ORNL/PPA-2017/3

Laboratory Directed Research and Development Program

FY 2016 Annual Summary of Completed Projects

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March 2017

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

ORNL/PPA-2017/3

Oak Ridge National Laboratory

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM

FY 2016 ANNUAL SUMMARY OF COMPLETED PROJECTS

March 2017

Prepared by
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CONTENTS

ABBREVIATED TERMS

CRISPR	clustered regularly interspaced short palindromic repeats
DNA	deoxyribonucleic acid
HBCU/MEI	historically black colleges and universities/minority educational institution
IEEE	Institute of Electrical and Electronics Engineers, Inc.
I/O	input/output
OLCF	Oak Ridge Leadership Computing Facility
RNA	ribonucleic acid
SPP	Strategic Partnership Projects

Federal Organizations

DHS	US Department of Homeland Security
DOD	US Department of Defense:
AFRL	US Air Force Research Laboratory
AFOSR	Air Force Office of Scientific Research
ARL	US Army Research Laboratory
ARO	US Army Research Office
DARPA	Defense Advanced Research Projects Agency
NRL	US Naval Research Laboratory
ONR	Office of Naval Research
ONI	Office of Naval Intelligence
DOE	US Department of Energy
DOI	US Department of the Interior
DOT	US Department of Transportation
FBI	Federal Bureau of Investigation
HHS	US Department of Health and Human Services
IARPA	Intelligence Advanced Research Projects Activity
NASA	National Aeronautics and Space Administration
NGA	National Geospatial-Intelligence Agency
NIH	National Institutes of Health
NCI	National Cancer Institute
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
USDA	US Department of Agriculture
USGS	US Geological Survey

DOE Laboratories

ANL	Argonne National Laboratory
BNL	Brookhaven National Laboratory
INL	Idaho National Laboratory
LANL	Los Alamos National Laboratory
LBNL	Lawrence Berkeley National Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
PPPL	Princeton Plasma Physics Laboratory
SNL	Sandia National Laboratories
SRNL	Savannah River National Laboratory

DOE Offices and Programs

AMO	Advanced Manufacturing Office
ARPA-E	Advanced Research Projects Agency–Energy
ASCR	Office of Advanced Scientific Computing Research
BER	Office of Biological and Environmental Research
BES	Office of Basic Energy Sciences
BETO	Bioenergy Technologies Office
BTO	Building Technologies Office
BTP	Building Technologies Program
EERE	Office of Energy Efficiency and Renewable Energy
EM	Office of Environmental Management
FE	Office of Fossil Energy
FES	Office of Fusion Energy Sciences
HEP	Office of High Energy Physics
JGI	Joint Genome Institute
LDRD	Laboratory Directed Research and Development
NE	Office of Nuclear Energy
NP	Office of Nuclear Physics
NNSA	National Nuclear Security Administration
NA-22	Office of Nonproliferation Research and Development
OE	Office of Electricity Delivery and Energy Reliability
SC	Office of Science
SULI	Science Undergraduate Laboratory Internships
VTO	Vehicle Technologies Office

INTRODUCTION

Oak Ridge National Laboratory (ORNL) is a US Department of Energy (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 Strategic Partnership Projects (SPP) program. Information about the Laboratory and its programs is available on the Internet at www.ornl.gov.

The Laboratory Directed Research and Development (LDRD) program at ORNL operates under the authority of DOE Order 413.2C, "Laboratory Directed Research and Development" (October 22, 2015), which establishes DOE's requirements for the program while providing the Laboratory Director broad flexibility for program implementation. The LDRD program funds are obtained through a charge to all Laboratory programs. ORNL reports its status to DOE in March of each year.

This report includes summaries of all ORNL LDRD research activities completed by September 30, 2016. It is sent to the ORNL Technical Officer for export control review and classification review prior to being uploaded to the Office of Scientific and Technical Information.

LDRD is a relatively small but vital program whose purpose is to meet the DOE mission. It allows ORNL and other DOE laboratories to improve their distinctive capabilities and to enhance their ability to conduct cutting-edge R&D for DOE and SPP sponsors. R&D projects funded through LDRD support the following general goals:

- maintain the scientific and technical vitality of the Laboratory;
- enhance the Laboratory's ability to address future DOE missions;
- foster creativity and stimulate exploration of forefront areas of science and technology;
- serve as a proving ground for new concepts in research and development; and
- support high-risk, potentially high-value research and development.

ORNL has established a program with three components to meet its LDRD objectives and to fulfill the particular needs of the Laboratory: the Director's R&D Fund, the Seed Money Fund, and the Distinguished Fellowship Fund (Householder, Russell, Weinberg, and Wigner Fellowships). As outlined in Table 1, these three 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 Distinguished Fellowship Fund allows the Laboratory to hire exceptional early career scientists to refresh its scientific

* http://energy.gov/mission

and technical capabilities. 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	Distinguished 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
Reviewers	Director's R&D fund Initiative Review Committees (IRCs), 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 Fellowship Review Committees (FRCs), composed of ORNL corporate fellows, senior technical managers, and subject matter experts
Review process	Preliminary and full proposal review, including a presentation to the IRCs 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, including a presentation to the FRCs and an annual review of progress
Review cycle	Annually	Monthly	Up to four times a year, depending on Distinguished Fellowship
Project budget	Typically ~$750,000	< $190,000	Typically ~$400,000
Project duration	24–36 months	12–18 months	30–36 months
LDRD outlay	~80% of program	~12% of program	~8% of program

Director's R&D Fund

The Director's R&D Fund is the strategic component of the ORNL LDRD program and is the key instrument 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.

To select the best and most strategically significant ideas submitted, the Deputy for Science Technology establishes committees for each of the annual LDRD initiatives to review the new proposals and ongoing projects. The committees are staffed by senior technical managers and subject matter experts, including external scientists.

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 of full proposals. In the second round, the committees review the full proposals and ongoing projects that are requesting second- or third-year funding. The committees provide funding recommendations