteration would return a result that is different from what is expected.

Information Shared

M. Stoyanov and C. Webster, *Numerical Analysis of Fixed Point Algorithms in the Presence of Hardware Faults*, Oak Ridge National Laboratory, ORNL/TM-2013/283 (2013).

J. Elliott, F. Mueller, M. Stoyanov, and C. Webster*, Quantifying the Impact of Single Bit Flips on Floating Point Arithmetic*, Oak Ridge National Laboratory, ORNL/TM-2013/282 (2013).

07085

Scalable Malware Repository (Pico) and Analysis Platform (Concordia)

J.M. Carter

Project Description

This proposal addresses a challenge in the malware analysis community, namely, maintaining and evolving a large-scale code repository and an associated knowledge base using a general-purpose interface that provides basic management and analysis capabilities. Forensic analysis of code remains a difficult, time-consuming human task that requires highly specialized training. In response to numerous challenges in this domain, we propose to develop a highly scalable federated system that versions all artifacts and metadata, and facilitates broad analysis by presenting an accessible, general user interface to an analyst community whose concerns are diverse. This project includes two major tasks: The first part involves developing architecture for a code repository that is anticipated to grow to contain billions of

instances; the second part involves maturing Concordia, a semantics-based learning platform for malware, and using it as an exemplar analysis system that integrates with the Pico platform.

Mission Relevance

Employment of code that continually changes is a ubiquitous and highly effective strategy employed by cyber criminals; detection and analysis of this code are difficult. If detected, an analyst could spend months trying to determine what it does and who created it. Analysts want to decrease the amount of time spent analyzing code, analyze larger code corpora, and gather high-fidelity intelligence that leads to attribution. Security companies and organizations are failing to provide products that detect software with unwanted and malicious functionality and services that identify adversaries. New methods for detection and analysis are actively being sought across industry and the government. Additionally, the digital forensics community continues to highlight the importance of scalable algorithms and data storage to improving our existing capabilities. This research addresses several unmet technical challenges in digital forensics: automated attribution cueing, identification of high-fidelity semantics-based classifiers for coding techniques, and scalability.

Results and Accomplishments

The first significant goal of this project is to establish a stable distributed architecture that incorporates the Hadoop Distributed File System (HDFS), Hadoop, and HBase (an open source implementation of Google's BigTable). These components form the foundation of the Pico storage and computation architecture. All these components have been installed and are working on a cluster of 12 machines. Scripts have been developed that allow new machines to be automatically configured when they are added to the cluster. Using our current catalog of malware (over 2 million samples), software has been developed that loads these artifacts into a single distributed catalog. When each artifact is added, metadata is extracted using special parsers and then added to table fields to facilitate improved aggregation and analysis. After loading over 60,000 artifacts (malicious files) and experimenting with some analysis codes, several problems were discovered. To correct these deficiencies, the storage architecture is currently being revised. Several analysis programs have been developed that provide valuable results that can be added to the persistent metadata store; additional analytics are in various stages of development including incorporating Function Extraction (FX) technology into the system. A web-based interface is currently under development that will allow external analysts to submit analysis jobs and additional artifacts to the Pico repository. In order to build a more comprehensive catalog, several new malware sources have been identified and work is ongoing with the Information Technology Services Division (ITSD) to facilitate safe downloading and incorporation of these artifacts.

Information Shared

None to date.

SUMMARIES OF PROJECTS SUPPORTED THROUGH THE SEED MONEY FUND

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BIOSCIENCES DIVISION

06352

A Fast Neutron Strategy for Creating Deletion Mutant Populations of *Sphagnum spp.*

D.J. Weston

Project Description

Recent advances in DNA sequencing (i.e., pyrosequencing) have been successful at supplying information on gene expression, even in non-model organisms lacking genome sequence data. However, gene expression alone does not allow us to assign gene function and must be accompanied by the generation and analysis of mutants. ORNL has novel facilities whereby fast neutrons can be generated from particle accelerator spallation sources and nuclear research reactors. Fast neutrons have previously been used to generate DNA deletion mutants in plant seeds but have yet to be used in mosses. We intend to leverage ORNL's unique resources in neutron science by proposing to develop a protocol for the generation of a deletion mutant population of *Sphagnum* using fast neutrons coupled with a novel phenotyping system.

The moss *Sphagnum*, is especially important in high-latitude ecosystems due to its unique physiology (e.g., low tissue pH) resulting in the storage of up to 30% of the earth's terrestrial carbon. This has led to the claim that *Sphagnum* mosses are the most important species governing C cycle dynamics, yet there are virtually no genetic and genomic resources available for this organism despite DOE interest in high-latitude ecosystems.

Mission Relevance

The DOE Office of Biological and Environmental Research currently sponsors two next-generation research activities that aim to better quantify the chemical, physical, and biological underpinnings of plant and ecosystem responses to a changing climate. The NGEE – Arctic (http://ngee.ornl.gov) project seeks to characterize the consequences of climate change on the vast amount of stored carbon in permafrost of the arctic tundra in Alaska. In addition, the SPRUCE (http://mnspruce.ornl.gov/) project will assess the response of northern peatland ecosystems to increases in temperature and exposures to elevated atmospheric CO_2 concentrations. The DOE also funds the development of climate models where process-level information derived from ecosystem studies is incorporated for improved climate projections. Both arctic tundra and high-latitude peatland ecosystems have provided vast sinks in terrestrial carbon with an estimated 1672 and 400 gigatons of stored carbon in permafrost and peatlands, respectively. A pivotal question for these projects will be: Will these ecosystems continue to provide immense sinks in terrestrial carbon or transition to carbon sources with changing climate conditions?

Results and Accomplishments

The primary goal of this seed project was to establish a population of deletion mutants and design a strategy to survey genetic and associated phenotypic differences within the population. Our first attempt at NA mutants resulted in no viable spores due either to the age of the sporangia (collected the previous summer and refrigerated for storage) or the dose received. Fresh materials of *S. magellanicum* collected in July 2013 and an available September beam time allowed us to expose a new set of sporangia, of which a minimum of two out of seven survived the exposure to produce viable spores for population establishment. This effort has resulted in the generation of a 500-member mutagenized population as well as a 500-member control (no neutron exposure) population, both of which were used to leverage a successfully funded genome sequencing project from the DOE Joint Genome Institute.

Methods developed for establishment of the model moss *Physcomitrella patens* in tissue culture have been successfully applied to both *S. magellanicum* and *S. fallax*. We initially planned to survey the *Sphagnum* genotypes using single nucleotide polymorphism (SNP) developed for *P. patens*; however, a pilot survey revealed that the SNPs are so highly conserved they did not vary among the samples we ran (composed of three species and five genotypes). With follow-on funding from PI Weston's new LDRD project, we will employ a set of markers derived from oligonucleotide probes for the sequence capture of ~40,000 and ~100,000 regions of the *Sphagnum* genome.

Information Shared

None.

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 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 BER. For biofuels, new isolates with interesting properties for either fuel synthesis or 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, to better understand the barriers to bacterial uptake of heterologous DNA for metabolic engineering. While high-performance LTQ-Orbitrap mass spectrometry was not as useful as hoped, DNA sequencing-based approaches provided the necessary information to perform the analyses. Further, we have synthesized or cloned many genes for enzymes that will allow us to circumvent these same barriers. 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. Utilizing this approach, we have successfully demonstrated genetic transformation using a number of different plasmids and antibiotic resistance genes in a novel lignin-degrading organism, which could serve as a platform to engineer lignin bioconversion to fuels and chemicals. We further deleted a gene in this organism, laying the foundation for metabolic engineering in this organism. We have also made substantial progress toward genetically modifying a microbe capable of biochemical upgrading of ethanol to biodiesel precursors. By enabling systematic and rational genetic modification of new organisms, we are making the diversity of microbial metabolism more amenable to biotechnological utilization.

Information Shared

None.

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 strategies for cost-effective, sustainable production of plant biomass. One recent breakthrough in the field of plant biology is the discovery of strigolactones as a new class of plant hormones controlling plant architecture. More importantly, the synthesis of strigolactones in plants is regulated by the nutrient availability in soil and strigolactones exuded by roots serve as host recognition signals for symbiotic fungi. Therefore, strigolactones are viewed as integrative signaling molecules that couple nutrient availability and microbial symbiosis to the control of 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, we take an integrative approach using bioinformatics, metabolomics, physiology, and microbiology to define strigolactone pathways and decipher their 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 the 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, such as the U.S. Department of Agriculture (USDA) and the National Science Foundation (NSF). Specifically, study of the molecular mechanisms of plant-environment interaction is one of the primary focuses of USDA National Institute of Food and Agriculture Plant Sciences Program and Sustainable Bioenergy Competitive Grants Program, and of NSF Plant Genome Research Program and Sustainable Energy Pathways Program.

Results and Accomplishments

The major objective of this project is to determine the existence and operation of strigolactone pathways in *Populus*. We conducted a genome-wide search of sequence homologues of strigolactone pathway genes in the genome of *Populus*. By using *Arabidopsis* strigolactone pathway genes as templates, we identified *Populus* sequence homologues for each of those four founding members of strigolactone pathway genes, namely, *MORE AXILLARY GROWTH1* (*MAX1*), *MAX2*, *MAX3* and *MAX4*. In total, we identified two *Populus* paralogous genes each for *Arabidopsis MAX1*, *MAX2,* and *MAX4*, and one *Populus* homologous genes for *MAX3*. Furthermore, we found that *Populus MAX* paralogous genes are differentially expressed across various tissues and organs, suggesting that the expression level of individual *Populus MAX* gene may play an important role in its functioning. We found that when transformed into corresponding *Arabidopsis max* mutants, each *Populus MAX* gene can partially complement *max* mutants' shoot branching phenotypes. These findings provide genetic evidence to support that *Populus MAX* genes likely function similarly to control shoot branching in *Populus* and that strigolactone pathways likely exist and operate in *Populus*. In order to seek further support, we wanted to identify strigolactones in *Populus*. To this end, we first applied liquid chromatography–mass spectrometry/mass spectrometry (LC-MS/MS) to analyze GR24, a synthetic analog of strigolactones, in order to determine the detection limit of the instrument. Then, we used LC-MS/MS to detect strigolactones in the roots of *Populus* plants. Preliminary analysis indicated that strigolactones may be present at an extremely low level in *Populus*. Enhanced detection systems are being sought to determine strigolactones in *Populus*, and a user proposal had been submitted to DOE's scientific user facility Environmental Molecular Sciences Laboratory.

Information Shared

Z. Li, O. Czarnecki, K. Chourey, J. Yang, G. A. Tuskan, G. B. Hurst, C. Pan, and J. G. Chen, 2013. "Strigolactone-regulated proteins revealed by iTRAQ-based quantitative proteomics in Arabidopsis," *Journal of Proteome Research*, 2013 (submitted).

J. G. Chen and W. Muchero, "Detection and quantification of strigolactones in *Populus*," DOE's scientific user facility Environmental Molecular Sciences Laboratory user proposal, 2013 (submitted).

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 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 western United States 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

Multiple *Agave* species (e.g., *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 low-temperature-tolerant species) were investigated for conversion of the biomass into ethanol. Tests are conducted on the whole plant (above gound) and not centered upon the core piñas, which is traditionally used for alcoholic beverage production. Also, we are using 2–3 year old plants to simulate short rotations rather than 10 year old plants used for alcoholic beverage production. Tests have included alteration of the fermentation approach and the use of a set of detoxification methods to improve the poor performance observed in all species except *Agave tequilana*. The most promising approach is the use of different enzymes for the breakdown of the complex carbohydrates, such as cellulases, hemicellulases, pectinases, beta-glucosidases, and other similar enzymes. The addition of just one commercial enzyme targeted at one plant component significantly improves ethanol production in the recalcitrant strains. An invention disclosure has been filed that is based on this finding.

Information Shared

Manuscript in preparation.

06637

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

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

Project Description

Nerve agent bioscavengers are enzymes that can degrade highly toxic organophosphorus (OP) nerve agents such as sarin. However, the activity of these enzymes toward OP substrates must be improved through protein engineering to be sufficiently useful in real world applications. In this work, we are investigating the biochemical mechanism(s) of the bioscavenger DFPase toward various OP nerve agents using high-performance computer simulations. We are studying wild-type and mutant diisopropyl fluorophosphatase (DFPase) using hybrid quantum mechanical/molecular mechanical (QM/MM) free energy simulations. We are also analyzing protein structures and sequences of DFPase and related enzymes using bioinformatics techniques to suggest mutations that may improve enzymatic activity toward specific nerve agent substrates.

Mission Relevance

The recent use of sarin in Syria highlights the importance of our work, which is also relevant to DOE missions in global security, high-performance computing, and biological sciences. We have also received funding from DOE-NNSA ($50K for FY 2013 and we expect to receive $100K in FY 2014), which supplements and extends the scope of this project. The work is also aligned with the missions of other federal agencies, including, for example, DoD and DHS. Indeed, a recent BAA from DoD 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.

Results and Accomplishments

We have performed QM/MM free energy simulations of wild-type DFPase with the substrates DFP and sarin. Importantly, our simulations showed that DFPase hydrolyzes DFP and sarin by two distinctly different biochemical mechanisms, which will have obvious implications for designing bioscavengers for specific nerve agents.

For DFP hydrolysis, a pentavalent phosphoenzyme intermediate is formed, followed by fluoride dissociation to form a tetrahedral intermediate, which is then hydrolyzed. In contrast, for (*S*)-sarin an enzyme-activated water molecule, rather than the enzyme itself, hydrolyzes the substrate. We traced the origin of these mechanistic dissimilarities to differences in the electrophilicity of the phosphorus centers of the two substrates.

Information Shared

T. Wymore, M. J. Field, P. Langan, J. C. Smith, and J. M. Parks, “Hydrolysis of DFP and the nerve agent (S)-sarin by DFPase proceeds along two different reaction pathways: Implications for engineering bioscavengers,” submitted to *J. Phys. Chem. B*.

06746

Butanol Production from Multiple *Agave* Species

A. Palumbo, J. Mielenz

Project Description

There are two primary drivers for alternate transportation fuels: so-called drop-in fuels and production of biomass for renewable fuels on non-agricultural lands (food vs fuel). We have been successfully investigating with DOE seed funding the fermentation of woody biomass into butanol, one of the drop-in fuel candidates. This work addresses the first driver. Additionally, *Agave* is one of the most water-use-efficient plants in the world due to its crassulacean acid metabolism (CAM), and an ongoing ORNL seed project in my lab has been developing a unique fermentation process using whole *Agave*, as opposed to the central bolus, for ethanol production. This mini-seed proposal seeks funding to demonstrate the production of butanol from multiple *Agave* species with the butanol-producing *Clostridium beijerinckii* bacterium using the newly discovered process that has been successful for *Agave* ethanol production. The diminished funds and specific Statement of Work for each aforementioned project precludes examining this unique marriage of two seed projects without additions funds. Funding of this project will permit the reduction to practice of a never before accomplished process using the whole *Agave* plant to produce a drop-in fuel butanol. These results will permit the filing of a strong patent application as well as a breakthrough publication.

Mission Relevance

Butanol is a valuable drop-in biofuel because it is readily blended with gasoline and diesel. It is also nearly immiscible with water, permitting shipping via pipelines. Finally it can be used both by automobiles and heavy duty trucks, expanding its markets beyond ethanol. Butanol can be produced by fermentation from renewable materials where it is called biobutanol. To date most of the processes use corn-based glucose in high concentrations to produced biobutanol using various *Clostridium* species. With seed project funding from the US DOE Office of the Biomass Program (aka now Biomass Technologies Office), we have shown a patented *Clostridium beijerinckii* from the University of Illinois can produce high levels of butanol from *Populus* biomass by fermentation. Therefore the use of non-food biomass for butanol production has been demonstrated. However, *Populus* and other dedicated energy crops require reasonable levels of precipitation (>31 in.) for proper growth. The use of a biomass crop from semi-arid United States to produce butanol would be completely new and provide a unique benefit to the biofuels industry.

Results and Accomplishments

We completed the testing of production of butanol by *Clostridium beijerinckii* from 10 species of water-efficient *Agave* plants from the semi-arid west and Mexico, specifically *A americana,* "big blue," *A. americana* var marginata, *A americana* var. gainsville, *A salmiana* var. ferox, *A tequilana*, *A univitatta* var. truncata, *A parryi* var. Compacta, *A. neomexicana, A. havardiana*, and *A. lechuguilla*. The latter four grow well in the western United States having sufficient cold tolerance. We used 2–3 year old plants and investigated the use of different enzymes for the breakdown of the complex carbohydrates, such as cellulases, hemicellulases, pectinases, beta-glucosidases, and other similar enzymes. Results from *Populus* testing showed *C. beijerinckii* fermentation of biomass is best accomplished with initial hydrolysis of the biomass with these enzymes followed by fermentation by *C. beijerinckii* of the liberated sugars. We showed all the species contained significant levels of fructose as well as considerable levels of cellulose. As a result of this observation, a new process was developed that preserved the fructose, which is heat and acid labile, while permitting the cellulose to be optimally accessed with a high-temperature

pretreatment. Among the US-derived species, the *A. neomexicana* was the most productive regarding butanol production due to high levels of soluble sugars as well as ample cellulose, while *A. lechuguilla* showed poor fermentation results.

Information Shared

An invention record was filed July 31, 2013.

06764

Renewable Hydrogen Production from Biomass Pyrolysis Waste

A.P. Borole

Project Description

Production of drop-in fuels from biomass is one of Department of Energy's (DOE) major goals. The current thrust is on the thermochemical route via biomass pyrolysis, to produce transportation fuels. The process uses natural gas for generating hydrogen required to upgrade bio-oil, the product of the pyrolysis process. Despite supplementation with natural gas, the overall energy efficiency of the process is 49%. The problem is the presence of partially oxygenated organics in the bio-oil such as carboxylic acids and furan aldehydes and phenolic molecules, which require large amounts of hydrogen for deoxygenation and also cause other problems such as corrosion. A novel solution to the problem is proposed. It uses a process called microbial electrolysis to convert the oxygenated organic molecules to hydrogen. This has the potential to eliminate the use of natural gas, improve stability of bio-oil by removal of polar molecules, and reduce corrosion during subsequent hydrotreatment. The project team has expertise in biochemical engineering, electrochemistry, pyrolysis, and process development.

Mission Relevance

DOE Energy Efficiency and Renewable Energy (EERE) BioEnergy Technologies Office and Fuel Cell Technologies Office seek to develop a capability to generate renewable hydrogen. It is a significant need of the future, which can enable modern society to meet its transportation needs and minimize extensive use of fossil fuels, thereby impacting climate change as well. Hydrogen is also required for production of drop-in fuels, which can prolong the use of our current fleet of vehicles, for example, production of hydrocarbons from biomass via pyrolysis process. Hydrogen is required to deoxygenate the biomass to generate high heating value fuels, which can be blended with petroleum-derived fuels. An intermediate product of the process, bio-oil, requires upgrading and hydrotreatment to obtain drop-in fuels and uses significant amounts of hydrogen for this purpose. A large component of the bio-oil is made up of oxygenated compounds. Existing technologies used in conventional petroleum refining are being modified to upgrade the bio-oil and improve fuel yield. Reforming of fossil fuels such as natural gas is the most economic way of providing hydrogen for upgrading and hydrotreatment at present. This contributes to the greenhouse gas emissions and requires three times as much water as the amount of fuel produced, plus treatment of the water prior to disposal. An alternate path to produce drop-in fuels without using natural gas-derived hydrogen is via renewable hydrogen. A novel process to generate hydrogen from the water-soluble, acidic component of the bio-oil is being proposed. This has the potential to increase the energy efficiency and sustainability of the process.

Results and Accomplishments

1. Biocatalyst development: An electrogenic microbial catalyst was developed to transform organics in bio-oil to electrons and protons, which could then be used to generate hydrogen at the cathode. The biocatalyst was characterized via 16S rRNA method and revealed a diverse population with presence of known electrogens.

2. Microbial electrolysis cell (MEC) design and construction: A MEC design was developed and used to generate and collect hydrogen. It included a lexan body, a carbon felt anode, and a Pt-deposited carbon cathode.

3. Demonstration of hydrogen production: The effect of applied potential on hydrogen production was assessed. The amount of hydrogen produced was measured via gas chromatography (GC). A rate of over 1.5 L/L-day of hydrogen production was achieved.

4. Preliminary energy balance using MEC-derived hydrogen: A baseline energy balance was developed for the thermochemical pyrolysis process using data from Pacific Northwest National Laboratory's report on fast pyrolysis. A overall energy efficiency of fuel production was obtained at 49%. The use of MEC for hydrogen production has the potential to eliminate use of natural gas completely while increasing energy recovery from biomass in the form of liquid fuels.

The seed funding was effectively used to show that it is possible to use the waste from the pyrolysis process to generate hydrogen. The results were used in a proposal to EERE Bioenergy Technologies Office, resulting in a project award of $ 2,135,000.

Information Shared

A. P. Borole, "Generation of renewable hydrogen from pyrolysis derived bio-oil aqueous phase via microbial electrolysis," 2013 (manuscript in preparation).

BIOLOGY AND SOFT MATTER DIVISION

06639

Detection and Characterization of Meso- and Nano-scopic Bubbles on Patterned and Native Metal Surfaces Using Neutron Small-Angle Scattering and Reflectivity Techniques

Y.B. Melnichenko, E. Popov, N. Lavrik, L. He, G. Smith

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, focuses 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 nano- and meso-scopic 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 nano- and meso-scopic 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 DOD and 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 DARPA and ONR) and nanofluids for biomedical applications (of interest to NIH and DARPA). The principal target source of follow-on funding will be the anticipated DOE BES call for proposals in the general area of mesoscale science.

Results and Accomplishments

During FY 2013, the team continued experimental studies of the bubble formation on nanostructured hydrophilic and hydrophobically modified surfaces of silica wafers. Two new nanostructured samples

were fabricated by N. Lavrik and I. Kravchenko at CNMS. A proposal was submitted and beam time was allocated at General Purpose SANS. Experiments with D_2O-saturated and contrast matching mixtures of (H_2O + D_2O) were conducted in April 2013 using a new set of samples. The experiments have confirmed results of preliminary experiments performed in Germany in that the filling degree of hydrophilic and hydrophobic nanopores was different and reproducible to within experimental error. At the moment the results are being analyzed in conjunction with results of computer modeling, and preliminary data revealed a surprising result of very little filling degree of nanopores with water, which is an important observation that may shed light onto the nanobubbles formation problem at ambient temperatures. The USANS proposal for studies of the shape of nanobubbles as a function of temperature was allocated 6 days of beam time, and experiments are scheduled in May 2014. The SANS beam time proposal has been submitted, and the results will be known later in the year. A proposal for neutron reflectivity experiments at SNS has been submitted, and new set of samples for this technique has been fabricated. A dedicated temperature controller with horizontal temperature gradient as well as sample holders required to perform in situ boiling experiments were fabricated and ready for experimentation.

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

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 opto-electronic conjugate polymer, P3(EO)4T, and the charge transportation properties using a thermodynamically controlled polymeric system that can provide us morphology controllability with sub-nanometer precision. The unique contribution of this research lies not only in providing a knowledge of the relationship 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.

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. 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. This method, once established, can be extended to design more general polymer electronics. Therefore, we believe that this research is within the scope of BES DOE mission.

Results and Accomplishments

During FY 2013, the project made considerable progress. First, in order to understand the templating block copolymer system L62/water, both simulation and SANS experiments were performed. The

mesoscale simulation, based on density functional theory (DFT), provided phase behavior of block copolymer systems up to a few hundreds of a micrometer length scales and a few tens of a microsecond timescales. In previously published literature, more than six combinations of parameter sets were used by different groups of researchers. In our project, results from SANS data analysis were used to validate the parameter sets used for the mesoscale simulation, and the most reasonable parameters for the mesoscale simulation could be deduced. The results have already been published in a peer-reviewed scientific journal. Second, the self-assembled system of water-soluble conjugate polymer (PEOT) and L62/water block copolymer template were made and measured by SANS. The preliminary data analysis shows that the structure of templating block copolymer system remains as a lamellar structure with the water-soluble conjugate polymer, which indicates that PEO may be confined within the hydrophilic domains of the lamellar structure as we proposed. Further data analysis and additional characterization will soon result in another publication.

Information Shared

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CENTER FOR COMPUTATIONAL SCIENCES

06566

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

O.E. Bronson Messer, 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 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. NSF and NASA also support Type Ia SNe investigations.

Results and Accomplishments

We have performed a series of simulations to understand how resolution and dimensionality might affect the long-standing practice of suppressing burning in a numerical shock (Papatheodore & Messer 2013). Our results show that, in one dimension, prohibiting burning in the shock is important wherever the carbon burning length is not resolved, in keeping with the results of Fryxell et al. (1989). In two dimensions, we find that the prohibition of shock burning effectively inhibits the development of cellular structure for all but the most highly resolved cases.

We assert that these results may influence the fidelity of large-scale Type Ia SN simulations, especially for the case of delayed-detonations. Gamezo et al. (1999) found that pockets of incompletely burned

material, created by the presence of cellular structure, can increase the size of the oxygen- and silicon-burning regions by a factor of 1.6 and 1.3, respectively. They argued that this could increase the critical density at which a DDT is likely to occur in models since the production of intermediate-mass elements would be possible at higher densities. Our results suggest this effect can be hidden due to a particular treatment of burning within the numerical shock, leading to an incorrectly informed sub-grid model.

The initial installation of the XNET nuclear kinetics module has been accomplished in the FLASH code, including OpenMP threading. The code continues to be tested against the "standard" networks available in the public version of FLASH.

We have performed an initial port of our nuclear burning module (XNet) to the GPUs on Titan. The matrix solve dominates the time for the computation, especially for larger networks. For smaller networks, we see that building the Jacobian on the device has a non-negligible impact on the computation. As the network size grows, the performance of the GPU in building the Jacobian approaches that of the serial code in the host-interface.

Information Shared

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O. E. B. Messer, J. A. Harris, S. T. Parete-Koon, and M. A. Chertkow, "Multicore and Accelerator Development for a Leadership-Class Stellar Astrophysics Code," *Lecture Notes in Computer Science* **7782**, 92 (2013).

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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. State-of-the-art methods of neutrons and x-rays scattering, spin-polarized scanning electron microscopy, and first-principle calculations will be used to characterize the coupling between the structural and magnetic order parameters under the application of stress and magnetic field. We expect this project to launch a new field at ORNL, attracting future research programs that exploit the link between physical properties and mechanical behaviors in the design of functional 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 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 its high polarization efficiency facilitates in situ characterization of the material state during application of external magnetic fields. In addition to neutron scattering measurements, we have measured the magnetic susceptibilities of the Ni-Mn-Ga single crystals at various temperatures from RT 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. The kinetics of twin boundary motion at low temperatures was measured by in situ high-energy synchrotron diffraction under magnetic field. It was shown that the temporal evolution of twin reorientation during the application of a magnetic field is described by the thermally activated creep motion of twin boundaries over a distribution of energy barriers. According to our theoretical analysis, the creep occurs as a result of competition between the longer range elastic fields from twin boundaries and the short-range elastic fields from twinning disconnections. Large magnetic-field-induced strain in MSM arises from strong magnetic anisotropy, which was obtained from both the experiment and the relativistic electronic structure calculations. The anisotropic classical Heisenberg model Hamiltonian was adopted to describe the magnetic properties of the Ni-Mn-Ga single crystal. The applicability of the obtained Hamiltonian was verified by comparison with experimental spin waves measured by inelastic neutron scattering at SNS.

Information Shared

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CENTER FOR NANOPHASE MATERIALS SCIENCES

05965

Thermopower at the Atomic Scale

P. Maksymovych

Project Description

This proposal has developed a nanoscale measurement of thermopower, a critically important variable in thermoelectric energy conversion. Today there exists a tremendous gap between our ability to nanostructure materials and evaluate thermoelectric performance at the length-scales commensurate with the nanostructuring procedures. As a result, the effect of single defects, dopants, quantum dots, and molecules in thermoelectric energy conversion and thermal energy flow remains poorly understood or altogether elusive. In this project, we developed a unique approach for measuring thermopower down to the atomic scale based on scanning probe microscopy. In contrast to almost any other thermoelectric characterization methodology, we do not make mechanical or thermal contact to the studied object. This enables us to measure electronic and thermoelectronic properties simultaneously, and characterize thermal gradients at the nanoscale.

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 has developed 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.

Results and Accomplishments

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. Specifically, we have proven that (1) it is possible to decouple the properties of the tunnel junction from the sought thermoelectronic properties of the material if the width of the tunneling gap can be systematically varied while measuring thermovoltage; (2) the properties of the junction can be optimized to significantly enhance the observed thermovoltage contrast and increasing the spatial resolution of thermoelectronic

imaging; (3) thermal gradient between the contact leads in a tunnel junction can be determined without explicit temperature calibration, which is presently not achievable by any experimental technique.

In the second part of the project, the developed techniques were applied to model systems, including metal nanoparticles and a canonical thermoelectric Bi_2Te_3. We revealed that previous theoretical descriptions (such as the Stovneng-Lipavsky model) do not provide a transparent way to account for experimental trends in measured thermovoltage. We therefore developed and verified a new approach which combines experimental tunneling spectroscopy and Landauer formalism to obtain quantitative values of thermopower at any temperature. We have successfully interpreted the difference in nanoscale thermoelectric response between different metals and were able to measure the density of states component of thermopower on Bi_2Te_3 as a function of quasi-Fermi level. One of the interesting consequences of these experimental analyses is that all-metal junctions can be very competitive with the presently known molecular transport junctions with respect to thermopower, and they can likely be superior in terms of overall efficiency of thermoelectric energy conversion or cooling applications.

Information Shared

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CHEMICAL SCIENCES DIVISION

06624

High-Rate High-Capacity Reversible Multielectron Cathodes

C.A. Bridges, M.P. Paranthaman, G.M. Veith, R.R. Unocic, K. Unocic, L. Baggetto

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 associated 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°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 Office of Basic Energy Sciences (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 to BES, 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. A coating of lithium phosphorus oxynitride (LiPON) was investigated to understand the impact of an electronically resistitive, ionically conductive solid electrolyte on the cycling performance. The surface modification via LiPON deposition failed to demonstrate a notable improvement in electrochemical performance. Further development has demonstrated the difficulty in obtaining pure fluoride and nitride anion-doped powders in the bulk. However, the new synthetic approach to electrode synthesis has demonstrated a notable enhancement in rate capability and cyclability in cycling tests with CR2032 coin cells. The project has developed a new synthetic approach for preparing nitride and fluoride surface-doped β-Fe_2O_3 crystallites with a rhombic dodecahedral morphology and well-developed facets. The β-Fe_2O_3 polymorph is rare, with only two previous preparation approaches in the literature leading to a material free of any other polymorph. The electrodes show a capacity of ~800–1000 mAh/g at lower cycling rates for a minimum of

100 cycles, depending upon preparation conditions and cycle number, which is close to the theoretical capacity of 1007 mAh/g. Further testing is required to demonstrate 1000 cycles or above. The results were recently presented at the Electrochemical Society Fall 2013 Meeting in San Francisco under the title "A new approach to the preparation of high capacity conversion electrodes." A provisional patent application (No. 61/873,129; UTB ID#2801.0) has been filed entitled "Nitride- and oxide-modified electrode compositions and their methods of making."

Information Shared

None at this time. A journal publication on β-Fe_2O_3 synthesis and electrochemical properties is in preparation.

06630

Inexpensive Efficient Hybrid Neutron Sensor

M.P. Paranthaman, C.A. Bridges, 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 both ITO-coated glass substrates and 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 poly3-hexylthiophenes, 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

06673

Secure Two Factor Authentication Using Quantum Random Numbers and Enhanced Hashing

R. Pooser, P. Evans, N. Paul

Project Description

Recent attacks against RSA Inc. uncovered weaknesses in RSA two-factor authentication (2FA) tokens, leading to high-profile cyber attacks on several corporations and government agencies. We propose to build a token-based 2FA prototype that combines true random seeds obtained from a quantum random number generator (QRNG) and a new, enhanced hashing algorithm. The proposed scheme will be more secure than current 2FA methods for several reasons. First, unlike the traditionally used pseudo-random number generators (PRNG), a QRNG is non-deterministic and thus yields non-reproducible seeds. Second, novel features in the hashing algorithm such as time-dependent seed rotation and hash chain switching provide additional layers of security. Finally, accessing the list of random seeds will also be rendered more difficult by hardware safeguards that are currently lacking in 2FA systems. The final prototype will combine all of these features into a new, secure 2FA system.

Mission Relevance

This research is relevant to DOE both for its scientific discovery and for its direct application to cyber security. Authentication tokens are in widespread use across all DOE labs. Bolstering the security of these devices will have a broad impact on DOE operations by making its labs less susceptible to attacks that exploit token weaknesses. The proposed research into a new type of quantum random number generator (QRNG) is also interesting for DOE from a scientific discovery standpoint, due to the interest generated in the scientific and cyber security communities each time a new QRNG is proposed and demonstrated.

Results and Accomplishments

Our main accomplishment on this project has been to produce a proof-of-principle design for a 2FA system that uses a forced time delay between each subsequent one-time password requested from the server. It also implements seed switching on the token so that hash chains can easily be switched if a seed becomes compromised. We have held discussions with RSA and Noetics about joint research efforts. We have also filed a patent application for the design. For the remainder of the project, we need to integrate our QRNG into the design so that tokens and servers rely on it for a source of one-time passwords. Another accomplishment has been the discovery of bias removal algorithms – essentially hardware extractors – which allow the QRNG to output more secure one-time passwords at a higher bit rate. We plan to publish a paper on the subject in conjunction with results on the operation of the QRNG.

06674

A Distribution-Oblivious Scalable Approach for Large-Scale Scientific Data Processing

S.K. Seal, S.B. Yoginath, M.K. Miller

Project Description

Applications capable of rapidly analyzing enormous quantities of data on modern high-performance computing platforms are needed to close a widening gap between data acquisition and data processing speeds in multiple scientific disciplines. Few scientific data processing (SDP) applications are able to scale, resulting in vastly sub-optimal usage of leading data acquisition technologies as well as computing capabilities. One of the central issues in the scalable design of efficient SDP algorithms is the sensitivity of their execution times to data distribution. Runtimes of SDP methods vary depending on the distribution of the data elements in the space in which they are defined, even if the number of data elements remains constant. This project will directly address a key algorithmic challenge of designing parallel SDP frameworks with data-distribution-oblivious performance characteristics, a bedrock of robust and scalable high-throughput SDP frameworks. The approach proposed here will be implemented to demonstrate both scalability as well as distribution-independent performance on large parallel machines. As proof-of-principle, this new capability will be used to analyze massive atom probe tomography (APT) datasets in unprecedented runtimes.

Mission Relevance

High-throughput data acquisition capability and high-performance computing are both strengths of DOE. However, a lack of matching high-performance data analysis capability stymies the process of scientific knowledge discovery. Left unaddressed, this mismatch will only grow. Unused data ultimately translates to wasted resources and manpower. The research proposed here is designed to provide a proof-of-principle of the pivotal role that scalable spatial queries play in relieving a fast-growing bottleneck poignant to multiple DOE missions that require analysis of massive spatiotemporal data sets. At the core of these analyses approaches are spatial queries that need to be satisfied numerous times during the execution of most high-level data analysis methodologies. This project highlights the criticality of efficiently satisfying these fundamental region queries for parallel scalability.

Results and Accomplishments

As part of this ongoing project, a parallel compressed octree construction algorithm, built on sub-algorithms for multiple parallel operations like sorting, spatial indexing and bit algebra, has been developed and tested using varying workloads. Two key results – distribution independence and small parallel runtimes – have emerged. Parallel compressed octrees were constructed on two data sets, each of size 10 million but with widely differing spatial distributions, using processor counts ranging from 16 to 256. One of the data sets consisted of a uniform distribution of points, and the other consisted of points distributed exponentially along each spatial dimension. The runtime ratio of the tree construction algorithm on the uniform to that on the exponential distribution of points was about 0.9 (the ideal ratio is 1.0). This resilience in the parallel execution times supports the fact that the communication overhead in our approach remains bounded and depends only on the data size, rather than on the spatial distributions of the data. In fact, time spent in communication was found to be within 3%–9% of the total parallel runtime in all the test executions. The proposed algorithm took less than 2 seconds using merely 16 processors and less than half a second using 128 processors to build a compressed octree on 10 million points. These small runtimes are very significant since higher-level analysis algorithms, which typically build data-indexing trees multiple times, benefit immensely from small turnaround times. Design and

implementation of parallel algorithms for spherical region queries using compressed octrees are underway.

Information Shared

Results in this ongoing project are being compiled in preparation for planned publications.

06781

A New Integrated Signaling-Encryption Technique to Reduce Error Propagation in Wireless Communications

M. Olama, M. Bobrek, E. Ferragut

Project Description

The goal of this project is to develop a conceptual design and analytically demonstrate proof of principle of a new integrated signaling-encryption technique that is secure and enables improved throughput, latency, and bit-error rate (BER) in wireless communication channels. This technique minimizes the number of steps with in a traditional encryption technique to tremendously reduce its drawbacks and use signaling that does not suffer from performance deterioration in wireless channels as compared to traditional encryption algorithms. Thus, the reliability and throughput of the communication link will be improved while the security is preserved at reduced complexity. This work will result in a new encrypted communication system that is as secure as traditional encryption systems but with improved quality of service (QoS). The project also focuses on validating the proposed integrated signaling-encryption scheme using end-to-end models and algorithms and analyzing their performance in terms of BER, throughput, and other QoS metrics.

Mission Relevance

The DOE Office of Electricity Delivery and Energy Reliability (OE) Smart Grid Program along with the DOE Industrial Wireless Program have shown interest in secure and reliable electric power grid and industrial wireless communications systems.

Other potential sponsors for the developed technology include DOD (ARL, NRL, AFRL, DARPA, etc.), DOT (RITA, FHWA), DHS, and NASA. Interest in secure communications is government wide, as well as in the commercial sector. Secure and reliable communication systems are already planned for many military, space, homeland security, smart grid, vehicle-to-vehicle, and commercial applications.

Results and Accomplishments

A conceptual design is produced using Matlab for the new integrated signaling-encryption technique. This design model is used to evaluate the performance of the proposed mechanism in terms of throughput for binary phase shift-keying (BPSK) modulation signal and in additive white Gaussian noise (AWGN) environments. The generated numerical results show that there is 10–20% improvement in throughput by using the proposed mechanism compared with the traditional advanced encryption standard (AES) cipher algorithm.

We are currently conducting performance evaluation of the proposed mechanism in multipath fading environments. We expect the throughput improvement to be much higher than in AWGN channels, since

the performance of the current techniques (such as AES) will severely deteriorate due to the avalanche effect in contrast to the proposed mechanism.

Information Shared

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COMPUTER SCIENCE AND MATHEMATICS DIVISION

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. Our research tasks are designed to develop building blocks and collect preliminary assessment results, which are necessary for external funding applications. We are collecting data from ORNL leadership compute platform –Titan – and working to improve widely used scheduling algorithms, which increase 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 DOE and the National Science Foundation (NSF). We consider this project especially fits the DOE Exa-scale programs and the NSF Computing and Communications Foundation (CCF) program. The PIs have had successful experience applying for external funding, with ORNL staff member submitting a NSF proposal via a joint faculty position at University of Tennessee.

Results and Accomplishments

In this project, we developed IOSI (I/O Signature Identifier), 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-scale compute platform at ORNL. IOSI leverages existing infrastructure at HPC centers that nowadays has mandatory functions of periodically logging high-level, server-side I/O throughput. 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 2 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. Note that IOSI is not intended to perform fine-grained recording of per-application I/O operations. Instead, it derives an estimate of their bandwidth needs along the execution time line to support future I/O-aware smart decision systems.

We have accomplished three major tasks in the project. (1) We extracted per-application I/O workload information from existing, zero-overhead, server-side I/O measurements and job scheduling history. Further, we obtain such knowledge of a target application without interfering with its computation/communication, or requiring developers/users' intervention. (2) We implemented a suite of techniques to identify an application's I/O signature, from noisy server-side throughput measurements. These include i) *data preprocessing*, ii) *per-sample wavelet transform for isolating I/O bursts*, and iii) *cross-sample I/O burst identification*. (3) We evaluated IOSI with real-world server-side I/O throughput logs from the Spider storage system at the Oak Ridge Leadership Computing Facility (OLCF). Our experiments used several pseudo-applications, constructed with the expressive IOR benchmarking tool, and S3D, a large-scale turbulent combustion code. Our results show that IOSI effectively extracts an application's I/O signature despite significant server-side noise.

Information Shared

Y. Liu, R. Gunasekaran, X.. Ma, and S. Vazhkudai, "Automatic Identification of Application I/O Signatures from Noisy Server-Side Traces," to be presented at the12th USENIX Conference on File and Storage Technologies (FAST 2014). Santa Clara, CA.

06623

Joining Neutron Scattering and Simulations towards Improved Lipid Models

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 requires 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, 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 (CL). We have completed parameterization and validation of the force fields for DHPC, POPS, DDM, and CL. We have published one paper that reported on revealing detailed molecular interactions between cholesterol and ether lipids (DHPC) by a combined use of scattering and molecular dynamics simulations. We have two additional manuscripts on POPS and CL lipids in preparation. Combined with neutron scattering, our simulations reveal a larger lipid area for POPS than its zwitterionic phosphatidylcholine (PC) counterpart, which was not known previously. We also find over-binding of ions to lipid head groups, a serious artifact in simulations of PS lipid bilayers. We have developed new force field parameters that successfully address this issue and reproduce small-angle neutron and X-ray scattering data. Our work on DDM models have directly helped another project on neutron scattering study of Photo System I from *T. elongatus* solubilized in DDM solution.

Information Shared

J. Pan, “Interactions between ether phospholipids and cholesterol as determined by scattering and molecular dynamics simulations,” *J Phys Chem B* **116**(51), 14829–38 (2012).

J. Pan, “ Molecular Structure of a Phosphatidylserine Bilayer Revealed by Scattering and Molecular Dynamics Simulations,” *J Phys Chem B*, in preparation, 2013.

R. Le et al., “Determination of the Solution Structure of Thermosynechococcus elongatus Photosystem I in n-dodecyl-β-D-maltoside Detergent Using Small-Angle Neutron Scattering and Molecular Dynamics Simulations,” *J Phys Chem B*, submitted for publication, 2013.

06675

Attacking the Supernova Problem: Nonlinear Moment Models for Simulated Neutrino Radiation

C. Hauck

Project Description

The death of massive stars in core collapse supernovae is one of the most important links in our chain of origin from the Big Bang to the present. Core collapse supernovae are the dominant source of elements in the periodic table between oxygen and iron, and there is evidence they are responsible for producing half the elements heavier than iron.

The transfer of energy by neutrino radiation is commonly believed to play a fundamental role in the supernova event, but to date, the confirmation of this hypothesis and a detailed understanding of the physical mechanisms still eludes the astrophysics community. This is due to the computational cost required to accurately simulate neutrino fields. However, advances in numerical algorithms and computer hardware will present new opportunities for exploration. The work proposed here is the first step in the development of such algorithms.

Mission Relevance

Supernova modeling requires a kinetic treatment of the neutrino radiation—that is, an accurate representation of the neutrino distribution in six-dimensional position-momentum phase space at each instant in time. In particular, shock revival by neutrino heating, the current paradigm we and others investigate, is very sensitive to the neutrino energy spectra. Thus, three-dimensional radiation hydrodynamics simulations that resolve the energy spectra of the neutrinos are required and would mark a quantum leap in sophistication and realism, and may also provide a solution to the supernova problem. *The development of a practical yet realistic approach to simulating neutrino radiation will be the key to unlocking such success.* This is the ultimate challenge, and risk, we face.

From a computational perspective, neutrino transport exemplifies many of the thematic challenges of simulating non-equilibrium behavior in particle-based systems. First, the neutrino field requires a kinetic, phase-space treatment. Second, the neutrinos exhibit strong multi-scale phenomena: some neutrinos can stream freely while others diffuse through the surrounding matter. Third, neutrinos are tightly coupled to magneto-hydrodynamic equations as part of a complex, multi-physics problem. These complications are common to many physics and engineering systems including dilute gas dynamics, neutron and photon transport, plasmas, charged-particle transport, charged-particle transport in semi-conductors and biological channels simulations, multi-phase flows, and chemically reacting flows. These systems, in turn, comprise some of the basic components of key DOE energy applications, including fission and fusion reactors, combustion, and solar cell design.

Results and Accomplishments

We have designed a high-order numerical method for simulating particle flows in phase space using Discontinuous Galerkin methods and Strong Stability Preserving, Runge-Kutta time integrators. The method is conservative, preserves maxima and minima, and can be applied to arbitrary coordinate systems, including general metrics and application-specific geometries. The method has been implemented in a parallel HPC framework and tested on TITAN.

Information Shared

E. Endeve, C. D. Hauck, and Y. Xing, "Positivity-Preserving DG Methods for the Boltzmann Equation," in preparation for submission to the *Journal of Computational Physics*.

06678

Method for Fiber Path Length Alignment to Enable Coherent Combination of High-Power Fiber Laser Sources

W. Ray

Project Description

We proposed a proof-of-principle experimental demonstration of a novel approach to achieve sub-10-micron path length matching between elements of a fiber laser array. This technology is vital to coherent beam combining of high-power fiber lasers and interferometric sensing applications. Current methods use free-space sampling of the signal beam of interest. The primary innovation here is the use of a secondary probe beam to sense path length differences. This probe beam co-propagates with the signal beam in each fiber amplifier. The proposed architecture (1) does not require knowledge of the combined signal beams, (2) ruggedizes the detection scheme, (3) is applicable to pulsed and continuous-wave systems, and (4) operates in an orthogonal manner to existing methods. Experimental proof-of-principle has been carried out by testing the proposed technology with a two-laser passively coupled fiber laser array. This capability could immediately impact high-bandwidth coherent beam-combining programs, since minimal modification to today's fiber amplifier structures would be required for system integration.

Mission Relevance

This research is relevant to the Global Security Science and Technology initiative, particularly to the advancement of power and efficiency of continuous-wave and pulsed laser sources for remote sensing technology. This research broadly benefits Department of Defense thrusts towards the generation of highly efficient, small footprint laser sources via coherent combination of high-power fiber lasers. These sources are relevant for long-range optical power delivery applications, which include directed energy sources and communications systems in addition to sensing.

Results and Accomplishments

Both objectives of the proposed effort were successfully completed and generated favorable results. The objectives involved (1) calibrating the proposed technology in a two-laser cavity when only the sensing beam was operational and (2) evaluating the effectiveness of the technology when both the signal and sensing beams were present. We found that the proposed system came close to the proposed benchmarks during calibration. We were furthermore able to independently verify the accuracy of the proposed sensing technology through a separate measurement that was not considered at the time of proposal. Certain modifications to the design of the sensing source were required in the case where the signal beam was present. These modifications were motivated by the need to separate the signal and probe sources in the detection portion of the scheme.

The key finding of this effort was that the proposed technology works as prescribed and can possibly be implemented in a number of relevant high-power coherent beam-combining systems. Based on our results, we believe that this technology would be best suited for master-oscillator power amplifier array geometries with active light conditioning. What remains to be determined is the possible spectral

separation of the probe and signal beams as this determines the ease of integration into today's systems. It will not benefit the passively coupled laser arrays studied here since path length matching would have to be extended by another two orders of magnitude. Future directions include algorithms to achieve better matching and establishing the utility of this method in high-power systems.

Information Shared

None to date.

06763

Development of Ultrafast High-Peak-Power Mode-Locked Broad-Area Laser Diode

B. Liu

Project Description

High-power mode-locked laser diodes are extremely attractive for commercial and defense use in a variety of applications, including signal processing, material processing, free space communication, range finding, and bio-medical tools. The maximum output power of a semiconductor laser is proportional to mode size, and it is limited by catastrophic optical damage (COD) of facet. A broad-area laser diode (BALD) has a wide emitter, and the cost of a BALD is low due to relatively simple fabrication process. A mode-locked BALD is a good candidate to boost the output power. Its main drawbacks are an unstable multi-transverse mode and large capacitance. With a V-shape external cavity design and hybrid mode-locked schematic design, the optical team at the Center for Engineer Science Advance Research (CESAR) aims to deliver a high-peak-power mode-locked BALD, which is of great importance to the development of laser system capability at ORNL.

Mission Relevance

With an increase in high peak power, high repetition rate, and pulse energy of mode-locked BALD technology, this affordable technology can be promoted in a more competitive way. Development of a new, affordable, high brightness laser source is of significant importance to the Defense Advanced Research Projects Agency (DARPA), the Navy, the National Science Foundation (NSF), the Department of Homeland Security (DHS), and the National Institutes of Health (NIH).

Results and Accomplishments

We ordered a semiconductor saturable absorber mirror (SESAM) with an absorption reflectance coefficient of 6%. The laser diode was ordered with low anti-reflectivity (AR) coated broad-area laser diode with an emitter size of 100 μm and cavity length of 1000 μm. A V-shaped external cavity was set up according to our experimental design. In first step, diffraction grating was posted at the image plane, and we got a narrow spectrum emission from single broad-area laser diode. With a current drive of 2 Amps, the output power from the broad-area laser diode V-shaped cavity is about 1.2 Watts. We replaced the diffraction grating with SESAM. We fully aligned SESAM in a V-shaped cavity, and we measured the time series with fast photo-detector with a 12 GHz bandwidth and an oscilloscope with a 6 GHz bandwidth. When we tuned the drive current to 0.5 Amps, the output laser showed the 160 ps pulse-width pulsing, which corresponded to the measurement bandwidth of oscilloscope. When we tuned the drive current higher, the oscilloscope did not show the any AC oscillation. This was the truly exciting since there may be a very narrow duration pulse being generated. We have recently been in contact with

different groups that have the capability to measure the short pulse. We need borrow an auto-correlator to measure a pulse width in around the10 ps range. If we can confirm the pulse width and repetition rate, our designed experiment will be totally successful, and we will be able to deliver a high-peak-power, high-repetition-rate laser in an affordable way.

Information Shared

No publication to date.

07044

Chaotic Controller Enabling High-Power Scalability of Fiber Laser Sources

W. Ray, Y. Braiman

Project Description

Fiber lasers are recognized as a promising route to realize efficient high-power continuous-wave (CW) and pulsed laser sources with excellent beam structure integral to military applications. In 2011 a new transverse mode instability was identified in emerging kW-class fibers. This instability dynamically couples a significant fraction of amplified light to higher-order spatial modes and today presents the most significant hurdle to power scalability of fiber sources. The physical origins are only now beginning to be understood, and to date no practical method has emerged that quenches either the onset or the severity of this instability. We propose a proof-of-principle demonstration of a novel control system to suppress the impact of the transverse instability in high-power fibers. The primary innovation is the treatment of this instability in the context of a spatially extended chaotic dynamical system. A feedback system will be designed to stabilize the modal content emitted by the fiber. Our method will be validated in experiments and simulations. We anticipate that this technology will establish a unique ORNL capability broadly applicable to existing and future CW and pulsed laser systems.

Mission Relevance

This research is relevant to the Global Security Science and Technology initiative, particularly to progress the power and efficiency of CW and pulsed laser sources for remote sensing technology. Fiber-based sources are viewed as promising candidates for this technology due to their efficiency and flexible form factor. If successful, the research proposed here would allow significant power scaling of high-fidelity light from single fiber sources. This research broadly benefits Department of Defense thrusts towards the generation of highly efficient, small footprint laser sources for long-range optical power delivery applications, which include directed energy sources and communications systems in addition to sensing.

Results and Accomplishments

Approximately 25% of the proposed effort was funded during FY 2013. In this initial effort, progress was made towards setting up simulations and experiments necessary to study the transverse mode instability. We have forged a hybrid model description from existing models. This model features significant computational savings while still capturing the relevant physics behind the instability. The computational efficiency will greatly benefit the numerical exploration of control strategies in FY 2014. An experimental design was also developed in detail during in the initial effort. Equipment related to safety, power handling, measurement, and optical manipulation for system diagnostics was ordered.

Information Shared

None to date.

07055

Adaptive OFDM Radar Waveform Design for Enhanced Target Detection and Discrimination

S. Sen, J. Barhen, C.W. Glover

Project Description

Modern radar systems have become very sophisticated and advanced with more impetus being put forward on the improved detection, discrimination, and identification capabilities. In order to collect sufficient information to perform these tasks, we propose to employ a wideband orthogonal frequency division multiplexing (OFDM) radar signal. An OFDM signal not only has a higher level of spectral efficiency, but its multi-carrier nature also offers more detailed target information as different scattering centers of a target resonate variably at different transmitted frequencies. Consequently, use of OFDM radar enables us to better discriminate a target from the background clutter and noise by utilizing multiple frequency samples of each target response. In addition, we optimally design the OFDM spectrum in accordance to the estimated target and interference parameters, and thus obtain a significant improvement in system performance by adaptively matching with the operational scenarios.

Mission Relevance

DOE (and ORNL) plays a vital role in national security beyond being actively involved in energy resources, environment quality, and science. A methodology for accurately tracking and discriminating "targets" could be used to monitor from airborne or space-based assets the geospatial motions of, for example, vehicles, related to nuclear proliferation, even when they are outside direct line of sight.

Results and Accomplishments

We analyzed the statistical performance of a wideband OFDM radar signal in estimating the micro-Doppler frequency of a target having multiple rotating scatterers. Being a frequency-diverse waveform by nature and having a set of orthogonal subcarriers, OFDM signal not only enabled us to independently characterize the micro-Doppler behaviors at different frequencies but also provided additional target information as different scattering centers exhibit varying frequency responses. First, we developed a parametric measurement model for a rotating target due to multi-frequency OFDM signaling. Then, to characterize the estimation accuracy of micro-Doppler frequency, we evaluated the Cramér-Rao Bound (CRB) on the error of the angular-velocity estimate, while considering the target scattering responses as deterministic (unknown) parameters. Additionally, to improve the accuracy of the estimation procedure, we formulated and solved an optimization problem by minimizing the CRB on the angular-velocity estimate with respect to the OFDM spectral coefficients.

We simulated several numerical examples to demonstrate the CRB variations with respect to the signal-to-noise ratios, number of temporal samples, and number of OFDM subcarriers. The CRB values not only decreased with the increase in the SNR values but also reduced as we increased the number of subcarriers, implying the significance of frequency-diverse OFDM waveforms. The improvement in estimation accuracy due to the adaptive waveform design was also numerically analyzed. Interestingly, we found

that the relative decrease in the CRBs on the angular-velocity estimate was more pronounced for a larger number of OFDM subcarriers.

Information Shared

S. Sen, J. Barhen, and C. W. Glover, "Cramér-Rao bound on micro-Doppler estimation and waveform design using OFDM radars," *IEEE Signal Processing Letters*, submitted.

S. Sen, J. Barhen, and C. W. Glover, "Performance bounds on micro-Doppler estimation and adaptive waveform design using OFDM signals," submitted to SPIE Defense, Security, and Sensing Conference, Baltimore, MD, May 2014.

07066

Shaping High-Power Diode Laser for High-Efficiency Spin Exchange Optical Pumping (SEOP)

B. Liu, X. Tong, Y. Braiman, R. Lee

Project Description

Stable, narrow spectral line-width high-power diode laser is highly desired for optical pumping purpose, especially for ^{3}He, ^{129}Xe spin exchange optical pumping (SEOP). External VBG (volume Bragg Grating) cavity provides the compact design. When the spectral line width of a high-power diode laser is narrowed to be comparable with Rb's D1 absorption line width, any spectrum drifting significantly reduces the pumping efficiency. Stabilization of narrowed high-power diode laser spectrums is crucial for achieving high-efficiency SEOP. A high-power diode laser with a narrow spectral line width and a stable spectrum is the key to achieving highly polarized noble gas using high-efficiency, low-cost SEOP. The collaborative effort of the optical team at the Computer Science and Mathematics Division (CSMD) and the polarized ^{3}He team at the Instrument and Source Design Division (ISDD) aims to deliver this new laser system for high-efficiency noble gas SEOP.

Mission Relevance

This project provides the narrow spectral line-width, stable, and compact high-power diode laser. The laser is very important to implement to a spin neutron filter in SNS. This project impacts two of the nine major initiatives under the "Excellence in Science and Technology" strategic objectives found in the ORNL FY 2012 Laboratory Agenda, namely to "Deliver science using neutrons" and to "Discover and demonstrate advanced materials for energy applications."

With this good-quality and low-cost diode laser system, highly efficient ^{129}Xe SEOP is possible and will be implemented for high-sensitivity nuclear magnetic resonance (NMR) spectroscopy and will enhance the sensitivity of NMR imaging. It will draw interest from National Institutes of Health (NIH).

Development of stable, compact, narrow line-width, high-power laser technology will benefit solid-state and fiber laser pumping. It will reduce the thermal management burden for pumping solid-state and fiber lasers, especially with wavelength around 885 nm and 969 nm. The stable, narrow line-width pumping laser will interest the Army Research Office, Office of Naval Research, the Defense Advanced Research Projects Agency (DARPA), and other agencies.

Results and Accomplishments

We had a portion of funding ($25,000) allocated in FY 2013. We decided to use all available funding to purchase the experimental equipment. The biggest portion was used to purchase a high-power laser diode bars from the laser diode company LaserTel. Special requirements of the collimation correction of laser diode bar were sent to LaserTel in order to match our proposed design. A variety of laser diode bar packages (conductive cooling mount and water cooling mount) were required. The different laser diode bar mounts have different temperature stabilities and cooling capabilities. Normally, conductive cooling bar is compatible with TEC cooling, and it will provide the more accurate temperature control (~0.01 k) for laser diode bar. However, it limits the thermal load of the conductive bar at around 60 W. On the other hand, water cooling mount provides a high thermal load and allows 100 W diode power. The temperature stability is totally dependent on the water chiller with fluctuation around (~0.06 k). The temperature fluctuation of the laser diode bar will affect the laser center wavelength drifting. The objective of our proposal is minimizing the wavelength drifting. We purchased the water chiller (ThermoCube) from Solid State Cooling System, and a high power current supply from Ametek. The laser system was set up, and the water cooling system and laser diode power supply system were tested. The cooling plate and temperature control system for volume Bragg grating (VBG) were also made. We will start the experiment in this fiscal year.

Information Shared

No publication update.

07076

Standoff Trace Chemical Sensing Using Two-Dimensional Ion Dip Spectroscopy

F. Rudakov

Project Description

Standoff detection of explosives and chemical warfare agents is of paramount importance for defense and homeland security. Most techniques for standoff trace chemical sensing are based on remotely probing vibrational spectra of target molecules using IR and Raman spectroscopies. Yet vibrational spectroscopy alone is often insufficient for reliable identification of large organic molecules in complex environments.

In a recent publication we presented a novel method for standoff trace chemical sensing that is based on structure sensitive photoionization of target molecules through Rydberg states followed by detection of laser-induced plasma with microwave radiation. We refer to this technique as Radar-RFS (Rydberg Fingerprint Spectroscopy). The complexity of Rydberg spectra does not scale with molecular size, making the technique well suited for detection of large organic molecules (such as those of explosives). Radar-RFS reveals highly resolved spectra and is orthogonal to well-established standoff sensing techniques such as IR and Raman spectroscopies.

The proposed work is focused on demonstrating the feasibility of two-dimensional standoff sensing (Rydberg spectrum along one axis and vibrational spectrum along the other axis). The proposed technique will overcome the major challenges faced by well-established techniques and will deliver unprecedented reliability of detection by providing sensitivity to both local and global molecular structure. The technique can be potentially applied to detection of nitro-containing explosives in complex environments. Using

vibrational spectroscopy, the nitro-compounds will be detected while Radar-RFS will discriminate between them and identify the explosive material.

Mission Relevance

The proposed technique for standoff detection is scientifically novel and may find multiple applications. For example, due to its high sensitivity, the proposed design can be used for the detection of airborne chemicals (i.e., for pollution monitoring). Rydberg spectroscopy is insensitive to molecular vibrational motion. Therefore, the proposed design may be applicable for studying combustion reactions. Besides, since the complexity of the Rydberg spectra does not scale with the size of the molecule, the technique is very applicable to characterization of large biomolecules organic molecules and clusters. The proposed design may also find applications in nuclear cycle monitoring and nonproliferation control.

Results and Accomplishments

We demonstrated that a) the lifetimes of the excited electronic states may be strongly dependent on the amount of energy available to the molecule and b) this effect can be used to acquire molecular spectra by depositing energy into vibrational modes through optical excitation to higher Rydberg states followed by internal conversion back to the S_1 state. This spectroscopic approach has several unique features: First, while multiphoton ionization usually requires laser power densities on the order of 10^{10}–10^{12} W/cm^2, Rydberg ion dip spectra can be acquired at laser power densities of ~ 10^7 W/cm^2 or less. Indeed, ionization is performed via two-photon process through a very long-lived electronic state and the transitions between molecular Rydberg states have high cross sections and extremely narrow Frank-Condon envelopes. Secondly, the technique can be applied to probe any vibrational or electronic transition as long as the transition results in deposition of energy into vibrational degrees of freedom.

Information Shared

F. Rudakov, Y. Zhang, X. Cheng, and P. M. Weber, “Standoff Trace Chemical Sensing via Manipulation of Excited Electronic State Lifetimes,” *Opt. Lett.* **38**(21), 4445–4448 (2013).

P. M. Weber and F. Rudakov, “Combustion of Highly Strained Hydrocarbons: Non-Intrusive Isomer Specific Detection of Complex Combustion Intermediates,” CBET NSF 09/01/2013-31/08/2016, proposal funded $300K.

P. M. Weber and F. Rudakov, “Standoff Detection of Effluents from Nuclear Processing via Structure Sensitive Photoionization and Microwave Scattering,” DTRA 01/01/2014-12/31/2016, proposal funded $470K.

ELECTRICAL AND ELECTRONIC SYSTEMS RESEARCH DIVISION

06627

Systems Approach to Steganalysis

J.D. Allen, V.C. Paquit, X. Liu

Project Description

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.

This project investigates image formation models to detect steganographic embeddings (i.e., secret messages in innocent-looking images). Our approach relies on a novel detection method called Long-Range Correlation (LRC), which aims at understanding how the steganographic routines are modifying the image encoding. Our hypothesis is that state-of-the-art steganographic algorithms modify image encoding without preserving pixel dependencies and therefore change long-range correlations.

Mission Relevance

Often used by terrorists to create covert 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 the years steganographic routines have become increasingly hard to identify, and despite millions of dollars invested in this quest, the 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 to be 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 the Intelligence Advanced Research Projects Activity (IARPA), the Defense Advanced Research Projects Agency (DARPA), and the Air Force Research Laboratory (AFRL).

Results and Accomplishments

To address the challenges of identifying steganographic images, our research plan includes six main tasks: (1) understanding steganographic routines, (2) creating a synthetic images database for known image formation processes, (3) implementing image processing algorithms on GPU platform to rapidly analyze billions of images, (4) collecting large database of real images for benchmarking, (5) defining an image formation model allowing a large variety of digital cameras to be characterized, and (6) detecting embedded messages by identifying the additive noise to the cover image as a function of the hidden message payload.

The image model is the core of our approach. It is a combination of statistical models – with various complexities – that best replicated the behaviors of the most commonly used post-processing algorithms applied to digital cameras' RAW image data (demosaicking, white balancing, gamma correction, optional image enhancement, and JPEG compression). The steganalysis decision is based on a similarity score between the image generated with our model after image matching and the target image. Our preliminary results indicate that modeling accurately LRC correlation will benefit steganalysis methods, but also that the image formation model is a lot more complex than the one investigated in this project.

Interesting finding: flipping all the least significant bits of an image containing a message with F5 will corrupt the JPEG image, whereas it does not happen when applying this operation on an image without an embedded message. This simple steganalysis method achieves 92% accuracy on a variety of synthetic and real images.

Information Shared

No publications at this time.

06633

Digital Hydraulic Actuator

L. Love, R. Lind, B. Richardson

Project Description

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. 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. The proposed digital hydraulic actuator enables discretely variable cross section controlled by ORNL's new multi-stage digital valves. If successful, this technology will provide a pathway to more than double the net energy productivity of fluid-powered systems. 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 power accounts for approximately 2 to 3% of energy consumption in the United States. Furthermore, the efficiency of fluid-powered systems is extremely low, with an average below 20%.

Hydraulics and pneumatics are a foundational technology for manufacturing. Therefore, improvements in fluid power efficiency directly impact DOE's Advanced Manufacturing Office (AMO). The team has briefed DOE AMO on these results and is working with the National Fluid Power Association on developing a fluid power institute. In addition, the Department of Defense uses fluid power on many of their systems. The Office of Naval Research (ONR) is presently funding ORNL to use some aspects of this technology for an energy-efficient underwater robotic system. Furthermore, ONRL has briefed US Special Operations Command (SOCOM) on energy-efficient hydraulics for wearable robotic applications.

Results and Accomplishments

The project successfully demonstrated through simulation studies the ability to control power flow through variable displacement actuators and digital control valves. Furthermore, the results of this investigation supported the development of a new, low-cost thermal control valve that has been successfully demonstrated on additive manufactured joints. The combination of energy-efficient valves and controls significantly improved the efficiency of a robotic platform and opens up many opportunities for new, high-efficiency control strategies.

Information Shared

None to date.

06634

Image Analysis for Calibration and Comparison of Hyperspectral Retina Fundus Camera Data and Ocular Phenomena

T.P. Karnowski, J. Baba

Project Description

The objective of this project 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 U.S. 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 that 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

The project began in FY 2012 with a limited amount of funds ($10K, or roughly 5% of the total budget), and thus results and accomplishments were 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.

In FY 2013, the project funding was again shifted so that more funds were scheduled for FY 2014. For FY 2013, the collaborations continued but the decision to postpone Doheny participation was made because the collaborative partner (Dr. Amir Kashani) was not reporting there until late in the summer when his residency in Michigan ended. Nevertheless, significant efforts were undertaken at ORNL and good progress was made. An additional ORNL researcher, Dr. Justin Baba, joined the project team. With his participation, the following accomplishments were achieved.

Software porting to Python was investigated. Given the initial project phasing, however, we have determined that Matlab is a more viable development environment for seed money goals and objectives. In accordance with this, additional software testing and evaluation were performed at ORNL, although additional steps will be needed in FY 2014.

- Additional data sets were delivered to ORNL by Dr. Kashani. Some initial analysis has been provided by him, although further in-depth information will be needed in FY 2014.

- A key element of the collaboration is the use of in vivo data, in that we may utilize not only existing data, but Dr. Kashani can collect additional samples as needed along with data created by surgically implanting different material into tissue as needed. The following accomplishments are expected to benefit from, as well as advance, the utility of in vivo data collection.

    - An image resolution assessment of in vivo data was created. The assessment is based on the extraction of the system response to a line edge, which is a common method in many machine vision applications. This assessment represents the first measurement of the hyperspectral fundus camera spatial resolution response.

    - A method and specification for a reflectance and diffuse reflectance standard for in vivo implementation was developed. This measurement is an additional step needed to characterize the response of the hyperspectral fundus camera so that accurate comparisons between tissue specimens can be made.

    - A color assessment standard for the in vivo data collection was developed. This allows an assessment of individual wavelength responses across the hyperspectral fundus camera bandwidth.

Finally, work on an assessment of oxygen saturation (O2-sat) quantification was begun. While the HFC is expected to perform more than oximetry, this application is a known use of the instrument and can serve as a stepping stone to more complex and unique measurements.

The project will conclude in FY 2014, with a remaining budget of $105K.

Information Shared

None at this time (September 2013).

06641

Adaptive Emissivity Surface Using Sub-Pixel Averaging

S.R. Hunter, P.G. Datskos

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 demonstrated 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 explored in the present project involved 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 was to modify the apparent emissivity of these 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

Extensive modeling studies were performed of the temperature and emissivity requirements that lead to good apparent temperature matching between the variable emissivity surface and the background conditions. A range of outdoor atmospheric conditions, pertinent to the optimal operation of the adaptive emissivity surfaces, were measured including air pressure, air temperature, high and low sky temperatures, relative and absolute humidity levels, percentage cloud cover, cloud type, and apparent cloud temperature. These parameters were measured periodically over an 8 month period to record a range of environmental conditions. These measurements were then used to determine when the use of the adaptive emissivity surfaces is feasible and when they will function less than optimally in real world operating conditions. A variety of structures and surfaces were created which demonstrated that apparent variable emissivity surfaces can be created using surfaces with varying ratios of high- and low-emissivity

materials. The emissivities and apparent temperatures of these surfaces were observed to be in good agreement with the modeled surfaces over a range of modeled real-world atmospheric conditions. Infrared imaging, temperature, and emissivity measurements in real-world situations demonstrated that sub-pixel averaging, along with cold sky reflectivity, allows a range of black body conditions to be temperature matched to varying backgrounds. Black body temperature matching was found to be feasible over the temperature range from <0°C to >60°C. Additionally, non-uniformities in the structure surfaces and aliasing effects in the infrared camera introduce apparent "noise" in the surface emissivity and measured temperatures that can be matched with the temperature fluctuations observed in real-world infrared imagery, allowing the structures to blend perfectly into the thermal background.

Information Shared

There have been no publications resulting from this work to date.

06642

Machine Vision for Underwater Explosive Ordnance Detection

T.P. Karnowski, R.A. Kerekes, A. Davis

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 very 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 U.S. 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 of 2012, 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.

For FY 2013, we completed the processing of the PC-NSWC set which included "ground truth" indicators of where MLOs were actually located. The PC-NSWC set consisted of test runs of "MSTIF" files, which are specially tagged TIF files that had to be converted to regular image files using custom software. This data set was referred to as the "Panama City Dataset." The SPAWAR set was referred to as the "Reorg" set as it was effectively a "reorganization" of the original set to remove the problem where training and testing samples were mixed. The focus therefore was on developing and testing machine learning / image processing methods that would work well on both the data sets. The Panama City data set required a high level of contrast enhancement, and an algorithm was implemented to improve the image quality. There are other effects that offered impediments, including distortions (likely resulting from maneuvers in the vehicle). A deep machine learning method, convolutional neural networks, was investigated, but the overall data set was too small to make this method effective and the training was too long. A better method proved to be shallow neural networks and random forest methods. Both worked well on the Panama City set (e.g., a typical neural network performance was sensitivity 99.5% and specificity 97.9%), but this was only when the anomalies of distorted image data were removed.

Overall, the methods used showed considerable promise. An integrated, embedded approach coupled with feedback and vehicle autonomy would provide benefits, particularly when considering the dearth of data examples for the field. As an example, images obtained when the vehicle is performing a complex maneuver must be re-performed under a more stable navigation method. Synthetic examples could be generated using image transformations or modeling, but these must match the expected imaging performance of the target SSS system. Finally, we have begun the process of sharing these results with potential sponsors and collaborators, including the Joint Improvised Explosive Device Defeat Organization (JIEDO), the Department of Homeland Security, and the Strategic Environmental Research and Development Program (SERDP).

Information Shared

None as of September 2013.

06680

Hardware Implementation of Space-Time Coding for WiMAX Protocol

M. Bobrek

Project Description

Wireless channels suffer greatly from multipath fading, and diversity is an efficient way to combat this fading. Several methods such as time diversity, frequency diversity, receive diversity, and transmit diversity have been proposed recently. However, time diversity and frequency diversity both require additional bandwidth to maintain the same throughput (bit rate). Receive diversity adds to design complexity and increased power consumption at the receiver. Compared with these diversity schemes, transmit diversity offers a potential improvement of both system design complexity and bandwidth efficiency. Space-time coding (STC) is based on transmit diversity, where information is staggered over multiple symbols and transmitted using multiple antennas. Thus, STC offers diversity gain in the channel because of the multiple antennas and paths. However, the challenge is to maintain high information rates. Several schemes have been proposed to optimize both the diversity and the rate. In most existing schemes, the channel state information is assumed either to be known to the receiver or to be accurately estimated.

Ongoing research efforts at ORNL have been focusing on implementing transceivers for various wireless protocols deemed suitable for specific environments and applications. These protocols include Worldwide Interoperability for Microwave Access (WiMAX) and Long Term Evolution (LTE), which are the basis for modern Fourth Generation (4G) cellular standards. However, the current implementations at ORNL do not consider STC, which is an inherent part of the 4G standard. This limitation in our implementations does not allow our transceivers to take full advantage of the improvements that the 4G standards offer. The completed work implements an advanced STC technique within our existing WiMAX protocols in software and hardware and evaluates the enhanced WiMAX system simulation against the performance specifications of the associated 4G standard.

We focused on demonstrating the STC algorithm by implementing a multiple-input multiple-output (MIMO) orthogonal frequency division multiplexing (OFDM) system in hardware for the WiMAX protocol. The uniqueness of our approach is the implementation of STC in a model-based design environment using Matlab Simulink® and Xilinx System Generator SYSGEN®. This will give us the flexibility to investigate new ideas in the area of STC.

Mission Relevance

The research was based on a novel communication technique for increasing channel capacity. The STC technique offers unique contributions to the field of diversities for communication. However, existing research results are mostly based on simulation. There is a legitimate gap between the basic concept and the challenges for its application to practical systems. The proof-of-principle research that we conducted bridges this gap by showing that the technique can be implemented for real-time hardware platforms in a scalable format.

The DOE Office of Electricity Delivery and Energy Reliability (OE) Smart Grid Program has shown interest in robust (works under severe channel conditions), fast (higher channel capacity), and energy-efficient (requires less transmit power) wireless communications systems. Other potential sponsors for the developed technology include the DOD (ARL, NRL, AFRL, DARPA, etc.), DHS, and NASA. Robust, fast, and energy-efficient communications are in general of interest Government wide, as well as in the commercial sector. OFDM-based communication systems are already planned for many military, space,

homeland security, and commercial applications. Specifically, the DARPA STO organization has a strong interest in STC research.

Results and Accomplishments

Initially, a Matlab Simulink® software model for a multiple-input multiple-output (MIMO) orthogonal frequency division multiplexing (OFDM) system for the WiMAX protocol was developed and simulated. Instead of the commonly used STC diversity scheme, an alternative Space-Frequency Coding (SFC) scheme was developed for use in frequency-selective fast-fading channels. The model includes SFC algorithms for two-transmit-one-receive MIMO systems. Specifically, a two-transmitter space-frequency encoder was developed, together with an OFDMA-based space-frequency decoder on the receiver side.

In the second phase of the project, the developed software model was implemented on an ML605, a Xilinx FPGA-based hardware platform, using SYSGEN® library of standard FPGA processing blocks. The transmit chain of the OFDM MIMO system includes two OFDM transmitters connected to the space-frequency encoder. The output of the transmitter feeds a classical OFDM receiver equipped with the space-frequency decoder. The hardware simulations fully confirmed the results obtained by the software simulation in the first phase of the project.

The space-frequency encoder and decoder blocks have been archived in the RF, Communications, and Intelligent System (RFCIS) Group's internal library archive of SYSGEN® blocks for future reuse. In addition, a paper abstract related to this research has been submitted and accepted for the Virginia Tech Wireless Symposium 2013.

Information Shared

M. Bobrek, "FPGA Implementation of Space-Frequency Coding for Fixed WiMAX Systems Using Simulink-Sysgen Design Environment," abstract accepted for Virginia Tech 2013 Symposium, Blacksburg, VA.

06783

Application of Plenoptic Computational Photography to Improve Off-Axis Iris Recognition

H.J. Santos-Villalobos

Project Description

Computational imaging methods such as plenoptic cameras are revolutionizing the imaging industry. Plenoptic cameras capture a light field, which imparts 3D information such as the position and the direction of rays coming from a scene. The information embedded in the light field allows for images to be refocused after they are taken and coarse depth estimates of points in the scene. ***The goal of this seed money is to determine if plenoptic cameras can be applied to centimeter-scale objects to estimate their 3D shape with micro-scale resolution***. More precisely, our goal is to reach a depth resolution of 20 µm. If successful, this effort will have the required basis for future research proposals to address current challenges for biometrics, advanced manufacturing, homeland security, defense, and many others.

Mission Relevance

We are targeting biometrics—in particular, the recognition of off-axis irises, because biometrics will immediately benefit from the proposed plenoptic camera, we have existing unique experience in this area of biometrics, and have a high probability of follow-on funding for that application area. Off-axis iris recognition is an open problem, and determining a solution will be a major step toward ubiquitous identification and verification systems. Such systems are crucial to protect and safeguard national landmarks, nuclear facilities, sensitive data centers, the soldiers in the battlefield, and other security personnel. Government agencies, such as the Department of Energy, the Department of Homeland Security, the Biometric Identity Management Agency, and the Army, to name a few, will benefit from and are interested in this technology.

Results and Accomplishments

System minimum requirements

As a two-phase LDRD SEED project, we document our progress and accomplishments for the first phase of the project. The deliverable for this phase is a definition of the plenoptic camera optical components, such as the main lens aperture and focal length, the microlens array grid pattern, pitch, aperture size, and focal length, the imaging sensor dimensions and pixel size, and the distances between each component. In addition, we need to show that the optical recipe meets the performance needed (e.g., field of view (FOV) and lateral and depth resolution) for the project goals.

The FOV and lateral resolution requirements can be defined from the literature. It is well known that the human iris diameter is between 10 mm and 13 mm and at least 140 digital image pixels across the iris diameter are required for recognition [Daugman 2004, "How Iris Recognition Works"]. Consequently, the minimum requirements for the camera FoV and lateral resolution are 10 mm and 70 µm/pixel, respectively. Computationally, we determined that the minimum required depth resolution is 20 µm/pixel.

Plenoptic optical recipe

The first step to define the optics of the system is to select the sensor. We selected a monochromatic sensor with a large imaging area (width = 36.17 mm, height = 24.11 mm, and pixel size = 5.5mm) and high quantum efficiency for 850 nm wavelengths. For the main lens, we have several off-the-shelf alternatives, such as the Canon MP-E 65 mm f/2.8 1-5× Macro Photo lens. The main lens must have low aberrations, short focus distance, and at least 2× magnification. The microlens array (MLA) optical specifications were obtained via a brute force algorithm that evaluates the performance of several configurations in order to find the optical parameters that make the system meet the minimum requirements. After the best optical configuration is found, the parameters are introduced in Zemax to measure geometric aberrations, refine the parameters, and validate the MLA optical properties. The final optical properties of our microlenses are ROC 0.258 mm, aperture diameter 0.198 mm, pitch 0.620 mm, FOV 1.66 mm, sagittal 0.0197 mm, distance from MLA to sensor 0.855 mm and distance from MLA to virtual image 2.29 mm. This produces microlenses with a focal length of 0.505 mm, sagittal of 0.0197 mm, working F# of 3.5, and largest baseline 1.24 mm. Based on these optical properties and the main lens having at least 2× magnification, we obtain an effective pixel resolution of 9.8 µm after considering diffraction and depth resolution of 18.1 µm, which exceeds our new 20 µm goal.

Information Shared

J. Thompson, H. Santos-Villalobos, M. Karakaya, D. Barstow, D. Bolme, and C. Boehnen, "Off-Angle Iris Correction using a Biological Model," IEEE Biometrics Theory, Applications and Systems (BTAS), Washington, DC, September 29, 2013.

J. Thompson, P. Flynn, K. Bowyer, and H. Santos-Villalobos, "Effects of Iris Surface Curvature on Iris Recognition," IEEE Biometrics Theory, Applications and Systems (BTAS), Washington, DC, September 29, 2013.

07073

New Protocols for User Authentication and Key Distribution for Smart Grid Applications Using Physical Unclonable Functions

M. Bobrek

Project Description

Existing communication infrastructure for control and data transfer in Smart Grid includes a heterogeneous mixture of communication media such as optic fibers, twisted pairs, coaxial cables, and the free space. The infrastructure is utilizing existing commercial protocols such as T1, Ethernet, Celular, WiMAX, WiFi, ZigBee, Bluethoot, etc. A common approach to improve the cyber security in electric power industry is to add security features to the standard communication protocols such as TCP/IP, Distributed Network Protocol ver.3 (DNP3), and Object Linking and Embedding for Process Control (OPC). Some of these features include packet-filtering firewalls, Network Address Translation, and Virtual Private Networks [1]. Integral part of these features is data encryption which is the main tool for data protection against cyber-attacks. While the existing encryption standards such as Advanced Encryption Protocol (AES) offer sufficient protection, the user authentication and the key management remain the most vulnerable parts of the system. In addition, the existing authentication and key management protocols are not always practical as they include generation and distribution of multiple keys. For example, the key management and user authentication protocols for the reader-meter communications can be cumbersome, with nearly eight keys per meter, and vulnerable to cyber-attacks as there may be thousands of meters connected to a single aggregator. Also, they may not offer sufficient level of security as they were usually designed for IP-based applications.

This proposal presents an efficient and secure method for the key generation and distribution and for user authentication within Smart Grid applications using Silicon-based Physical Unclonable Functions (PUFs) [2, 3]. Due to the production variations (PV) in silicon circuits, PUFs offer a unique, verifiable signature that is irreproducible by the adversary. The keys are generated locally on each node, eliminating the need for traditional key generation and management requirements for smart grid applications. The goal of this proposal is to validate PUF-based authentication and key distribution protocol using Field Programmable Gate Array (FPGA)-based hardware platform.

Mission Relevance

As stated in the DOE's Energy Delivery Systems Cyber Security Roadmap for the Smart Grid, the cyber security is one of the top emerging and standing issues facing the electric sector over the next 10 years. Current efforts of the US Government, the research community and the energy companies in the area of Smart Grid cyber security is to develop and implement robust cyber security technologies to prevent cyber threats to energy delivery systems that can impact national security, public safety, and the national economy. This is a proposal to contribute to these global efforts by introducing and validating a new method to increase the cybersecurity of Smart Grid communications using Silicon PUFs.

Results and Accomplishments

There were no research activities in FY2013 on this project. The FY2013 budget of $5,000.00 was used to purchase the hardware and the software needed for the project.

Information Shared

R. Parks et al., *Network Security Infrastructure Testing*, Sandia National Laboratory Report, October 2005.

R. Pappu, B. Recht, J. Teylor, and N. Gershenfeld, "Physical One-Way Functions," *Science 297*, November 2002.

R. Maes and I. Verbawhede, "Physically Unclonable Functions: a Study of the State of the Art and Future Research Directions," book chapter in *Towards Hardware-Intrinsic Security*, *Information Security and Cryptography*, 2010.

ENVIRONMENTAL SCIENCES DIVISION

06767

Toward Improved Understanding of HGMS Separation for Aerosol Particle Collection

M.-D. Cheng, L.R. Avens, G.M. Ludtka

Project Description

Collection of airborne particles for environmental protection and human health assessment using magnetic means has not been prevalent, because mechanisms controlling magnetic collection of ultrafine particles from the air using complex matrix morphology are poorly understood. We propose to improve our understanding of the control mechanisms for the design of a next-generation aerosol collector using high-gradient magnetic principle under selected environmental conditions. We are interested in aerosol particles consisting of common environmental non-magnetic and magnetic materials with a diameter less than 200 nm.

Mission Relevance

The results of this research are of interest to environmental monitoring of ultrafine particles that are of importance to the protection of human health, air quality, and emissions control. The US EPA has long been interested in an effective control method for the removal of airborne particles smaller than 200 nm with minimal power requirement. Small particles have also been identified as an important player in atmospheric cloud life cycle that could be important to changes in regional climate, which is a direct DOE BER research mission.

Results and Accomplishments

Magnetic removal of aerosol particles is an air pollution control mechanism that has rarely been taught in school. The topic is not found in all air pollution control engineering textbooks. We have conducted several tests on the collection of three types of particles representing a range of magnetic susceptibility from diamagnetic to ferromagnetic that are commonly found in the environmental samples, using the proposed magnetic collection technique. We tested the collection under different wind speeds simulating calm to light wind conditions in the ambient environment. Comparison of magnetic collection was made to the negative control where a non-magnetic device was used. As predicted, the magnetic force has no effect, statistically, in the collection of sodium chloride aerosols that are weakly diamagnetic. The magnetic force applied in the collection process enhanced collections of para- and ferro-magnetic particles. This use of magnetic force was required to meet a capture efficiency of greater than 99% at higher wind speed conditions for magnetic particles.

Information Shared

The work has been presented to interested agencies, but has not been submitted for publication. A manuscript is being prepared.

ENERGY AND TRANSPORTATION SCIENCE DIVISION

06638

Blue-Energy Harvesting by ORNL Mesoporous Carbon Electrodes

C. Tsouris, 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 MC electrodes can be used to reach high energy-recovery efficiencies. An experimental assembly has been set up, and preliminary data of seawater electrosorption have been obtained. Neutron imaging experiments provided insight into ion transport rates in the electrodes. 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 was carried out using two flow cells with a pair of ORNL MC electrodes in each cell, for capacitive energy extraction, and the required electrical circuit. The first cell was used for in situ neutron imaging of blue-energy experiments, while the second was used in laboratory-scale experiments. The setup for both electrodes simulates capacitive deionization systems. Two tanks with freshwater and high-salinity water were connected to a feeding pump. Each experiment consisted of four steps:

(1) charging using high-salinity water, (2) switching step I from high-salinity to low-salinity water, (3) discharging, and (4) switching step II from low-salinity to high-salinity water. The voltage across the electrodes, current, and conductivity of the solution was continuously monitored throughout the entire duration of each experiment. The experiments were conducted to determine if there was a voltage increase across the electrodes during the switching step I, when freshwater was flushed through the CDI cell.

Results demonstrated the proof of principle, but more work is needed to produce a practical device that can efficiently recover the energy of mixing of high-salinity and low-salinity waters. For experiments conducted at 1.2 V, no increase in voltage was observed during step 2, and the potential across the electrodes kept dropping after the external potential was removed. For the cycles carried out at 0.6 V and 0.9 V applied voltage, we observed an increase in voltage during step 2 when water was flushed through the cell. Thus, it can be deduced that a voltage range of 0.6–0.9 V is suitable for the operation of the capacitive blue energy cycle.

Neutron imaging, using LiCl in D_2O, revealed information on the transient behavior of ions during the different steps of the blue energy cycle. The transmission profiles across the electrodes provided insight into the rate and direction of ion transport as a function of time, and showed that during step 2 of the cycle, the concentration of counterions inside the electrodes decreases and the electrical double-layer thickness increases. This expansion of the double-layer thickness increases the capacitive energy stored in the electrochemical cell.

This small Seed Money project demonstrated a proof of principle of harnessing the energy of mixing high-salinity and low-salinity solutions. Monitoring tools have been established to provide a better understanding of the behavior of the electrodes, during the energy-harnessing cycle, and quantitatively evaluate capacitive blue-energy devices. These tools can be used in future work than needs to be focused on maximizing the energy recovery by optimizing the electrode structure and operating parameters. Future work is expected to lead to capacitive cells that can efficiently harness blue energy in delta areas, where rivers with low-salinity water flow into seawater.

06669

Printed Engines to Enable Characterization of Combustion Processes of Small-Scale Internal Combustion Engines

M.D. Kass, M. Noakes, R. Dehoff, L. Love, B. Kaul, K.D. Edwards

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 AM 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

A titanium engine head was printed and evaluated on a 4-cc single cylinder two-stroke engine. The head was equipped with a printed in sensor port to evaluate the combustion process and measure the heat release rate. The printed titanium head was successfully operated over 20 hours without failure. The engine was mapped from 2000 to 7000 RPM on a motoring dynamometer at maximum torque with both the stock aluminum head and the printed titanium head. Analysis of the power curves showed that peak power was not reached in this speed range; however, the maximum brake torque (MBT) reached a peak for speeds of 3000 and 3500RPM. The engine air-fuel ratio was rich for all speeds, but approaches stoichiometry at 6000 RPM. Interestingly, the MBT for each speed setting occurred at less-rich conditions with the titanium head than with the aluminum head. The reduced thermal conductivity associated with the titanium head allowed for more complete combustion of the fuel, and hence, leaner operation. The titanium head produced improved fuel efficiency only at 2000 and 2500 RPM; at higher speeds, the engine operated more efficiently with the stock aluminum head.

The calculated brake work efficiency of the 4-cc single cylinder two-stroke glow plug engine was 7.5 and 5.5 % for the aluminum and titanium heads, respectively, at 6000 RPM. These efficiencies dropped to 4.2 and 4.8 % when the engine speed was increased to 7000 RPM. The 1st and 2nd Law analyses also showed that very little energy is available in the exhaust that can be recovered. Most of the available energy is lost through walls and from blow by. This observation, along with the incomplete fuel combustion, indicates that the efficiency and performance can be greatly improved by using stronger, more heat resistant materials and tighter tolerance between the piston-wall gap.

Information Shared

M. D. Kass, M. Noakes, L. Love, B. Kaul, B. Dehoff, and J. F. Thomas, "Experimental Evaluation of a 4-cc Glow-ignition Single Cylinder two-stroke Engine," SAE Technical Paper Series, March 2014.

06757

Intelligent Supervisory Power Management Control in PEVs

A. Malikopoulos, S. Pannala

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. Recently, plug-in electric vehicles (PEVs) have attracted considerable attention due to their potential to reduce fuel consumption and emissions. The high costs associated with their energy storage systems and concerns with the PEV battery range and predictability have been significant barriers to extensive market penetration of PEVs. This project will directly address these barriers through overall PEV optimization, including the capacity and lifetime of the battery. The overarching goal of the proposed research is to establish a virtual energy storage system that can be integrated in a PEV simulation model and develop an intelligent supervisory controller that will optimize fuel economy and battery utilization and lifetime. The long-term potential benefits of the proposed research are substantial. Overall PEV operation will be improved in terms of fuel economy and battery capacity utilization, and thus increased range or smaller batteries will be possible, reducing initial PEV overall cost of ownership. The combined approach optimizes the available lifetime of the battery packs, which has significant implicationson the cost and warranty.

Mission Relevance

The research conducted in this project aims to address overall PEV optimization including the impact on the battery system energy utilization and lifetime. This problem is important because (1) if overall PEV operation can be improved, the chosen battery design capacity can be less conservative, thus reducing the PEV cost, and (2) if the lifetime of the battery system can be improved, this will reduce the overall cost of ownership. By addressing these issues, an extensive market penetration of PEVs will be achievable. Thus the expected outcome is directly consistent with the DOE mission to promote scientific and technological innovations that advance the national, economic, and energy security of the United States.

Results and Accomplishments

Although previous research reported in the literature has aimed at enhancing our understanding of power management control optimization in PEVs, the battery system has been considered as a ideal “buffer” which can be used either to store or utilize energy at any time. The optimization approach developed in this project addresses overall PEV optimization, including the capacity and lifetime of the battery. PEV operation was modeled as a controlled Markov chain using the average cost criterion, and we treated the stochastic optimal control (SOC) problem as a multiobjective optimization problem.

For a target SOC value, the battery SOC was compared for the case of an ideal battery and for the case of including the capacity and lifetime of the battery in the optimization problem formulation. Considering the battery lifetime in addition to the engine and the motor has a clear positive impact on the battery SOC. The case that includes the battery capacity and lifetime demonstrates a SOC that is preserved close to the target value, while the ideal battery case demonstrates rapid change in the SOC. A direct result of preserving the SOC close to the target value is the improvement of the end of driving cycle battery average estimated range. The elimination of the rapid change in the SOC directly improves the battery average temperature, and at the end of the driving cycle, the battery temperature is improved significantly. These improvements in the battery performance characteristics come at the expense of the cumulative fuel consumption. Consequently, the results show a tradeoff between the battery performance characteristics, for example, lifetime and range, and the fuel consumption.

The optimization approach adopted here facilitates better understanding of associated trade-offs between the performance of the engine and the battery. A significant improvement in the battery performance characteristics can be achieved if the battery behavior is considered in the optimization problem. However, a trade-off arises between the battery performance characteristics and fuel consumption.

Information Shared

A. A. Malikopoulos, "A Duality Framework for Stochastic Optimal Control of Complex Systems," *IEEE Transactions on Automatic Control*, in review.

M. Shaltout, A. A. Malikopoulos, S. Pannala, and D. Chen, "A Duality Framework for Optimal Control of Battery Management Systems in Hybrid Electric Vehicles," Proceedings of the 2014 American Control Conference, Portland, Oregon, June 4–6, 2014 (in review).

A. A. Malikopoulos and V. Maroulas, "A Multiobjective Optimization Analysis for Stochastic Control of Complex Systems," Proceedings of the 2014 American Control Conference, Portland, Oregon, June 4–6, 2014 (in review).

06766

High-Throughput, Super-Selective Membranes to Improve Biofuel Economics

M.Z. Hu

Project Description

We seek to establish proof of principle of a membrane concept combining high flux and high selectivity that can impact several large-scale, energy-intensive processes. The novel High-Performance Architectured Surface Selective (HiPAS) technology combines a superhydrophobic surface selectivity layer with an architectured high-flux membrane layer. Because these two nanostructured layers can be integrated with established ORNL inorganic membranes as supports, there is a good potential for scale-up and implementation in follow-on efforts. This effort will focus on ethanol-water separation and address the central proof-of-principle questions regarding achievable selectivity and permeability based on the HiPAS concept. We will (1) fabricate HiPAS membranes with tailored surface selectivity and nanopore architectures, (2) develop essential separation performance data (selectivity and permeability for ethanol), and (3) compare results against target performance data.

Mission Relevance

The proposed HiPAS membrane is relevant to the mission of DOE's Bioenergy Technology Office (BETO). The goal of the Seed project aims directly at the potential improvement of economics in ethanol production due to possible higher separation efficiency. The HiPAS membrane could be developed further for extended biofuel separation applications such as bio-oil processing, and thus could impact the future drop-in fuels.

Results and Accomplishments

The key component of this Seed project includes HiPAS membrane synthesis/fabrication (i.e., membrane support, nanotextured top layer, and the surface chemistry development) and membrane permeation studies. In FY2013, we have established a die press-sintering process that allows fabrication of membrane support in the form of porous alumina ceramic discs of desirable dimension. Various methods on nanotexturing have been investigated on particle deposition and substrate etching. A series of surface-

modifying surfactant ligands were evaluated and selected. Our fabricated inorganic membrane surfaces have demonstrated the superhydrophobicity with a contact angle from 167–172°. We also have obtained video evidence on fundamentally important phenomena that the HiPAS membrane surface repels the water droplet beads away from the membrane surface, while allowing the ethanol droplet to wet and permeate into the membrane surface. Our preliminary pervaporation permeation test has shown that a 10.7 wt.% ethanol-water mixture solution was reduced to ~1.5 wt.% ethanol, while the ethanol concentration was concentrated on the other side of membrane. Such a proof-of-principle result needs to be further verified in FY 2014 by more pervaporation tests (under various conditions) using more refined HiPAS membranes. On the external program development, the principal investigator has actively interacted with the DOE/BETO through our ORNL biomass program manager and established proposal collaboration with NREL. Our proposal convinced BETO to consider sponsoring the investigation of HiPAS membranes in bio-oil processing applications. At this time, we expect to receive future possible funding ($300,000, for FY2014) via a BETO AOP process.

Information Shared

M. Hu, M. Sturgeon, T. Aytug, M. P. Paranthaman, and J.T. Simpson, Super-Surface Selective Nanomembranes Providing Simultaneous High Permeation Flux and High Selectivity, patent application declaration filed January 2013, Application No.: 13/666,217, UTB ID Ref. No.: 2622, NDQ Ref. No.: 19079.0348 (6321-420).

07074

Oxygen-Stabilized Flame Propagation to Improve SI Engine Efficiency and Performance

M.D. Kass, B. Kaul, C.S. Daw

Project Description

The objective is to improve combustion efficiency of spark-ignited (SI) engines through improved flame stabilization. Engine efficiency and emissions reduction are limited by flame instabilities at high-dilution and high-boost pressures; however, the spark plug energy levels needed to achieve stable ignition under these conditions are not feasible using current technologies. We propose to experimentally demonstrate a novel means for extending the dilution and pressure limits of spark-ignited internal combustion by increasing oxygen concentration in the immediate vicinity of the spark plug. Theoretical considerations indicate that such localized oxygen enhancement in the spark region should enhance flame kernel nucleation and subsequent flame propagation, thereby extending the limits of stable combustion under dilute and high-pressure conditions relevant to advanced engines. We plan to conduct our proof-of-principle experiment using an existing specially designed SI combustion chamber. Fuel-air mixtures will be added to the vessel, and pure oxygen will be injected through a specially constructed channel in the spark plug directly into the electrode gap to determine if combustion stability can be enhanced under more dilute and higher pressure conditions. Flame kernel formation and subsequent propagation will be assessed by precise measurement of combustion chamber pressure and direct visual observation. Successful demonstration will open up additional R&D opportunities in the areas of improved engine control and novel spark plug designs. Such novel technologies for advanced engines would fit very well with the priorities of sponsors in DOE's Vehicle Technologies Office and current industry partners.

Mission Relevance

Advances in engine development will require technologies and methods that extend the operational range of stable combustion and flame propagation. Highly efficient combustion achieved via high dilution is limited by flame kernel propagation at conditions of both lean and high exhaust gas recirculation conditions. Improved engine efficiency is a hallmark of the DOE Vehicle Transportation program. Pushing flame stabilization to higher limits allows a greater range of engine operation under highly efficient combustion regimes. Oxygen-assisted flame kernel growth offers the potential to extend the dilution limits of spark-ignited engines.

Results and Accomplishments

This effort was initiated in late September for a total FY 2013 allocation of $5K. During this time, instrumentation was procured and other resources were lined up for the subsequent FY 2014 effort.

07077

Sulfur Trioxide Point Measurements via Regenerable Fiber Tip Luminescence

R.M. Connatser, W.P. Partridge, Jr., S.A. Lewis, Sr., J.M.E. Storey

Project Description

Sulfur species in high-temperature applications, such as automotive catalysis, stationary power generation, and industrial processing, pose an environmental threat and can decrease engine energy efficiency by accelerating component corrosion and compromising the catalysts utilized to mitigate harmful emissions (i.e., smog-forming NOx). Among sulfur's combustion products, sulfur trioxide (SO_3) is particularly difficult to measure. High reactivity and an aggressively hygroscopic nature lead to an inability to make effective and quantitative measurements due to adsorption to or reaction with transfer lines and spectroscopic windows. This limits detailed understanding of SO_3 formation and reaction chemistry and its impact on other processes such as catalysis and materials corrosion. To address intractable problems when measuring SO_3 emissions, an innovative in situ measurement will be developed to eliminate extraction-system losses and thereby improve sensitivity and measurement speed. The single insertion point probe is based on luminescence detection of SO_3 via association with an oxidation-state-sensitive sol gel-adhered copper zeolite. The probe will be engineered for gaseous and thermal regenerability after strong $SO_3/H_2SO_4(g)$ adsorption. Expected outcomes include a robust, regenerable probe design for faster and improved SO_3 quantitation relative to existing methods for SO_3 estimation. This proof-of-principle on a laboratory scale will lead to further development for use on engines and catalyst bench reactors with commercial and developmental monolithic catalyst to enable key insights into catalyst reaction and poisoning mechanisms in realistic circumstances. Catalysis and materials improvements increase automotive fuel economy and reduce operating costs in power generation, industrial and biomass processing, and additive manufacturing, especially in non-domestic markets with higher sulfur fuels. Fundamental understanding gains include SO_3 reaction chemistry across a range of temperatures, pressures, and gaseous environments.

Mission Relevance

Opportunities for substantial progress remain in developing materials, computational models, and component controls for automotive and stationary power aftertreatment applications to simultaneously meet efficiency and emissions regulations. Sulfur and its compounds comprise one family of pollutants in

the emissions from power generation, both stationary and automotive. Sulfur released from the burning of hydrocarbon fuels can cause acid rain, corrosion of engine components, and deactivation of catalysts that clean up other harmful substances. The insights the proposed proof-of-concept SO_3 probe will lend to emissions control, and thereby energy efficiency improvements, touch several areas of vehicle technologies, power generation, and biomass utilization. All of these are major thrust areas in DOE EERE's mission, to invest in clean energy technologies that strengthen the economy, protect the environment, and reduce dependence on foreign oil. Monitoring of industrial processes could also be improved in both quality and resource efficiency. Finally, certain aspects of the gas-liquid sulfur-sulfate equilibrium are essential elements of these proof-of-principle experiments. This opens a door to more fundamental study of several aspects of sulfur interactions. Follow-on funding includes DOE's Office of Energy Efficiency and Renewable Energy—Gurpreet Singh (Vehicle Technologies Program) and Kevin Stork (Fuels & Lubricants Program). Work-for-Others follow-on funding will be sought from stationary power companies, automotive manufacturers (Ford letter attached), engine companies (Cummins letter attached), and catalyst component suppliers.

Results and Accomplishments

During these first 2 months, probe fabrication was improved, and intra- and inter-probe reproducibility was studied. A small reactor was designed to generate the SO_3. In addition, the primary laser source for luminescence excitation in the catalyst material detection was upgraded, and two capillary gas dividers for delivery of test gases were repaired. Early iterations of the copper ZSM5 catalyst-tipped probes suffered from a lack of physical robustness, that is, their tip coating were extremely fragile and would flake off the optical-fiber tip upon scratching against the reactor or catalyst channel wall. One of two strategies implemented to improve probe robustness was intensive cleaning of the fused silica optical fiber tip with peroxide then boiling with sulfuric acid, followed by copious deionized water rinses, and a final activation via protonation of surface silanol sites. These modifications alone have yielded much more robust connections between catalyst sol gel material, deposited in the liquid phase, and the solid fused silica surface of the optical fiber. The second improvement tested during these early stages of work was the standardizing of a protocol for delivering liquid sol gel mixed with catalyst material to the surface of the optical fiber. A fine mist of the material was generated, allowing for the formation of a porous film of the sol gel upon drying, while not being so fine as to deliver solvent-free material to the surface. With too much removal of carrier solvent, wetting of the optical fiber tip can be compromised and robustness again disrupted.

A second area of progress relates also to probe robustness but also includes evaluation of response characteristics. Preparations were made, and initial experiments carried out, to measure the differences in probe response to exposure to ammonia, an exhaust species that poses less of a health hazard than SO_3. These data are currently being collected and analyzed and will be reported in the annual survey. Finally, discussions began with catalyst after-treatment colleagues on utilizing a diesel oxidation catalyst to use in-line with the probe reactor for in situ generation of SO_3. Not only is this the safest way to introduce the analyte for measurement by our probes but it is also the most representative and realistic, since the probe will first be applied in engine exhaust to SO_3 measurement.

Information Shared

R. M. Connatser, W. P. Partridge, and J. E. Parks, "Ammonia & Oxidation State Sensing Based on Catalyst-Tipped Optical Fibers," poster presented at the Southeastern Chapter of North American Catalysis Society Meeting, Asheville, NC, September 29–30, 2013.

NUCLEAR SECURITY AND ISOTOPE TECHNOLOGY DIVISION

06791

Investigation of Underwater Bulk Detection of Explosives Using Neutron Interrogation

A. Nicholson, D. Hornback, D. Archer

Project Description

Monte Carlo calculations were performed to analyze and assist in the determination of requirements for an underwater neutron interrogation system for explosives detection. Multiple federal agencies are concerned with unexploded underwater munitions and are actively seeking proposals for techniques for the detection and classification of underwater explosives. Neutron interrogation for explosives detection is an established technique for terrestrial explosives detection, and the possibility exists to extend this technology for underwater application. However, both the underwater environment and operational scenarios provide additional challenges relative to a land-based system. 3D radiation transport calculations (MCNP – Monte Carlo N-Particle) will provide quantitative guidance to the applicability of this underwater neutron interrogation. Specific questions to be answered by this effort include the deliverable neutron flux to an underwater target at different stand-off distances, the required neutron flux to create a minimal signal for detection, and the requirements for detection (such as needed detector resolution) to guide detection system design.

Mission Relevance

There is a widespread need for the remediation of underwater explosives for both legacy underwater, unexploded ordnance and threat mitigation in homeland security. Several federal agencies are engaged in efforts to detect and identify bulk explosives in the underwater environment. As members of the Nuclear Material Detection and Characterization Group, we are actively engaging multiple sponsors that have previously funded or are currently funding active interrogation in the marine environment. The information gleaned from this project's calculations has directly provided key additional technical expertise for ongoing proposal efforts.

Results and Accomplishments

A general MCNP model was created to understand neutron interactions and overall flux attenuation in several different bulk materials. A mission-relevant geometry for underwater operations was implemented in the model to study realistic active interrogation system configuration and performance. This includes the packaging of a neutron generator and associated detector materials into a contained active interrogation system, including shielding material to reduce the overall neutron flux in the detector. The active interrogation system was then placed in operationally relevant scenarios, including relevant amounts of explosives in several different configurations within a ship hull.

Neutrons were generated in a pulsed fashion, reflecting the next-generation high-output compact neutron generator design currently under way at ORNL. Detector signals are then tallied from each neutron pulse. In all scenarios, calculations are performed with and without explosives present in order to calculate relevant background rates. Several scenarios of varying water and air distances were explored. Small positive net signals are detected in all explored configurations, with explosives 1 meter from the ship hull and the active interrogation system 30 cm from the ship hull. Additional variations in explosives geometry and size, as well as detector response, will ultimately permit a rigorous statement in the required dwell time required for positive detection and characterization. Initial results suggest timescales on the order of less than a minute (e.g., ~60 pulses).

Information Shared

None.

INSTRUMENT AND SOURCE DIVISION

06765

Superconductor Shielded Triangular Magnets for Spin Encoding in Elastic Neutron Scattering Applications

J. Zhao, B. Kadron,W. Hamilton, T. Tong, L. Crow, P. Jiang, L. Robertson

Project Description

In elastic spin echo scattering applications, precession magnetic fields are required to have inclined entrance and exit faces. The quality of these precession fields directly determines the instrument resolution. In this project, we conducted proof-of-principle investigations using superconductor shielded triangular magnets. We built a set of four closed-loop, C-shaped magnets with triangular poles. We use high-technetium superconducting films around the magnet poles which function as Meissner shields to define the magnetic boundaries. These Meissner shields are thin films deposited on sapphire substrates, which are not expected to create any background problems for scattering experiments. The combination of the closed-loop C-magnet and the Meissner shields will reduce stray fields to a minimum, eliminating the needs of the π-flipper before the sample, since the precession fields after the sample can now be placed in the opposite direction to those before the sample without creating a zero field crossover along neutron's path.

Mission Relevance

In elastic neutron scattering experiments, the neutron momentum transfer range of $Q = 10^{-6} - 10^{-3}$ Å^{-1} is inadequately covered by any existing instruments. The spin echo small-angle neutron scattering technique (SESANS) and its variants (SERGIS, SESAME) are a new and promising technique. SESANS is ideally suited for accessing the above mentioned Q-region. In the last 15 years, significant progress has been made in developing this technique. Nonetheless, SESANS instruments are still too premature for prime-time usage by the general user community. The main difficulty lies at creating high-quality, well-delineated precession fields. In the conventional setup, the need for a high-performance (and broad band) spin flipper creates an additional hurdle. The proposed work aims at solving both these difficulties at the same time.

Results and Accomplishments

We have procured superconducting films required for the Meissner shields, and superconducting tapes needed to make the coils for the magnets. The triangle magnets have been designed and manufactured. Preliminary tests indicate that magnetic fluxes are well confined within the yoke. Spin-echo test of the magnets are being prepared and will be conducted in the near future.

MATERIALS SCIENCE AND TECHNOLOGY DIVISION

05957

Separation of Carbon Dioxide from Flue Gases

B.L. Bischoff, 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 FE and EERE for follow-on funding.

Mission Relevance

DOE Secretary Chu, in his letter to the Office of 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 post-combustion CO_2 capture targets of 90% CO_2 capture at less than a 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 micrometers thick) aluminum oxide separative layer to the inside surface. The supports have a pore size of approximately 4 micrometers. 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 three 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 re-treatment 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 impossible 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 the 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

B. Bischoff and L. Powell, “Selective Separation of Carbon Dioxide from Flue Gases,” AIChE Annual Meeting, October 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. 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 in achieving DOE's 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

This research was focused on the fabrication of zeolitic membranes due to their molecular sieving properties, resistance to radiation degradation, and low energy requirements compared to cryogenic distillation. The proof-of-concept feasibility of zeolite membranes was demonstrated using several zeolite materials including MFI, DDR, and SAPO-34. The membranes were synthesized on porous α-alumina support discs, and single-gas permeance was measured for a number of gases such as CO_2, CH_4, N_2, H_2, He, Ar, Xe, Kr, and SF_6. Since the kinetic diameter of krypton is 3.6 Å and that of xenon is 3.96 Å, zeolites SAPO-34 (nominal pore size 3.8 Å) and DDR (nominal pore size 3.6 Å) were studied because their nominal pore sizes are between or equal to the kinetic diameters of krypton and xenon. Gas permeance and selectivity of zeolite MFI (average pore size 5.1 Å) were measured to establish a baseline for comparison.

Permeance measurements with MFI and DDR zeolite membranes showed their inability to separate Kr and Xe with the desired high selectivity. However, SAPO-34 zeolite membranes were able to separate Kr and Xe with an average Kr/Xe ideal selectivity of 11.8 and an average Kr permeance of 19.4 Gas Permeation Units (GPU) at ambient temperature and a 1 atm feed pressure. Based on these results, SAPO-34 membranes can separate an equimolar Kr/Xe feed into a 92% Kr/8% Xe permeate stream in a

single stage. An analysis of the SAPO-34 membrane defect permeance showed that the average Kr/Xe selectivity decreased by 53% at room temperature due to unselective defect permeance by Knudsen diffusion. However, sealing the membrane defects with polydimethyl siloxane (PDMS) increased Kr/Xe selectivity by 32.8% to 16.2, and retained a high Kr membrane permeance of 10.2 GPU at ambient temperature. Overall, this research has shown that high-quality SAPO-34 membranes can be fabricated to achieve a Kr/Xe ideal selectivity >10 and Kr permeance >10 GPU at ambient temperature and 1 atm feed pressure. Based on the recent SAPO-34 membrane results for separating Kr and Xe, further research is warranted to develop SAPO-34 membranes for separation of ^{85}Kr and Xe from nuclear reprocessing off-gas.

Information Shared

There are no publications for FY13 at this time, but publications are anticipated in FY 2014. This research was presented at the FY 2013 ORNL Poster Session on September 24, 2013.

06259

Determination of Coating Mechanical Properties Using In Situ High-Temperature Digital Holographic Imaging

S. Dryepondt, 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 (DH) 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 DH 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 a component's surface quality.

Results and Accomplishments

A high-temperature (up to 1500ºC) stage was purchased and inserted in the DH 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 sand papers and 0.3 μm alumina powder. First heating trials revealed that DH imaging of the coating surface was successful up to ~1000ºC, but at higher temperatures, oxidation of the coating surface started to degrade the signal significantly. Flowing inert gas through the hot stage during heating was not sufficient to prevent oxidation, and a vacuum pump would need to be used.

The system was instead used to characterize the martensitic transformation of NiPtAl alloys with compositions similar to high-temperature coatings, because the transformation occurs at a temperature low enough to avoid surface oxidation. This transformation can generate high stresses in coatings that could result in coating failure. The formation of surface relief during heating due to the martensite-to-austenite transformation was monitored, and post-processing of the images yielded 3D movies showing martensite plates ~100 nm deep, and a macroscopic deformation of the specimen ~1μm in height for a scan area of ~100 × 100 μm. DH imaging also revealed that after repeated thermal cycling, the surface relief due to the martensite-to-austenite transformation was exactly the same each time, but the reverse transformation during cooling would lead to surface relief patterns slightly different from one cycle to another. These slight microstructure changes led to the formation and propagation of cracks in some grains after 15 to 50 thermal cycles from room temperature to ~140ºC.

Information Shared

B. P. Thiesing, C. J. Mann, and S. Dryepondt, "High Temperature Measurements Of Martensitic Transformations Using Digital Holography," *Journal of Applied Optics* **52**(19), 4426–4432 (2013).

Second paper expected to be submitted in November 2013.

06262

Electrochemical Energy Storage in Solutions of Renewable Organic Quinonoid Species for Energy Dense Flow Batteries

W.E. Tenhaeff, P. Bonnesen

Project Description

Redox flow batteries with high-energy densities that are low in cost hold the promise of transformative electrical energy storage (EES) systems. In this project, a novel hybrid 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, which are primarily mined in foreign countries, these organic species can be produced domestically. This will result in greater energy independence. The technology is applicable to energy storage for electric vehicles and could displace conventional internal combustion engines, leading to less CO_2 pollution. Specific offices within DOE that would benefit include the Office of Basic Energy Sciences (BES) and the Office of Electricity Delivery and Energy Reliability. Specific programs include the Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Program.

Results and Accomplishments

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. However, we were unable to develop coating technologies to inhibit the adsorption and promote the reversible cycling of concentrated solutions.

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. However, reversible cycling at these concentrations was not demonstrated.

During the project, a design for protected lithium metal anodes was developed. Protected lithium metal anodes consist of a lithium metal electrode hermetically encapsulated by a solid electrolyte on one face of the lithium electrode and a current collector on the other for electrical contact. Deposition masks were designed and fabricated, and the synthesis protocols were established. Due to time constraints, the operation of protected lithium metal anodes in aqueous electrolytes was not evaluated. However, these efforts established and tested key fundamental design principles, which can be further improved and characterized for future research projects. The fabrication masks and protocols were transferred to other researchers in the lab.

Also, initial experiments were performed to test the environmental stability of commercially available lithium ion conducting glass ceramics in aqueous media. Previous studies have revealed substantial impedances for the interface between ceramic and liquid electrolyte phases. These impedances were not observed in our experiments. However, an aging mechanism was observed, where a gradual increase in the overall resistance of the ceramic|aqueous system with time was observed. The aging mechanism will require further investigation for the practical, long-term operation of these materials in relevant liquid electrolyte compositions

Information Shared

None.

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 departments such as Basic Energy Sciences, as well as Energy Efficiency and Renewable Energy, will benefit substantially from this research.

Results and Accomplishments

We identified from theory numerous magnetic compositions that may have favorable magnetic properties. In particular, we 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.

Unfortunately, our Co_3WN synthesis efforts produced a compound, which while attaining the proper stoichiometry, forms in a different (hexagonal) structure and does not appear to exhibit evidence of magnetism. This lack of magnetism is a surprising result given the high Co concentration of this compound. Synthesis efforts for this SEED program were very difficult, and it was only in Quarter 4 of 2013 that we succeeded in synthesizing the Co_3WN.

While we did not succeed in discovering new high-performance magnetic materials, we do have several positive results from theory to report. Theoretical results from this research effort were included in four publications on magnetic properties of rare-earth free magnets (listed below), including one in *Physical Review Letters*. This is significant given that typical DOE metrics for publications have a guideline of $100,000 per publication, while we achieved four publications at a net SEED cost of $190,000. In addition, results from this research effort were sufficiently promising that the Materials Science and Technology Division (MSTD) Advanced Materials Group received follow-on funding from the Critical Materials Hub at a funding level of 1 FTE per year for 5 years.

Information Shared

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M. S. Osofsky, L. Cheng, W. E. Bailey, K. Bussmann, and D. Parker, "Measurement of the transport spin polarization of FeV using point-contact Andreev reflection," *Appl. Phys. Lett*. **102**, 212412 (2013).

06640

Development of High-Performance Lithium-Ion Hybrid Ultracapacitors

J. Nanda, C.-N. Sun, F.M. Delnick

Project Description

The goal of the project is to develop a lithium-ion hybrid ultracapacitor (LIHUC), a hybrid energy-storage device, that can sustain the high-energy density of lithium-ion batteries with the 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- or sodium-ion-based cathode that potentially doubles the voltage window, thereby increasing the energy density by a factor of four 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 an energy densisty four times higher than 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 30 Wh/kg and 650–700 W/kg, respectively, 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 follow-on funding since 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

We have made good progress toward our goal of increasing the energy density of double-layer capacitors by four times. This is made possible by our new electrolyte, which has a 4 V window and is stable. The current state-of-the-art electrolytic double-layer capacitor (EDLC) is based on an electrolyte system that uses tetraethyl ammonium tetrafluoro borate in acetonitrile solvent that has an effective potential window of 2.5 V. Our new sodium-based electrolyte has a window close to 4 V. Since the energy stored in a capacitor is given by $U= ½ CV^2$, doubling the voltage increases the energy by four times alone! In this work, a sodium electrolyte system was adopted to avoid the complexity caused by the intercalation process associated with lithium in carbon; instead, we expect a sodium deposition on the electrode approaching close to a sodium potential. The electrolyte consists of sodium triflate (NaOTf) and sodium hexaflurophosphate in organic ether-based solvent tetraethylene glycol dimethyl ether (TEGDME). Various additives are included to increase the conductivity of the electrolyte. Cyclic voltammetry experiments (CVs) of the TEGDME/NaOTf showed that this electrolyte is stable up to 4 V without any side reactions on the current collectors. The working electrode, in this case, is a glassy carbon disk electrode, and the counter electrode is a sodium metal smeared on the nickel electrode. As a result, the reaction taking place at the counter is fixed as $Na^+ + e^- \leftrightarrow Na$ and therefore minimizes the possible contamination created by electrolyte or salt decomposition. To see the possible reaction in the entire range, we use a 5 V potential window in a CV with a scan rate of 10 mV/sec. The obvious rise in the positive current was observed at a voltage beyond 4.5 V vs Na/Na^+, presumably due to the electrolyte decomposition. The negative current started to increase at a potential below 0 V vs Na/Na^+ indicating the sodium deposition. The CVs with a scan rate of 1 mV/sec were also performed to reduce the capacitive current and confirm that TEGDME possesses a 4 V electrochemical window with NaOTf and $NaPF_6$ salts. We have tested the new electrolytes in a symmetric carbon-based capacitor in pouch configuration, and the preliminary results are promising. The next step is to use this electrolyte in a asymmetric configuration where one of the electrode is a Na-ion battery electrode.

Information Shared

J. Nanda, C.-N. Sun, and F. Delnick, "Electrolyte for High Energy Density Ultracapacitors," one invention disclosure currently in the system (to be submitted November 17).

C.-N. Sun, J. Nanda, F.Delnick, T. Zawodzinski, and N. J. Dudney, "A 4V electrolyte system for high energy ultra capacitors," in preparation.

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. This project consists of two parallel efforts: 1) improvement of mechanical strength of bulk TE

materials and 2) development of TE fibers. In the first part, TE materials reinforced by carbon nanotubes (CNT) are fabricated through a powder metallurgical approach, which is expected to maintain the TE performance of the base materials while improving the mechanical integrity. In the second part, continuous TE fibers are developed via an extrusion technique. These fibers have large aspect ratios and high Seebeck coefficients. With improvement in electrical conductivity, these fibers could have great potential in small-scale applications.

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, development of TE technology can benefit other government agencies including NASA, who is currently using TE generators for powering deep space probes, and the Army and Navy, who are developing portable sources for their field missions. TE fibers may be used to fabricate small form power generators, serving as power sources for many advanced electronics.

Results and Accomplishments

Bismuth telluride-based TE materials (p-type $Bi_{0.4}Sb_{1.6}Te_3$ and n-type $Bi_2Te_{2.7}Se_{0.3}$) were synthesized from pure elemental materials and cast. The cast ingots were then ball milled. Small amounts (up to 1 wt.%) of multiwall carbon nanotubes (MWCNT) were then incorporated into the TE powders, followed by hot pressing. Microstructures of all hot pressed samples were dense while CNTs were evenly distributed at the grain boundaries.

The addition of CNTs tended to increase the Seebeck coefficient while decreasing the electrical and thermal conductivities. The dimensionless figure of merit however did not change significantly at CNT doping levels of 0.5 wt.% and 1 wt.%. The dynamic Young's modulus seemed to decrease with increasing CNT concentration. Room temperature fracture testing was performed on both undoped and doped (0.5 wt.%) $Bi_{0.4}Sb_{1.6}Te_3$, which showed a dramatic increase (~ 200%) in fracture strength when CNT was added. This result demonstrates our approach is successful.

In a parallel effort, TE powders were mixed with dissolved polymers to form a composite paste. Through an extrusion process, green fibers with a submillimeter diameter were fabricated in a continuous manner. Foot-long fibers were easily made and then sintered under vacuum or argon atmosphere to remove the polymer binder. The sintered fibers possessed a pure TE phase with residual porosity. An in-house measurement apparatus was set up to characterize the properties and performance of TE fibers. The Seebeck coefficients of fibers were comparable to those of bulk materials, but the electrical resistivity of fibers was much higher. It is suggested that the microstructure of the sintered fiber be improved in future studies to enhance the electrical conductivity. CNT doping may be another approach, as suggested by our preliminary results.

The findings from this project are very encouraging. It has been shown that a very small amount of CNT addition will significantly improve the mechanical strength of TE materials without sacrificing their functionality. In addition, improved mechanic properties means higher yields of devices and less waste, which may lower the overall cost. Therefore, this result could be transferred to companies making TE materials and devices.

The TE fiber developed in this project is very unique. Its large aspect ratio gives it an advantage in maintaining the temperature gradient, which is problematic in bulk or thin film materials. This approach

will also provide future opportunities to fabricate TE devices of complicated geometry via additive manufacturing. As mentioned above, the TE fiber technology has much potential and will be of interest to other agencies. Therefore, good opportunities exist for ORNL to attract investment from many outside funding sources.

Information Shared

F. Ren, H. Wang, P. Menchhofer, and J.Kiggans, "Method of Fabricating Thermoelectric Fibers," ORNL Invention Disclosure #201303024, DOE S-Number S-124605, Feb. 26, 2013.

H. Wang, P. Menchhofer, J. Kiggans, and F. Ren, "Improving Mechanical Properties of Thermoelectric Materials by Incorporating Carbon Nanotubes", presentation at 2013 MRS Fall Meeting, Boston, MA, Dec. 1–6, 2013.

F. Ren, P. Menchhofer, J. Kiggans, and H. Wang, "Thermoelectric and mechanical properties of multi-wall carbon nanotube doped $Bi_{0.4}Sb_{1.6}Te_3$ thermoelectric material," manuscript in preparation.

06649

Titanium/Graphite/Graphene Composite Friction Materials

P.A. Menchhofer, J. Klett, P. Blau, T. Muth

Project Description

In this SEED project, titanium/graphite foam composites as friction materials for demanding applications are being evaluated. The extreme thermal conductivity of the graphite ligaments (more than 5× that of copper) yields thermal conductivities for the composites that are significantly higher than the base titanium metal and potentially surpass the mechanical and thermal performance requirements of 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 project evaluates the processing variables (powder size, concentrations, additives, and heat treatment conditions to start) and their effect on strength, thermal conductivity, density, and friction properties. Analysis of the data was conducted to develop an understanding of the fundamental relationships and the mechanisms by which the resulting properties were affected. The results are being used to attract funding from other government agencies.

Mission Relevance

There are many friction applications where the existing technology is well undersized. For DoD, efforts to up-armor vehicles for the army (LATV and HMMVV) have increased their weight so much that the current braking systems are inadequate. Other applications, such as automotive, heavy trucks, trains, and racing vehicles are often undersized to reduce mass. Most brakes employ cast iron rotors with specially formulated pads to attain the desired friction for braking, resulting in high mass. The advantage of the graphite foam particles is that they are extremely thermally conductive (up to 1700 W/mK, compared to 180, ~180, and ~1200 W/mK for aluminum, powdered graphite, and pure diamond, respectively). Thus, a lower concentration of the conductive filler is required to achieve dramatic increases in thermal conductivity, thereby yielding higher mechanical properties from the higher volume fraction of metal that will be realized.

The novel composites explored mainly compared the effects of the graphite foam particle size on the final composite properties while also varying the percentage of the highly conductive graphite foam component added. The goal sought to improve thermal conductivity, reduce mass, and improve strengths. Additionally a limited number of other samples explored the addition of minute amounts of graphene powder for comparison purposes.

Results and Accomplishments

Dry, blended powders of titanium (matrix) and ground graphite foam (additive) were prepared (with samples containing between 10 and 50 volume % ground graphite foam additive), followed by mechanical and thermal properties characterization.

While a 50% improvement in the thermal conductivity was achieved with the addition of only 10 volume% finely attritted graphite foam, the strengths (38.5 KSI) remained sufficient for some applications, for example, brake rotor materials. By reducing particle size of the graphite foam powder, higher strengths were achieved than composites containing coarse-particle-size ground graphite foam.

Two samples were subjected to friction wear testing. An ORNL-designed sub-scale testing machine for brake materials (SSBT) was used to evaluate the friction and wear characteristics of a commercial semi-metallic lining material (Knorr-Bremse, Jurid 539 ™) sliding against cast iron, 100% titanium, and two composites of titanium and carbon (80/20 and 70/30 Ti/C) at both high and low contact pressures and speeds from 2 to 10 m/s. The friction coefficients of these tests were highest for the cast iron and titanium reference discs, and as low as 0.16–0.22 for the composites; thus, the traction of these materials would need to be improved in order for them to function as brakes, which typically require friction coefficients of 0.3–0.5. While less sensitive to the effects of pad pressure than cast iron, the composites produced intermediate levels of pad wear. Pad wear loss was highest for 100% titanium, slightly lower for the composites, and lowest for the reference cast iron test discs.

Information Shared

P. Menchhofer and J.Klett, “Metal Bonded Graphite Foam Composites,” ORNL Invention Disclosure ID 2608B, a patent application has been filed.

06677

Synthesis and Wire Development of Iron-Based Selenide Superconductors

A. Safa-Sefat, P. Paranthaman, C. Bridges, M. Tomsic, J. Mitchell, D. Hillesheim

Project Description

We propose to develop iron-based superconductor wire technology at ORNL, using powder-in-tube method (PIT), based on AFe_2Se_2 (A: alkali metal, alkaline-earth metal; FS) selenide superconductors. With FS superconducting wires, it is possible to meet the desired performance of high-current density (10^5 A/cm^2) in magnetic fields ranging from 3 to 5 Tesla and at temperatures above 20 K, while producing wires that are low cost, lightweight, and free of critical rare earths and toxic arsenic. For this project we will (a) set up a new synthesis capability in order to produce FS superconducting materials, (b) draw wires of FS superconducting materials using PIT method, and (c) characterize the

superconducting properties of materials and wires. We will deliver several feet of FS wire with $T_C > 20$ K and high H_{C2} by the end of this project.

Mission Relevance

We propose to develop wires based on iron-based superconductors at ORNL, for the first time. The outcome of this project has the potential to enable cost-competitive, compact, and powerful generators. Such work is relevant to DOE's energy mission with respect to resources, environmental quality, and science. We foresee that programs such as Basic Energy Sciences (BES), Office of Electricity (OE), Office of High Energy Physics (HEP), and Advanced Research Project Agency-Energy (ARPA-e) to benefit from this project.

Results and Accomplishments

Ammonothermal intercalation of barium (or lithium) into FeSe structure results in two distinct but related crystallographic phases, differing primarily in the magnitude of the *c*-parameter. The relative proportion of larger cell (LC) depends on the reaction duration, with LC dominating under quick reaction times and superconductivity emerging the longer the product remains in a liquid-NH_3 environment. Superconductivity is observed with T_C in the range 35 to 38 K, with the superconducting fraction roughly scaling with the proportion of LC. As reaction duration lengthens, the superconducting and shielding fractions both decrease, as do H_{C1} and J_C as calculated from magnetization curves. Thermogravimetric analysis experiments show a two-step loss of NH_3, with $T_{onset} \sim 220°C$ and $\sim 370°C$, resulting in a formula of $Ba_x(NH_3)_{0.8}Fe_2Se_2$. These results indicate that shorter reactions times favor the LC phase, resulting in the most desirable superconducting properties. PIT wires, with T_C up to 20 K, have been drawn to several feet.

Information Shared

There are two publications that are currently in progress. The one that is ready for submission is entitled "Short ammonothermal reaction-time leads to optimal superconducting properties in $Ba_x(NH_3)_yFe_2Se_2$". After finishing a few last experiments, there will be another publication with tentative title of "Wires of iron-based selenide superconductors."

06679

Performance and Reliability Enhancement of Concrete Confinement Structures for Nuclear Applications through Improved Concrete/Steel Interfacial Bonding

J. Hemrick, F. Ren, D. Naus, J.-A. Wang, S. Sham

Project Description

This project will build upon existing knowledge and capabilities at ORNL, including structural evaluation of nuclear power plants, nuclear materials (fuel/cladding and pressure vessels), concrete manufacturing/processing, glass and ceramic science, and mechanical testing and analysis, to develop advanced manufacturing processes and composite structures for use in nuclear structural applications. Typical containments or shield buildings in conventional nuclear power plants (NPPs) are fabricated from reinforced concrete or a combination of reinforced and post-tensioned concrete. This project will explore a novel optimized design concept for such reinforced concrete structures utilizing enamel-coated steel reinforcement in ultrahigh performance concrete (UHPC). Improved material performance could allow

more flexible design, reduce construction cost, increase reliability, and prolonge design life. Such a novel capability would allow for new design concepts for advanced NPPs and would position ORNL for a leadership role in this area and other concrete-based structures.

Mission Relevance

Concepts are needed to increase safety and output of existing and future NPPs to reduce the number of nuclear-related accidents and to provide additional margin for response times to such accidents. Reinforced concrete is used in almost every aspect of NPP design and is the fundamental construction material for safety-related concrete structures in plants regardless of plant type. Novel materials for NPP constructions will be of great interest to the US nuclear programs and therefore can attract potential further development funding from programs within the DOE Office of Nuclear Energy, and US Nuclear Regulatory Commission.

Results and Accomplishments

To date, an enamel system has been developed and produced which is suitable for use on both standard and high-strength steel rebar. This enamel system is based upon an alkali borosilicate glass composition and has been used to coat samples of both types of rebar through commercial processes and coated samples have been embedded in both conventional and high-strength concrete. Samples have also been obtained of commercial epoxy-coated rebar and uncoated standard rebar.

Produced samples are being evaluated through several methods. The feasibility of using neutron diffraction techniques to image and analyze the bonding between concrete/enamel and enamel/steel is currently being evaluated. Mechanical evaluation of the bonding between the rebar and the concrete is also being performed. Pull tests are being performed on samples of enamel-coated standard steel rebar in both high-strength and conventional concrete, enamel-coated high-strength steel rebar in both high-strength and conventional concrete, bare rebar in both high-strength and conventional concrete, and epoxy-coated standard steel rebar in conventional concrete.

Based on the preliminary work from this project, a proposal was submitted in collaboration with the University of Houston to the 2013 NEET Advanced Methods for Manufacturing Call and was selected for funding. This project, entitled “Ultra-High Performance Concrete and Advanced Manufacturing Methods for Modular Construction,” will build upon the epoxy-coated rebar system utilized in high-strength concrete that was developed under the current SEED project.

Information Shared

None at present, but planned following completion of project.

06684

Corrosion Prevention of Magnesium Alloys via Surface Conversion Treatments Using Ionic Liquids

J. Qu, H. Luo, H.H. Elsentriecy, G. Song

Project Description

Magnesium alloys are great candidate lightweight materials for automotive applications, but they are susceptible to corrosion attacks. Limited studies in the recent literature suggest good potential for using

ionic liquids (ILs) to form a conversion coating on magnesium surfaces for corrosion protection. However, the mechanisms of the ILs-based conversion coating formation are not yet fully understood, and the effectiveness of reported treatments in corrosion prevention is moderate at most. This proof-of-concept project intends to conduct feasibility demonstration and mechanistic investigation of forming effective magnesium surface conversion coatings using selected ILs. Compared with conventional magnesium surface conversion chemistry, the ILs have several advantages including higher flexibility in molecular design, hydrophobicity, and potentially better bonding to paints. Unlike literature work that mostly involves extended exposure to ILs at room temperature or an electrical potential bias, this study proposes to apply thermal and/or mechanical stresses to promote the IL ions breakdown and their interactions with magnesium surfaces to allow a rapid conversion coating formation. If successful, the fundamental understanding and coating development gained in this project will be expected to generate great interest and opportunities from both government funding agencies and industry.

Mission Relevance

DOE has been promoting lightweight alloys for transportation to improve the fuel economy. Magnesium alloys are great candidate materials for automotive applications due to their low density and high strength-to-weight ratio. However, magnesium alloys are susceptible to corrosion because of their high reactivity and low electrode potential, which prevents them from widespread applications in automotive industry. This project proposes a proof-of-principle study to develop novel, effective anti-corrosion conversion coatings for magnesium alloys using ionic liquids.

Results and Accomplishments

In FY 2013, initial efforts successfully demonstrated the feasibility of using organophosphate ILs to produce a conversion coating for the Mg AZ31B alloy. A furnace-aided surface treatment has been developed, and a group of ammonium-phosphate ILs has been identified as the effective compounds in forming an anti-corrosion surface film. Electrochemical evaluation confirmed the passivation behavior of the IL-treated magnesium surface. Results suggest that the thermal stress likely promote IL decomposition and the consequent interactions between the decomposition products and the Mg alloy surface to form an anti-corrosion conversion coating. Effects of pretreatments including acid pickling and base conditioning were investigated. It was observed that aprotic ammonium-phosphate ILs have good synergy with phosphoric acid pickling, while protic ammonium-phosphate ILs work best without pretreatment. Cross-sectional TEM examination and XPS surface chemical analysis revealed the thickness, nanostructure, and composition of the IL-induced conversion coatings. The dominating compounds in the conversion coating are metal phosphates, metal oxides, and some organometallics. This supports our proposed mechanism on the IL conversion coating formation: IL molecules first break down under thermal and/mechanical stresses and then react with the alloy surface. One ORNL invention disclosure has been submitted and elected for patenting. One journal paper has been submitted, and another is in preparation. The planned tasks in FY2014 include (1) IL molecular structure modification for potential hydrophobicity, (2) further mechanistic investigation of IL conversion coating formation, and (3) direct comparison with a commercial conversion coating.

Information Shared

J. Qu and H. Luo, “Corrosion Prevention of Magnesium Alloys via Surface Conversion Treatments Using Ionic Liquids,” ORNL Invention Disclosure #201303046, submitted on March 19, 2013 (elected for patent filing).

H. H. Elsentriecy, H. Luo, H. M. Meyer III, L. L. Grado, and J. Qu, “Effects of Pretreatment and Process Temperature of a Conversion Coating Produced by an Aprotic Ammonium-Phosphate Ionic Liquid on Magnesium Corrosion Protection,” *Electrochimica Acta* (submitted).

06715

Synthesis of Tin-Doped Indium Oxide Nanofibers

S. Ozcan, A. Naskar

Project Description

The objective of this project is to develop new sol-gel precursor chemistry that will form flexible tin-doped indium oxide (ITO) nanofibers at diameters of 50–400 nm. This proof-of-principle type of research is designed to understand the mechanism of formation of ITO nanofibers and a flexible fiber web that have important future opportunities in the area of flexible electronics and replacement of specialized coatings. ITOs are of fundamental interest for the modern electronics industry because of the need for transparent electrodes in devices such as solar cells displays, organic light-emitting diodes, thin-film transistors, antistatic coating, and EMI shieldings. Although there is a high potential and large application spectrum, the poor flexibility and brittleness of ITO thin films limit extensive utilization. To address these limitations, this research program is investigating microstructure and processing characteristics of the inorganic precursors. Our ultimate goal is to demonstrate a conductive, flexible, and stretchable ITO nanofiber web, with significantly reduced reflectivity.

Mission Relevance

ITO is an enabling material for a growing number of applications that require a highly conductive and transparent surface, including solar cells, liquid-crystal, plasma, and touchscreen displays, electromagnetic shielding, and other applications. Various deposition methods (both solution and vapor) and sputtering techniques have been commonly used to produce ITO films. However, existing techniques are not scalable for large-volume lower cost fabrication. Lately, one-dimensional nano-structured materials such as nanowires, nanofibers, nanorods, and nanotubes have received attention for their potential applications in numerous areas because of their special properties, which are distinct from conventional bulk materials. For example, metallic nanowires and carbon-based nano-structures have been tried for transparent flexible electrodes, but the poor thermal stability of metal nanowires and poor conductivity of carbon-based nano-structures limit their application to displace ITO films.

Results and Accomplishments

The initial 40% of the project is complete. The formation mechanism of ITO has been investigated. Several films from various starting precursor solutions are prepared and casted as a film on quartz substrate using a spin coating method. Films were characterized using the methods X-ray Diffraction (XRD), Optical Transmittance, Electrical Resistivity measurements. XRD indexing was consistent with cubic In_2O_3, and samples were polycrystalline in nature. We achieved 80% transparency on films as measured by UV-vis spectroscopy. We achieved the electrical resistivity of 4.2×10^{-2} ohm.cm; however, this is still higher than our target of 1×10^{-3} ohm·cm. We believe this is due to film preparation technique and can be improved.

In a parallel effort, we have investigated the spinning of bicomponent nanofibers. Two bicomponent fiber geometries were used: sheath/core and islands-in-sea. Sheath/core geometry is less complex and was successfully employed first to develop familiarity with the bicomponent spinning system. However, islands-in-sea is required to produce the desired size of nanofibers. The next step is to produce nanofibers using the islands-in-the-sea method and apply the understanding we are currently learning from film study to form transparent, electrically conductive ITO nanofibers.

Information Shared

None to date.

06768

Effect of High Static Magnetic Fields on the Microstructure of Heat-Treated, Nodular Cast Iron

G. Muralidharan, T.R. Muth, G.M. Ludtka, T.R. Watkins, J.A. Haynes, R.D. England

Project Description

The drive to improve the efficiency and decrease the weight of automotive and diesel engines, while still keeping their costs low, has created the demand for alternate materials in the design of next generation engines. The replacement of forged crankshafts with cast crankshafts in high-performance (smaller, turbocharged, high power density) engines is one example of this paradigm shift. This is reflected in the proposed Department of Energy Funding Opportunity Announcement (FOA) DE-FOA-0000793 that identified Area of Interest 5 – Development of High-Performance Cast Alloys and Processing Techniques for Engine Rotating Components – as a topic area of interest. Ductile irons, potential lower-cost candidate materials for cast crankshafts, need significant improvements in tensile and fatigue strengths before they become attractive candidates for cast crankshafts. Previous work on the effects of high magnetic fields during high-temperature processing of ferrous alloys suggests that microstructural modifications of ductile irons may be feasible, with concomitant improvements in strength and fatigue resistance. The goal of this project is to evaluate the effect of applying high magnetic fields (up to 9 T) during standard simple heat-treat processes of a specific type of ductile iron, with particular reference to microstructure and property modification. If proof-of-concept work is successful, ORNL and Cummins will collaboratively compete for $1.5 million in further funding from DOE under the pending FOA to achieve improved strength properties for cast crankshafts.

Mission Relevance

Development of new materials with improved properties or new materials that achieve desired properties at lower cost are of interest to many DOE programs and other federal agencies. Examples include the Vehicle Technologies program, which focuses on the development of new materials for heavy- and light-duty on-road vehicle applications; the Fossil Energy program, which seeks new high-temperature materials for use in energy production processes from fossil sources; and the Advanced Manufacturing Office, which funds efforts on materials development for various industrial processes. A proposal entitled "Cast iron development for high power density internal combustion engine crankshafts" was submitted by Cummins Technical Center in collaboration with ORNL in response to DE-FOA-0000793. Although this project did not receive funding in the initial round of selection process, it is still under consideration for future funding subject to appropriations.

Results and Accomplishments

Ductile iron crankshafts, consisting of nodules of graphite dispersed in a matrix that can vary from soft (ferrite) to very hard (martensite) are desirable from a manufacturing and cost perspective for crankshafts but are lacking in mechanical properties. The proposed project was a proof-of-concept work to determine if high magnetic fields can be synergistically used with traditional heat-treatments to modify either the matrix microstructure or the nodule content (or both) for a given composition that is designed to produce pearlitic ductile iron. Heat treatments of interest consisted of a relatively high-temperature exposure

(850ºC–900 ºC) for durations of 1–2 hours (never before attempted) in the absence of a magnetic field and in a 9 T magnetic field, followed by a rapid quench. Such a treatment would normally result in a matrix microstructure that was extremely hard and with high strength. These heat treatments were performed in a unique prototype system comprising of a 200 KW dual-frequency induction heating power supply fully integrated with a polymer quenching system, an automated sample delivery system, and a cryogen-recondensing, ~ 8-in.-diameter, 9-in.-long uniform field, 9-T superconducting magnet. Parallel heat treatments were performed in a laboratory-scale box furnace for comparison of the baseline microstructures obtained in the two different experimental setups in the absence of the 9 T magnetic field. Comparison of microstructures showed that better prediction, measurement, and control of the temperatures must be achieved in the induction heated system to unambiguously separate out the effect of magnetic fields from that of temperature.

Information Shared

None.

06784

A Sacrificial Coating System for Magnesium Alloys

G.-L. Song, N.J. Dudney

Project Description

Corrosion is limiting the application of magnesium alloys, although the alloys are being considered as attractive lightweight materials for next generation vehicles. Currently, all the developed coatings are cathodic to magnesium alloys. If these coatings are accidently damaged, the corrosion of the substrate magnesium alloys will be dramatically accelerated. Inspired by the great success of galvanized steel in the battle against corrosion, this project explores the possibility of forming a sacrificial coating on magnesium. The proposed coating system consists of an inner conversion layer to passivate the magnesium substrate in case the coating is damaged, a middle sacrificial carbon-lithium layer to cathodically protect the magnesium in the coating-broken area, and an outer hydrophobic inert layer to guard the sacrificial coating. If such a coating system proves to be feasible for magnesium, it will easily find many applications. Its impact on industry will be as profound as the galvanizing technique for steel, because it can significantly extend the service life of a magnesium component.

Mission Relevance

DOE has been promoting lightweight alloys for transportation to improve the fuel economy. Magnesium is the lightest engineering metal. However, the poor corrosion resistance of magnesium limits practical applications. This project proposes a proof-of-principle study to develop a sacrificial coating for magnesium. It falls within the DOE Vehicle Technology Program.

Results and Accomplishments

First, magnesium was dipped in a concentrated metaphosphoric acid (HPO_3) to produce a metaphosphated film on it. Unfortunately, the deposited thick layer was non-uniform and porous, and immediately dissolved when exposed to water. Although a uniform magnesium surface could be obtained in a diluted metaphsophate acid, XRD analysis indicated the film is amorphous and extremely thin. However, if magnesium was immersed in diluted HPO_3 to obtain a clean surface and then dipped in 12wt.% $NaPO_3$, a

uniform film (likely to be a metaphosphated film, to be confirmed by XRD) formed on it. The composition of this film will be analyzed.

Second, a graphite layer was manually applied using a dropper, although not very uniformly (the non-uniformity can be clearly visualized by the naked eye), on metaphosphated magnesium. Stabilized lithium powder was then mixed in the graphite layer. However, if this coated sample was exposed to water, intense reaction occurred and the coating was dissolved immediately. This means that the lithium-carbon coating is too reactive to effectively protect magnesium, as claimed in the GM patent (M.D.Bharadwaj, A.K.Sachdev., M.Verbrugge, Sacrificial Coating for Magnesium Components, US patent, US7713618B2, May 11, 2010). Due to the high activity of lithium-carbon, the metaphosphated film is too slow in reacting with dissolved Li^+ to passivate the substrate magnesium. Therefore, a top layer that can separate the lithium-carbon layer from environmental solution will be critical in this project.

Third, a lithium-coated plastic film (SLMP-coated plastic film) has been tried. It was not soft and sticky enough to act as a top layer. Parafilm appears to be able to cover a coated sample. A scratched parafilm that can limits the access of water to the lithium-carbon layer will be tested on the lithium-carbon layer for its corrosion protection behavior.

Information Shared

No publication so far.

06788

Passive Impact-Resistant Battery Electrolytes

G.M. Veith, W.A. Tenhaeff, H. Wang, B. Armstrong

Project Description

This project obtains preliminary data on the use of a shear thickening fluid as a platform for a passive safety system for lithium ion batteries used in applications such as cars, planes, and larger personal electronic devices. This electrolyte is envisioned to stiffen instantly during an impact (e.g., accident), preventing cell deformation and short circuiting. This will prevent chemical fires originating from the battery, which is a significant safety issue in batteries for transportation and other applications. Specifically, we will measure lithium ion conductivity values and rheological properties for 11 silica-loaded polyethylene glycol–based electrolytes. In addition, we will perform a simple pinch test to determine the ability to prevent electrical shorting. This data will be used to respond to proposal calls anticipated in the spring of 2013 [e.g., Advanced Research Projects Agency–Energy (ARPA-E) and the Office of Energy Efficiency and Renewable Energy (EERE)– BATT].

Mission Relevance

One of the critical challenges confronting the development and distribution of advanced high-energy battery technology is the stability and safety of the electrolyte system. An electrical short between the cathode and the anode results in a large amount of energy released spontaneously. This energy release often leads to combustion of the organic electrolyte and a fire. This risk of fire is one of the major challenges facing the widespread implementation of advanced batteries for automotive, aeronautic, and other applications, which are key drivers for various DOE missions related to energy storage and conversion. This project led to the team winning an ARPA-E grant on this electrolyte concept (total award of $450K).

Results and Accomplishments

We have developed the methodology to prepare shear thickening electrolytes. Specifically, we identified suitable particle sizes of silica that can be stabilized in carbonate solvents. These materials have a large visible shear response suitable for impact protection. We also identified synthesis procedures to prepare these suspensions. These results and the teamwork developed as part of this work resulted in a much stronger, and successful, proposal to ARPA-E.

Information Shared

None.

07054

Novel Tubular Battery with Solid Electrolyte Membrane

N.J. Dudney, B. Bischoff, J. Sakamoto

Project Description

This project explores a novel tubular structure for rechargeable lithium batteries. Using DOE legacy membrane fabrication technology, a thin ceramic lithium electrolyte will be coated onto a porous metal tube which serves as both a support and current collector. The ORNL metal tubes are thin, robust, and readily tailored for the application. A ceramic electrolyte powder of a highly conductive garnet compound will be used to form a thin and impermeable coating which is highly conductive for Li^+ ions. A successful outcome will be a clear demonstration of good lithium conductivity without any electronic shorts across the ceramic coating using impedance spectroscopy. With this proof of concept, further applicability for batteries will be demonstrated using metallic lithium films as the anode and selected solid or liquid cathodes adopted from other current ORNL battery programs. Novel battery designs using the robust electrolyte tubes will provide new ways to enhance safety and performance for electric vehicle and other applications.

Mission Relevance

There is a strong motivation to develop safer, lower cost, longer range batteries for vehicles. The DOE Vehicle Technologies road map calls out R&D for lithium-sulfur and lithium-air technology and also new battery architectures as 2020 targets for the next generation beyond lithium-ion batteries. An important piece of this is to develop stable and efficient lithium metal anodes that are safe and are free of side reactions that reduce capacity. One of the DOE-funded programs addressing means to stabilize and protect metallic lithium anodes is the Integrated Laboratory Industry Research Program (ILIRP) supported by the Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies (VT). This is a tightly directed and collaborative program with the specific goal of enabling use of metallic lithium in batteries. Other VT programs, specifically Batteries for Advanced Transportation Technologies and Advanced Battery Research, are also possible avenues for continued work if the concept can first be demonstrated. We anticipate a FOA announcement for Beyond Li-ion proposals in 2014 that will include solid electrolytes as a subtopic.

In addition, the Defense Advanced Research Projects Agency (DARPA) and Advanced Research Projects Agency–Energy (ARPA-E) have programs devoted to advanced electrical energy storage. The proposal PI participated in a 2012 ARPA-E workshop on Crash-Safe Batteries for EV, where the goal is to improve safety, and the perception of safety, in both normal operation as well as in a crash event. In the

course of this workshop, it was clear that, in pursuit of these safety objectives, vehicle manufacturers are responsive to considering radically redesigned battery systems if system-level cost and power and range performance are not substantially compromised. Successful outcomes from this Seed proposal would be the first step in establishing a new battery design paradigm to meet these cost, performance, and safety goals.

Results and Accomplishments

To date, three different powders have been obtained, characterized, and used for initial coatings of the tube including a proprietary lithium titanium phosphate from Ohara corporation (Ohara), and several powders with the garnet structure of lithium lanthanum zirconium phosphate (LLZO) from Sakamoto prepared at Michigan State University by solgel and hydrogel processes. The key factors for a satisfactory coating of the dry powders are the primary particle size and agglomeration. Only the Ohara powder and the precalcined LLZO solgel-derived powders were fine enough to anchor in the porous stainless support tube. Acetone slurries were prepared of several powders and applied by hand to the surface with various degrees of success. The best coatings obtained to date were from coating of the tubes directly with the sol suspension, prior to any significant gelation. Preparation of the sol was performed at ORNL in cooperation with postdoctoral researcher E. Rangasamy. The structure of the sintered coatings is under investigation with attention to the method of coating, the number of coatings, viscosity of the sol, and pre-coating of the tubes with dried powder. We anticipate greater flexibility in control of the viscosity with a hydrogel formulation in the future.

Information Shared

No publications at this time.

07069

The Role of Surface Oxygen Vacancies in Perovskite Oxide Catalysis

P.C. Snijders, T.Z. Ward

Project Description

Catalysis is arguably an essential industrial process: one-third of our material gross national product involves a catalytic process. The design of modern catalysis relies heavily on tailoring of catalyst properties using doping and defects as oxygen vacancies. However, despite progress in atomic-scale understanding of metallic catalysts enabled by scanning tunneling microscopy (STM) studies, controlling the atomic order, and the resulting electronic properties that govern the catalytic behavior at the very surface atomic layer of perovskite oxide catalysts, is in its infancy. Here we propose to control the surface concentration of oxygen vacancies in $CaMnO_3$, study their electronic properties, and correlate the location of catalytically active sites with the location of these intrinsic defects. Manganites are excellent candidates for exhaust gas NO reduction using CO as a reducing gas. $CaMnO_3$ is a model for perovskite oxide catalysts and is related to the compound responsible for the oxygen evolution reaction in photosynthesis. We will use our unique STM capabilities to directly image surface oxygen vacancies at the atomic scale. This will allow for the first-ever study of the catalytically relevant electronic properties of and near these vacancies using atomic resolution scanning tunneling spectroscopy. These results will be correlated with CO adsorption and oxidation experiments inside the STM as a litmus test for catalytic activity and will position ORNL well for obtaining follow-on funding that applies the knowledge gained here to research into solid-oxide fuel cells.

Mission Relevance

This project is directly relevant to the science mission of DOE: we will generate the knowledge needed to design and produce new materials with tailored properties, and obtain understanding of the relationships between electronic structure and properties of complex materials. This will push the field forward from catalyst discovery to true catalyst design – a goal stated in the DOE report *Basic Research Needs: Catalysis for Energy*. This project is highly relevant to the Office of Energy Efficiency and Renewable Energy (EERE) in that it will provide a methodology to understand and improve materials issues in solid oxide fuel cells. EERE has a Request for Information (RFI) and a Notice open in expectation of future Funding Opportunity Announcements (FOAs) concerning fuel cells (DE-FOA-0000855, DE-FOA-00009).

Results and Accomplishments

With the $7000 that was allocated to this project at the end of this FY 2013, we designed the UHV-compatible oxidation chamber and ordered some small parts.

Information Shared

None.

07075

A New Approach to Electrochemical Noise Analysis to Understand and Monitor Localized Corrosion

D.F. Wilson, R.A. Kisner

Project Description

Electrochemical Noise (EN) offers the possibility of achieving real time monitoring and analysis of localized corrosion. Stochastic corrosion events give rise to small differences between the mixed potential of coupled electrodes and result in voltage and current fluctuations (i.e., EN). Analyses involving statistics, frequency domain transforms, chaos theory, wavelet analysis, and neural networks have yielded limited reproducibility in the prediction of corrosion. This project will employ a higher data sampling rate approach (kilo- to mega-Hertz) than the traditional <10 Hertz to discern additional information associated with corrosion events and provide predictability, which will allow for widespread applicability of EN.

Mission Relevance

The project proposes the development of analytical tools and a monitoring system for the analysis and prediction of localized corrosion. Localized corrosion is the bane of many industries and results in unplanned outages and shutdowns. Long-term monitoring of plant and equipment health with real-time diagnostics and prognostics saves lives, natural resources, and financial cost. The proposed work is directly tied to the DOE mission “to ensure America’s security and prosperity by addressing its energy, environmental and nuclear challenges through transformative science and technology solutions.”

Results and Accomplishments

Work was performed to identify, isolate, ameliorate, and reduce non-signal noise associated with the electrical systems in the environment and the measurement systems. Using Faraday cages, doubly shielded cables, ferrites, common ground, and other passive electronic elements, the overall non-signal

noise in the assembled equipment was significantly reduced. Work on noise reduction continues toward meeting the target of being able to measure the Johnson noise at room temperature of a 5000-ohm resistor. Electrochemical noise is expected to be greater than the random fluctuations produced by a 5000-ohm resistor at room temperature. Achieving such a low non-signal noise background would allow for measurements of EN signals that would establish proof of principle that high-frequency sampling incorporates information that allows for a better understanding of the various phenomena and monitoring of initiation and propagation of localized corrosion.

Information Shared

None.

NUCLEAR SECURITY AND ISOTOPE TECHNOLOGY DIVISION

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 proposed 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 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

Undoped YAP crystals obtained from Materials Corporation were cut and polished at Oak Ridge National Laboratory (ORNL) and drawn into fibers by 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 is 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. 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. After receiving the fibers fabricated by Dr. Harrington, we studied methods for the controlled doping of fiber ends with cerium via thermal diffusion and physical deposition (e-beam evaporation) with subsequent thermal annealing. The thermal annealing for the purpose of diffusing trivalent cerium into the fibers was carried out under vacuum in a sealed quartz ampoule using cerium metal. An alternate method of introducing cerium into the fiber ends consisting of ion implantation followed by thermal treatments was considered but not implemented due to lack of

availability of a suitable cerium ion-implantation source. All of the cerium-treated fibers demonstrated photoluminescence upon excitation by an ultraviolet light source. Testing for scintillation was conducted using both alpha particles (Am-241 under vacuum) and gamma rays (Cs-137). The best results, in terms of scintillation efficiency, were found for those samples treated by thermal diffusion. These initial results suggest a viable path forward for the optimization of controlled cerium doping of YAP single-crystal fibers and eventual fabrication of a fiber-optic-based high-resolution scintillation detector.

Information Shared

J. S. Neal, L. A. Boatner, and J. T. Mihalczo, "High Spatial and Temporal Resolution Particle Detectors," INMM 53rd Annual Meeting, July 15–19, 2012, in Orlando, Florida.

U.S. Patent No. 8,258,483 B1, "High Spatial Resolution Particle Detectors," issued September 4, 2012.

Patent pending at the U.S. Patent Office: Pub. Number US2012/0318993 A1, "High Spatial Resolution Particle Detectors," Division in Part of application No. 3/101,741.

06685

Lanthanide Separations for Industry Applications of Rare Earth Radioisotopes

M. Du, C.W. Alexander, L. Lewis, C.E. Phelps, B.E. Lewis, Jr.

Project Description

The objective of this project is to develop a lanthanide separations approach designed to yield high-purity isotopes that meet known industrial requirements. The specific focus is on the separation of milligram quantities of ^{155}Eu from gram quantities of irradiated Sm with a yield greater than 80% and purity greater than 97%. The primary application of ^{155}Eu, a beta emitter, is as a power source for various long-life applications such as betavoltaic batteries due to its 5 year half-life, beta emission energy less than 250 keV, and low gamma emissions. This work is important because conventional chemical techniques do not meet the required production and purification levels of multi-curies of ^{155}Eu due to the complexity, effectiveness, radiolysis effects, and cost of separation of the adjacent rare earth pair (Eu-Sm) at a meaningful throughput. Two multi-process approaches were proposed and are currently under investigation with the goal of separating milligram quantities of europium from multigram quantities of irradiated samarium. Both are based on the fact that the reduction of $Eu^{3+} \rightarrow Eu^{2+}$ (-0.35V) is easier than $Sm^{3+} \rightarrow Sm^{2+}$ (-1.05V) in solution. Our efforts are focused on optimization of the trivalent europium reduction and quick separation of microscopic amounts of Eu^{2+} from the Sm^{3+} matrix in a solution.

Mission Relevance

By supporting the development of new beta emitter batteries of high-energy density, this project meets the need for new power sources by the Department of Defense (DoD) and the Department of Energy (DOE), as well as the National Aeronautics and Space Administration (NASA), and potentially other Intelligence Community (IC) sponsors. Once success is achieved in separating milligram quantities of ^{155}Eu from multigram quantities of irradiated samarium, the initial batch of this beta emitter will be used to synthesize a new type of phosphor. The new phosphor will be used to show the potential of ^{155}Eu-doped phosphors in power generation systems. If successful, it is anticipated that this work will result in additional funding for the production and purification of larger quantities of ^{155}Eu for use in a variety of power source applications. Potential sponsors include DOE's Office of Nonproliferation Research and Development (NA-22), the Defense Threat Reduction Agency (DTRA), and other government agencies.

Results and Accomplishments

In Year I of this Seed project, we completed the conceptual design for the two multiple-process approaches for separating milligram quantities of ^{155}Eu from multigram quantities of irradiated samarium. One process uses a Jones reductor attached to a cation exchange resin column (JR-CX column), while the other uses an electroreduction-filtration cell. Both approaches are designed for quick separation of divalent europium immediately after its reduction in the trivalent matrix and can be used for multiple runs of the same matrix solution (recycling runs are required due to the inherently incomplete reduction of the trivalent europium) with minimum solution adjustment.

In the first approach using the JR-CX column, cold and radioactive tracer experiments were conducted to optimize process conditions. The experiments focused on the following: 1) the effluent composition with the least resistance to flow through both the reductor column and the attached resin column; 2) particle sizes of zinc powders and resins; 3) flow rate required to minimize the radiolysis effects on the resin column; 4) stripping agents for complete removal of the rare earth (RE) from the CX column; and 5) proper methods of inert gas blanketing. So far we have demonstrated the effectiveness of trivalent europium reduction by the Jones reductor and achieved up to 46.6% recovery of europium with no samarium contamination in a single (no recycle) JR-CX column run. The size of the JR-CX column is presently being adjusted to transition from RE loadings of 1.5 mg to 20 mg. In addition, a new design for attaching the JR column to the CX column has recently been completed (detachable during elution).

In the electroreduction-filtration cell approach, a compact assembly has been made with both reduction and filtration functions. This assembly is ready for processing multigram quantities of irradiated samarium in a glove box or a hot cell. The optimal electroreduction conditions are currently under investigation by using nonradioactive europium of a visibly observable amount in precipitation to select the electrode materials, electrolyte compositions, compartment arrangement, stirring methods, and applied voltage. A University of Tennessee Ph.D. candidate student has recently joined in this work. Optimization of $Eu(II)SO_4$ formation conditions and its dissolution behavior will be studied as part of this approach.

Recently, a total of 13 rabbits containing several grams of ^{154}Sm oxide were irradiated at the High Flux Isotope Reactor (HFIR) and then transferred to Radiochemical Engineering Development Center (REDC). This material is ready for processing to recover and purify ^{155}Eu. A glove box has been prepared for processing the first rabbit (cut open, dose measurements, dissolution, and sampling for ^{155}Eu yield determination).

Information Shared

M. Du, C.W. Alexander et al., "Lanthanide Separations for Industrial Applications of Rare Earth Isotopes," a proposal Phase-1 report given to LDRD Committee, July 17, 2013, Oak Ridge, TN.

C. Romano, M. Du, C.W. Alexander et al., "Lanthanide Separations for Industrial Applications of Rare Earth Isotopes," a proposal presentation given to LDRD Committee, October 17, 2012, Oak Ridge, TN.

PHYSICS DIVISION

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 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, along with an associated 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 NSF.

Results and Accomplishments

Demonstrated collection efficiency post wavelength shifter at expected levels.

Information Shared

Summary publication in progress.

06635

Prototype of Compact Calorimeter Module for Beam Test

K.F. Read, T. Awes, C. Britton, N.D. Ezell, D. Silvermyr, P. Stankus, R. Warmack

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. 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 Brookhaven National Laboratory Relativistic Heavy Ion Collider.

Mission Relevance

As articulated in the Nuclear Science Advisory Long Range Plans and recommended 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

We performed calorimeter detector simulations, finalized multiple specifications, identified satisfactory vendors, 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 fabricated in sufficient quantity. Specifications of silicon sensor wafers were finalized after completing simulations, meeting with collaborators with past experience, and discussions with Hamamatsu Corporation. Tungsten absorber layers satisfying mechanical tolerances and chemical composition were purchased from a cost-effective vendor. In collaboration with colleagues at CERN, specifications were finalized for a custom Scalable Readout System appropriate for readout of this prototype, and the system was ordered.

Mechanical and electrical designs of the prototype were prepared to finalize connector and integration specifications. An innovative design for the detector panel was developed to ease assembly and allow scale-up. The silicon sensor wafers were received from Hamamatsu Corporation, mounted on tungsten absorber plates, and combined with custom readout flex-boards and summing boards. The ORNL flex-boards were wire-bonded to the Hamamatsu silicon pad wafers at Fermilab.

The assembly of the first of four longitudinal segments of the beam-ready prototype was completed in September 2013, with full completion of the assembly anticipated by late November 2013. ALICE colleagues (with outside funding available) intend to perform studies using this prototype at ORNL in early 2014. They anticipate testing this prototype at a CERN test beam in fall 2014.

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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 need for highly accurate and scalable flow dynamics computing algorithms is invoked by the increasing availability of large computing resources, and by the demand for accurate flow solutions in many applications (e.g., nuclear). This was the driving force 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. The software being developed is called PRATHAM (PaRAllel Thermal Hydraulic simulations using Advanced Mesoscopic methods) and will be used to demonstrate the LBM's applicability, accuracy, and scalability for realistic nuclear applications. To support this developmental effort with a mesh generation capability suitable for easily and timely producing computational domain lattices from CAD geometries, a Cartesian mesh generator was sought. The starting point was a GNU-licensed open source code (CARTGEN). However, it had to be further extended to fully support the specific preprocessing requirements, and therefore, CARTGEN has been strongly modified and upgraded in the course of this work.

Mission Relevance

In recent years, ORNL has become one of the nation's leading high-performance computing hubs by providing home to one of the largest computer clusters in the world – JAGUAR/TITAN (~300,000 cores). The availability of practically unlimited computing power posed the questions of developing highly scalable computing algorithms and improving their maturity so they can be applied to solve practical problems. The current practice shows that very accurate flow solutions can be obtained only for relatively small computational domains, usually not representing practical interest. Those solutions are typically used to derive general relationships applied in the approximate (averaged) models and thereby to obtain a production level result. In this work, we attempt to apply existing, sound theoretical approaches to solve turbulent flows in typical nuclear application by employing LBM, thus providing accurate solutions with practical merit. The need for such results is driven by problems like flow-induced structural vibrations; enhancement of heat transfer; deposition of residues (crud) on heat transfer surfaces with an effect on power distribution and corrosion, etc.

Results and Accomplishments

The work on the project during the reporting period was very intensive, and more than planned was achieved. A short summary of what was achieved during 2013 per software package follows.

PRATHAM Code

The LBM Software package, PRATHAM, is characterized by the following development features.

(1) The code is a single-phase compressible solver for three-dimensional high Reynolds flows, typical for industrial applications. (2) It is written in FORTRAN90 and is fully parallel by using MPI. It has been tested on multiple platforms at ORNL: JAGUAR, OIC, MEGY, and FISSION at INL. (3) The Single and Multi Relaxation time schemes (SRT/MRT) are implemented together with Smagorinsky LES model. (4) Inlet and Outlet boundary conditions were tested and proved functionality for directional flows. (5) A midway bounce-back scheme for handling complex boundaries was added. (6) An unstructured mesh option for SILO post-processing and a restart feature were included.

CartGen++

Originally the code was serial written in Fortran and had several drawbacks related to extensive memory consumption, inefficient input/output and mesh format (serial as well), and some other less important features that were limiting the practical application of the code. A decision was made to convert the code to parallel and in order to improve the memory management, the code was rewritten in C++. A new name was given – CARTGEN++. The structure of data transfer between CARTGEN++ and PRATHAM allows the partitioning to be done at the level of meshing, and for the moment the data transfer goes through an I/O interface, but in the future the two codes with be fully coupled in parallel.

The major development effort in the current year was focused on providing an unstructured mesh format feature. The original voxel labeling (coloring) technique used for generating meshes for the LBM solver relied on keeping the entire domain grid in structured form. An algorithm was added, based on neighbor nodal search that extracts the mesh using the scalar labeling function. This feature is directed to expanding the code capability toward a general-purpose meshing software. Thus the generated meshes are generalized and can be read by any external software.

The mesh generation package, CartGen++, is characterized by the following development features. (1) The code was modified to provide portability across different compilers. (2) Changes were made to the subroutine importing binary STL files. (3) A boundary tagging approach was developed. (4) A feature was added to write output in SILO format (instead of VTK and PLT). (5) The output-file-writing segment of code was converted from serial to parallel using MPI. (6) The basic algorithm in CARTGEN was rewritten in C++. (7) Data structures were optimized to save memory (compared to CARTGEN). (8) The CARTGEN algorithm was converted to parallel using MPI. (10) The code output uses XDMF for “light” data and binary/HDF5 for “heavy” data.

Information Shared

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06645

Inverse Sensitivity/Uncertainty Methods Development for Nuclear Fuel Cycle

G. Arbanas, M.E. Dunn, L.C. Leal, 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 the DOE/NE Fuel Cycle R&D (FCR&D) Program and the DOE Nuclear Criticality Safety Program (NCSP) managed by NNSA/NA-00. 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

We have developed the formalism for the inverse sensitivity/uncertainty and have applied it for the first time on the pressurized-water reactor (PWR) fuel system that is sensitive to the thermal and intermediate-energy neutron cross sections. We have quantified the effect of the so-called "implicit" component of the sensitivity coefficients (which is known to be important for thermal and intermediate neutron systems) by comparing IS/U optimized uncertainties with, and without, including the implicit component. This comparison shows that inclusion of the implicit component yields uncertainties on the differential cross sections that can be significantly smaller than the uncertainties computed without it, thus demonstrating the importance of including the implicit component of the sensitivity coefficient.

Our second accomplishment is a self-consistent inclusion of integral benchmark experiments (IBEs) into the IS/U optimization method. We have demonstrated the advantage of incorporating the integral benchmark experiments (IBEs) into the IS/U method by comparing the results for a pressurized-water reactor fuel-rod array, with and without IBEs. We find that inclusion of IBEs leads to less stringent uncertainties that yield the same target uncertainty of the application's response. This is a useful

development in view of the fact that cross section uncertainties for U-235 and U-238 already exhaust the best precision achievable in the present-day measurements. Thus, larger uncertainties afforded by inclusion of the IBE into the IS/U method are seen as a practical advantage of this method that lead us to suggest that IBEs be routinely incorporated into the IS/U studies.

A funding for continuation of this work and its applications has been appropriated in the Nuclear Criticality Safety Program (NCSP) 5-year plan approved by the National Nuclear Security Administration (NNSA) for FY 2014–2018 at approximately $100,000/year starting in FY 2015. Furthermore, as a result of our collaboration with Prof. Abdel-Khalik (NCSU), which was initiated within this Seed project, we will submit a proposal to the recently announced FY2014 Consolidated Innovative Nuclear Research FOA (DE-FOA-0000998), which could lead to additional funding.

Information Shared

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06676

Enabling GPU and Multithreaded Concurrency in Denovo's Method of Characteristics Solver for Reactor Analysis and Nuclear Applications

J.J. Jarrell, W. Joubert, S.R. Johnson, T.M. Evans

Project Description

Denovo is a 2D/3D radiation transport code used for reactor core analysis (neutronics), radiation shielding, nuclear forensics, and radiation detection. The computationally dominant pieces of the Denovo code are the radiation transport solvers. Denovo provides parallel-capable solvers for the linear Boltzmann transport equation using both deterministic (discrete ordinates (SN), Method of Characteristics (MoC), and diffusion) and stochastic (Monte Carlo) solvers. This project will port the MoC solver from central processing units (CPUs) to NVIDIA graphics processing units (GPUs) and incorporate multithreaded concurrency. This should decrease the time to solution by a factor of 3–4. This proof of principle will demonstrate the feasibility of using GPUs to significantly speed the MoC solver.

Mission Relevance

The Department of Energy's (DOE) Consortium for Advanced Simulation of Light Water Reactors (CASL) would like to run simulations on the Oak Ridge Leadership Computing Facility (OLCF) Titan, which will rely on GPUs for maximum efficiency. In order to utilize this parallelism, the material processing will require GPU-enabled algorithms such as the MoC solver. The Nuclear Regulatory Commission (NRC) has shown a desire to accelerate the MoC solver for reactor criticality and shielding analyses.

Results and Accomplishments

With the development of new algorithms, both consumer- and scientific-grade GPUs accelerated realistic characteristic sweeps by a factor of 8× to 30× faster. However, because of the computational expense of other parts of the transport framework and solution algorithm, the overall effective speedup on a realistic problem was about 3× faster (which agrees with the initial project expectations). The low fraction of time now spent on the transport sweep during the transport solve, especially on desktop systems, suggests that the next step to take to accelerate the code would be to perform the linear algebra on the GPU. This would additionally improve performance by obviating the cost of transferring solutions and source vectors back and forth between the host (CPU) and device (GPU) memories. Along with this activity, memory management improvements could also increase the speedup, though by substantially less.

Along with demonstrating that the MoC algorithm can be successfully ported to the GPU, this project provided support for a number of radiation transport staff to learn the details of CUDA and GPU-based coding best practices. This knowledge base will lend itself to numerous projects and activities in the future, thus keeping ORNL capabilities at the forefront of the radiation transport area.

Information Shared

None.

06782

Complexity Reduction Code Package for Reactor Physics Modeling and Simulation of Reactor Systems

U. Mertyurek, H.S. Abdel-Khalik, M.A. Jessee

Project Description

This project proposes the development of a complexity reduction code package to increase the computational efficiency of costly nuclear engineering calculations required in support of design and safety (e.g., advanced reactor design, optimization of spent fuel transport/storage casks, and regulatory confirmation reviews, each typically require many executions of the models). In our context, efficiency means completing the calculations in sufficiently short execution times on desktop computers and/or small computing clusters. The ultimate goal of this project is to achieve robust, high-fidelity simulation while maintaining the computational efficiency required for the original evaluation. This objective will be enabled by reducing the model order and replacing the original expensive models with fast-executing surrogate models while ensuring that the reduction errors are upper-bounded by user-defined error tolerance limits. Currently no code package is available to offer these proposed capabilities for realistic non-linear multi-physics reactor models with millions of input parameters and output responses.

Mission Relevance

The main premise of this project is to reduce the computation time and memory requirements of reactor core simulators without sacrificing accuracy. Through this capability, ORNL will secure its leadership in reactor analyses and computational methods and maintain its role in collaborating on initiatives from major key sponsors including the DOE Office of Nuclear Energy (DOE/NE) and the NRC Office of Nuclear Reactor Regulation and New Reactor Office that require very detailed or massive amounts of core calculations. Although the proposed code package will be developed for nuclear engineering applications, given the generic nature of the code package, we believe the technology can be applied to

many scientific disciplines such as climate modeling, astrophysics, materials modeling, and computer machine learning.

Results and Accomplishments

The CRANE complexity reduction code has been fully integrated with the ORNL SCALE code system. Integration efforts included modification of existing SCALE modules to provide required data for the CRANE calculations, a SCALE compatible input interface, and substitution of third party software dependencies with SCALE modules.

A new control sequence code called POSEIDON has also been developed and implemented in SCALE to automate several stages of CRANE calculations and allow parallel execution under different platforms without user intervention. Due to the modular design used in CRANE and POSEIDON codes, computational and data processing components can easily be substituted with more advanced ones as research progresses. The modular design also allows easy integration with different code systems in the future.

For the second stage of the project, significant progress has been made in development of a new advanced surrogate model form and algorithm to allow for better error control and more accurate predictions of the target parameters in a given reduced-order problem space. Preliminary studies demonstrated superior accuracy and speed of the new algorithm compared to the originally proposed second-order form. The new surrogate model algorithm is currently being implemented in CRANE.

SUMMARIES OF PROJECTS SUPPORTED THROUGH LABORATORY-WIDE FELLOWSHIPS

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WEINBERG FELLOWSHIP

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 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 include 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 the foreign countries that are unstable both politically and economically, solar residential applications will enhance the nation's 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 modernization in the near future. However, switching to the locally generated power can reduce the modernization costs of the transmission and distribution infrastructures while also eliminating 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 maximum power point tracking techniques has been completed, and a method that automatically responds to the changes in both irradiance and temperature has been implemented within the current-source inverter. A single-phase phase-locked-loop has been 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 have been carried out and results have been documented.

06348

Universal Sensing Platform for Autonomous Data Correction in Building Technologies

C.C. Castello

Project Description

Thousands of sensors are used by Oak Ridge National Laboratory (ORNL) to help analyze energy-saving building technologies at the component, system, or whole-building level. Data acquisition activities at ORNL have demonstrated up to 14.59% of missing data from data logger or sensor failure. This rate does not include data inaccuracy from sensor fouling and calibration error. Current methods to correct such discrepancies are technically inadequate and costly. Therefore, I propose to utilize advanced statistical methods, filtering mechanisms, and machine learning techniques to facilitate an autonomous and scientifically defensible method for the correction and reporting of sensor data. I proposed to design a universal sensing platform (USP) for real-time data validation and correction. The ultimate goal is to design a universal device capable of being connected to a wide variety of sensors which preserves the original data value, but can validate and correct data quickly at the 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) commercial 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 completed the study of statistical, filtering, and machine learning techniques for data quality assurance (QA). Statistical techniques include (1) least squares, (2) maximum likelihood estimation, (3) segmentation averaging, and (4) threshold based. Filtering methods include Kalman and linear predictive coding (LPC). Machine learning algorithms include feed-forward neural networks and Bayesian networks. Results have been presented at Energy Informatics 2012 (Castello and New, 2012), GlobalSIP: IEEE Global Conference on Signal and Information Processing (Castello et al., 2013), and IEEE International Conference on Machine Learning and Applications (ICMLA'13) (Smith et al., 2013). The correction of temperature, humidity, energy, pressure, and liquid flow data are investigated using data from ORNL's ZEBRAlliance Project, which built four energy-efficient homes for research purposes in Oak Ridge, TN. The statistical, filtering, and machine learning techniques are able to model temperature, humidity, pressure, and liquid flow data with coefficients of variance (CV) being below 10%. Energy data are much more difficult to predict with filtering and machine learning techniques, resulting in CVs of approximately 100%. However, the least-squares statistical technique is able to predict energy data with a CV of 52%. This is due to energy data's high variance. This accuracy is sufficient to allow adaptive detection and health assessment for incoming sensor data. Currently, algorithms are being implemented on a BeagleBone low-power single-board computer for real-time data QA at the sensor node. Furthermore, additional funding has been acquired from DOE's EERE to develop and engineer software for sensor data QA.

Information Shared

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WIGNER FELLOWSHIP

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 allows 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), and 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.

A new detector and data acquisition system was assembled and commissioned for charge particle emitters. The new system was subsequently installed at the Dubna gas-filled recoil separator in fall 2013 and has been used to study the fusion-evaporation products of the reaction ^{48}Ca+^{nat}Yb. The shortest half-life yet observed at the gas-filled separator was ^{219}Th ($T_{1/2}$ = 1 μs). The system has been deemed ready to be used for new experiments to detect new isotopes of flerovium (Fl).

Information Shared

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05982

Adaptive Radar Waveform Design for Optimal 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 project has direct relevance to DOE's CESAR program, the DoD, and the DHS. 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 proposed to design a peak-to-average power ratio (PAPR) constrained radar waveform that achieves the optimal performance (following the Neyman–Pearson lemma) in detecting an extended target in the presence of signal-dependent interference. The direct time-domain approach allowed straightforward characterizations of the correlation and PAPR properties of the designed signals, which are critically important to analyze the system performance in the presence of multiple targets and to assess the transmitter power-utilization, respectively. On the contrary, traditional waveform design techniques provide only the optimal energy spectral density of the transmit waveform and suffer a performance loss in the synthesis process of the time-domain signal. Therefore, in order to obtain the optimal detection performance and to simultaneously maintain a good cross-correlation performance, we proposed to solve a bi-objective optimization problem involving these two objective functions. In general, the detection and cross-correlation performance criteria are conflicting in nature; we tackled this contradictory behavior by concurrently optimizing both the objective functions in a Pareto-sense subjecting to the PAPR and total energy constraints. By computing the Pareto-front (where all the Pareto-optimal solutions reside), we could easily understand the trade-off or relative importance of the two objectives involved in the optimization problem.

We simulated several numerical examples to characterize the performance of the PAPR-constrained signals with respect to the optimal and a couple of other existing signal design techniques. Our numerical results demonstrated that even with a small PAPR measure (e.g., approximately 1 dB) the PAPR-constrained waveforms had fairly better detection performance than the constant-envelope signals having PAPR = 0 dB. Once the PAPR constraint was further relaxed by allowing a higher PAPR value, we showed that the designed waveform could actually achieve the optimal detection performance; however, the associated high PAPR value might not be suitable in many radar applications. In addition, our Pareto-optimization-based design approach enabled us to quantitatively describe the deterioration of the detection performance with the simultaneous improvement in the cross-correlation performance.

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 interest in developing novel engineered materials and the natural extension to associated nanotoxicological effects continues 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 Northeastern 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.

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
Presentation, BESC workshop, Riverside, January 2012
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06245

An Accurate and Efficient Computational Methodology for Simulating Disordered Nanoscale Materials

M. 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

The proposed research will be useful in identifying the 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 and 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 DoD agencies.

Results and Accomplishments

Accomplishments in the last year have focused on the development of an efficient computational method for obtaining the Green function for a disordered nanomaterial. (The Green function contains information on both the static and dynamic system properties.) 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; it scales independently of 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 (which is under way). Other work has been the development of a theory for electron transport pathways through nanomaterials with more than two termini (such as "supergraphene"). While parts of these derivations were straightforward, their substantiation with quantum chemistry codes has proven problematic. Although basis set non-orthogonality has been known for several years to trouble electron transport calculations, the source of these numerical problems has remained elusive. Moreover, calculations of electron transport pathways seem to be particularly sensitive to these problems. As such, we have made considerable progress to understand these problems and can attribute them to an insufficient electrode size in the transport calculations. With this solution, we have solved an outstanding problem in the electron transport community and moved one step closer to understanding current pathways in nanomaterials.

Information Shared

M. G. Reuter, W. S. Thornton, and R. J. Harrison, “Removing the Stigma of Nonorthogonal Basis Sets from Computational Quantum Mechanics: Robust Frameworks for Translating Operator Expressions to their Matrix Representations,” in preparation.

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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 that are capable of sharp and reversible conformational and chemical changes controlled by external signals. We will focus on the synthesis and characterization of polymer brushes and thin films capable of altering their conductive properties in response to external stimuli such as pH, temperature, electric field, etc. As part of this work, polymer brushes and thin films will be prepared on various substrates such as gold, highly ordered pyrolytic graphite (HOPG) and characterized by atomic force microscopy (AFM), light scattering, ellipsometry**,** broad band dielectric spectroscopy, scanning electron microscopy, electrochemistry. Results from the experimental studies will provide valuable insight to understand the relation between restructuring and electron transport in polymer brushes and thin films upon exposure to external signal. Knowledge gained 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 stimuli in energy-harvesting devices will be evaluated. This effort is aligned with the DOE energy mission by addressing energy challenges through transformative science and technology solutions. As one of the possible applications, we propose to apply new stimuli-responsive materials to the problem of efficient conversion of biomass to energy in enzymatic biofuel cell. Research on enzymatic biofuel cell will provide the foundation to facilitate development of a green energy technology capable of producing clean, sustainable electrical power.

This research is focused on the development of new switchable interfaces capable of extreme conformational and chemical changes in response to external signals. It would be of interest to various agencies (including DOE, NIH, and DoD) providing support to programs that require "smart" materials, biosensors, drug delivery systems, micro-nanoactuators, regenerative systems, and tissue mimicking platform.

Results and Accomplishments

To date, various stimuli-responsive interfaces composed of polymer brushes and thin films have been synthesized, and we are in the process of characterizing them. Various AFM modes are used to characterize the topography and properties of materials such as conductive, mechanical, piezoelectric, etc. This research is conducted at the Center for Nanophase Materials Sciences under user proposal #CNMS2013-238 entitled "In situ probing of bias-induced structural (mechanical), and ionic transformations in polymerized ionic liquids" and is performed in collaboration with Dr. Kalinin (AFM),

Dr. Sumpter (theoretical simulation), and Dr. Kravchenko (Nanofab lab). Conductive polymer thin film is our starting point. The exciting findings that demonstrate restructuring of conductive polymers in response to external stimuli (electric field) were presented at the CNMS evaluation poster session this year. These results are the core of scientific publications that are presently in preparation.

To study the dynamics of the polymer interfaces, we use broadband dielectric spectroscopy. The dynamics of the polymers are well established for thin films. However, study of polymer brushes requires unique skills and an experimental setup. We are in collaboration with Dr. A. Sokolov (ORNL/UT) and Dr. J. Sangoro (UT) and have started with polymer brushes based on polyisoprene. This polymer has a relaxation time that is easy to follow experimentally. In the process of fabricating and characterizing the polyisoprene brush, we expanded our understanding of how molecular weight, composition, and method of preparation affect the its dynamics. Results obtained will be reported in scientific papers. To facilitate our collaborative effort with Dr. Sangoro, we have submitted a JDRD proposal this year.

The application part of our LDRD project includes measurements of the catalytic activity of enzymes embedded in thin films and polymer brushes to enhance the performance of biofuel cells. The importance of electrodes modification for an effective biofuel cell operation is described in a book chapter written by E. Katz et al. This work is conducted under CNMS user proposal CNMS2013-340 “Probing redox reactions of biocatalyst modified electrodes for biofuel cell applications using voltage modulated SPM” in collaboration with Dr. Kalinin and Dr. Rodgriguez (University College Dublin, Ireland). This work is in progress.

Additionally, we work with biodegradable and biocompatible polymers. Interfaces based on these polymers are important to extend the life of enzymes on the electrodes in biofuel cells and for various medical applications. We expect that the knowledge gained from the present LDRD project can be used to receive a follow-up findings from various agencies including NIH. Some preliminary work testing stimuli-responses of alginate to biological stimuli has been recently reported by S. Mailloux et al.

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 (e.g., 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 the stability and efficiency of these antenna systems. To address this issue, highly photostable chromophores, that is, fluorescent metallic nanoclusters, will be synthesized and organized using DNA self-assembly. 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. Additionally, surface nanostructuring and synthesis of new materials will be explored to achieve antireflective and self-cleaning coatings, transparent insulation, and lightweight materials, which will further enhance the energy efficiency of buildings and vehicles.

Mission Relevance

This research will lead towards developing new solar energy harvesting devices and enhancing the efficiency of the existing devices. Since solar energy is clean and available in abundance, this research strongly supports the DOE mission of increasing energy security and improving environment quality. Additionally, this research fits well with the DOE's Vehicle Technology Office (lightweight materials, self-cleaning coatings) and Buildings Technology Office (antireflective and self-cleaning coatings, transparent insulation, and lightweight materials) missions. This research is also well aligned with the mission (body armor and bulletproof vehicles) of Defense Advanced Research Projects Agency.

Results and Accomplishments

During the FY 2013, the focus of my research program was on nanostructured surfaces.

- The synthesis of hierarchical structures with absolute control of size and number of components has been demonstrated.
- The synthesis of silica nanoparticles ranging from diameter 10 nm to 1 μm has been accomplished.
- The synthesis of silica structures with addressable and local control of shape and diameter has been achieved.

The above-mentioned silica structures are of tremendous importance for surface nanostructuring in order to obtain antireflective, superhydrophobic, superhydrophilic, and antibiofouling coatings.

- The synthesis of silica nanofibers of unprecedented diameter (~25) was demonstrated using a less-energy-intensive technique.

These nanofibers are of substantial importance to lightweight materials, body armor, and aerospace applications.

Information Shared

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J. Sharma and P. Datskos, "Synthesis of silica nanofibers of unprecedented diameter," ORNL invention disclosure (#201303139).

07105

Large Timescale Atomistic Modeling of Metallic Glasses Deformation

Y. Fan

Project Description

The aim of this proposal is to study, understand, and hence predict the metallic glasses (MGs) deformation over large timescales, from nano-seconds to years, by means of state-of-art atomistic modeling methods. This is a formidable challenge in both scientific concepts and practical simulation. Although such a capability does not presently exist, advances in the study of slow dynamics suggest the difficulty of simulating the evolution of MGs at macroscopic timescales can be overcome. The aim of this project is to build the computational models, derive the analytic theory, and acquire the fundamental understanding needed to enable prediction of deformation mechanisms in MGs at large timescale. An atomistic modeling technique will be employed and further developed to determine the essential plastic units. The proposed synergistic research can shed light on the design of novel materials, from atomic to engineering scales, for desired properties and enhanced performance in energy applications.

Mission Relevance

The design of materials with unique functionality has become increasingly important to meet the urgent demand for new energy applications. For example, because of its large elastic limit, high yield strength, metallic glasses are emerging as a new category of materials for energy storage, and are required to have high-load-bearing capability. Developing such materials requires understanding and assessing materials deformation behavior at relevant, large timescales.

Results and Accomplishments

Since becoming a Wigner fellow on July 8, 2013, I have studied the relationship between the stabilities and structural properties in a MG system. It has been demonstrated the stability of amorphous system is more closely related to the organization of different atoms, rather than single atom properties. Even for a very similar distribution of single atom properties, the overall stabilities can be largely different. Particularly, my modeling system showed that the stability is strongly related to the distribution of the soft atoms with the lowest 5% shear modulus. These results suggest an alternative and novel way to unraveling the mysterious structure-property relation in amorphous materials, by selecting appropriate windows.

Information Shared

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07115

First-Principles Study of the Influence of Disordered Dopants on the Electronic Structure of Materials

T. Berlijn

Project Description

Doping and alloying, the removal, substitution, and insertion of chemical elements, into otherwise pure materials, are powerful ways to control the electronic properties. For the theoretical materials scientist, this raises the question, what does doping do? How do the dopants influence the Bloch states and band structure of the solid? At the simplest level, they will inject/remove electrons, as in the example of doped silicon, resulting in a shift of chemical potential. Additionally doping will exert chemical pressure by modifying the lattice constants. Dopants will also, inevitably, induce quenched disorder into the system. As a consequence, the disordered dopants will scatter electrons, giving them finite lifetimes and finite mean free paths as reflected in the energy and momentum broadenings of their band structure. Furthermore, entirely new degrees of freedom can emerge under the influence of disorder, such as impurity states and resonances, which often play a vital role in the functional properties of materials. In this project we address these questions and in particular study:(1) the breakdown of Luttinger theorem in functional materials; (2) the missing interlayer band in graphite intercalation compounds; (3) impurity in a superconductor; (4) band gap bowing; (5) lattice and magnetic fluctuations; and (6) the mobility edge from first principles.

Mission Relevance

Doping and alloying, the removal, substitution and insertion of chemical elements, into otherwise pure materials, are powerful ways to control the electronic properties of materials. The most famous example is doped silicon in which phosphorus/boron substitutions inject/remove electrons, resulting in n- and p-type semiconductors, which in turn form the basis of all modern electronics. The list of other materials with doping and alloying-induced functional properties is long and includes superconductors (e.g., the pnictides, cuprates, graphite intercalation compounds), dilute magnetic semiconductors (e.g., Ga1-xMnxAs, Zn1-xCuxO1-y), topological insulators (e.g., Bi1-xSbx), thermoelectrics (e.g., PbTe1-xSex), ferroelectrics (e.g., PbZr1-xTixO3), shape memory alloys (e.g., Ti-Ni alloys), photovoltaics (e.g., CuIn1-xGaxSe2), photocatalysts (e.g., Ga1-xZnxN1-xOx), and battery materials (e.g., Li1-xMxFePO4).

Results and Accomplishments

Since joining Oak Ridge National Laboratory 3 months ago, I have been working on several projects on disordered materials. One of them involves the influence of selenium vacancies in the recently discovered monolayer FeSe superconductors. These dopants turn out to display a very strong *breakdown of Luttinger theorem*. I found that, counterintuitively, selenium vacancies dope holes rather than electrons. This finding rules them out as the origin of the strong electron doping observed in these compounds. Another project I have been working on is the development of a method to treat an *impurity in a superconductor*. This method combines techniques from model calculations (Bogoliubov-de Gennes equations) with those of first-principles calculations (Wannier functions). The main purpose of this method is to compare it with experimental scanning tunneling spectroscopy to obtain insight in the nature of the superconductivity. My collaborators and I have applied the method to bulk FeSe as a first test case and were able to explain the so-called “dimer state” that is frequently observed in iron-based superconductors. This result highlights the unique capabilities of the new combined method such as the exhibition of global symmetry breaking and the inclusion of non-local contributions.

Information Shared

I have resubmitted a manuscript on the influence of selenium vacancies. Furthermore, I have been co-editing a preliminary draft of the manuscript on a new method for treating an impurity in a superconductor.

07149

Production of Renewable Hydrocarbon Fuels from *Saccharomyces cerevisiae*

D.M. Close

Project Description

This project focuses on the direct production of a liquid hydrocarbon fuel component from the model yeast *Saccharomyces cerevisiae* through introduction of a synthetic tridecane (C13 alkane) production pathway. This pathway is comprised of the tetradecyl (C14) aldehyde producing *luxCDE* genes of the bacterial bioluminescence gene cassette and an associated aldehyde decarbonylase gene that is capable of selectively reducing the provided aldehyde substrates to alkanes. Expression of this synthetic pathway will permit direct synthesis of a liquid hydrocarbon fuel component that is compatible with existing engines and infrastructure. Expansion of this system to allow for the production of alternate hydrocarbon products will provide an inexpensive and renewable means for producing fuel from a well-characterized, highly scalable, and industrially leveraged organism.

Mission Relevance

This project is of relevance to the DOE Office of Energy Efficiency and Renewable Energy's mission for the development of alternative, renewable energy sources to supplement or replace the United States' dependence on foreign oil. In addition, the proof-of-principle nature of the project contributes significantly to the understanding of hydrocarbon fuel production pathways in microorganisms, which conforms to DOE's support of basic science that can be used for renewable energy and environmental quality improvement.

Results and Accomplishments

To date, two separate hydrocarbon production pathways have been synthetically assembled and expressed in *S. cerevisiae*. The first utilizes the prokaryotic *Nostoc punctiforme* aldehyde decarbonylase gene that has been popularized in the literature, while the second utilizes a homologous aldehyde decarbonylase sourced from a eukaryotic organism that has not previously been investigated for biofuel production purposes. Due to differences in cellular organization between prokaryotic and eukaryotic hosts, the need for a supplementary reductive system consisting of two additional genes has been identified for expression of the *N. punctiforme* gene in *S. cerevisiae*, and this system has been synthetically assembled and co-expressed with the hydrocarbon production pathway. Several alternative alkane extraction methods have been competitively evaluated, and a procedure has been developed to rapidly prepare samples of hydrocarbon-expressing yeast strains for GC/MS analysis. Production of the target hydrocarbon product, tridecane (C13 alkane), has been identified in yeast strains expressing both the prokaryotic- and eukaryotic-based synthetic production pathways. Additional alkane and alkene products have also been identified, consistent with published literature detailing the evaluation of biohydrocarbon-producing bacterial strains. Basic growth characteristics of hydrocarbon production strains have been evaluated and analyzed using liquid chromatography to determine the extent of exogenous pathway

expression on sugar uptake and basic metabolism. A detailed metabolimic assessment using GC/MS has also been initiated to determine the full extent of pathway expression and hydrocarbon production on internal oxidation/reduction states and cellular function.

Information Shared

No manuscripts have yet been published from this work.

07150

Revealing the Functionality of Nanomaterials for Energy Applications at the Atomic Scale

W. Zhou

Project Description

The overarching goal of this research program is to reveal the functionality of energy-related materials at the atomic scale by developing novel analytical electron microscopy techniques that combine low-energy and low-dose operation regimes with in situ holders.

In order to achieve the overarching goal of this research program, I explore, develop, and optimize the best low-energy and low-dose techniques required to perform atomic-scale quantitative analysis in aberration-corrected scanning transmission electron microscopy (STEM) for different energy-related materials that are electron beam sensitive, that is, graphene, lithium-based cathodes, metal nanoparticles, and zeolites for heterogeneous catalysts. The low-energy and low-dose operation STEM, also known as *"gentle"* STEM, allows the *true* atomic structure, chemistry, bonding, and optical properties of energy-related materials to be revealed with unprecedented spatial resolution and with single-atom sensitivity. Moreover, when combined with various in situ sample holders, *gentle* STEM further enables the tracking of the structure, chemistry, and electronic structure evolution of materials under their relevant working conditions. The outcome of this research program aims to offer valuable guidance to the optimization of material synthesis and the design of new materials with enhanced performance.

Mission Relevance

The success of this program aims to position ORNL at the frontier of one of the most investigated areas of electron microscopy, low-energy and low-dose *gentle* STEM, and open new opportunities to probe the functionalities at the atomic scale in a much wider range of material systems, including two-dimensional materials, active carbon materials, polymers, battery materials, etc., that suffer electron beam damage under conventional TEM/STEM experiments. This program benefits material scientists at ORNL who are working on these materials. This program is well aligned with the mission of DOE on energy material research. The success of this program also aims to propel ORNL, both directly and through interagency collaborative teams, into a highly competitive position for funding from EERE and DOE BES and DARPA program offices.

Results and Accomplishments

Using low-voltage *gentle* STEM technique, we published the first direct imaging of grain boundary structures in monolayer MoS_2 in *Nature Materials*, and a more systematic study of various intrinsic structural defects in monolayer MoS_2 in *Nano Letters.* These two papers provide the most comprehensive atomic structural information for the study of defects in monolayer transition-metal dichalcogenide

(TMDC) materials, which are considered to be the most promising semiconductors for future flexible nano-electronics. Using dynamic *gentle* STEM imaging, we showed that the semiconducting TMDC layers can be locally converted into conductive nanowires using the electron beam, paving the way for direct patterning of conducting channels in semiconducting materials for flexible 2D integrated circuits. This study is under review at *Nature Nanotechnology*. We also develop a new method to perform layer-by-layer dopant distribution mapping in MoS_2 using *gentle* STEM imaging (paper under review at *Nano Letters*). Our *gentle* STEM technique also helped to understand the structure of stacking boundaries in bilayer graphene (published on *Nano Letters*), to identify a new type of interlaced crystal containing perfect Bravais lattices with interlaced chemical order (paper under review at *Nature Materials*), and to reveal the active sites in platinum-modulated cobalt nanocatalysts for low-temperature aqueous-phase Fischer-Tropsch synthesis (published on *JACS*). The PI is a lead author in all the above-mentioned works.

Based on the work funded by the Wigner Fellowship, the PI gave two invited talks at international conferences in 2013.

[1] Spectrum imaging of 2D materials at the single-atom level. *EDGE 2013 International Electron Energy Loss Spectroscopy Meeting*. Sainte Maxime, France.

[2] Probing defect physics of 2D materials at the atomic scale. *IUMRS International Conference on Advanced Materials*. Qingdao, China.

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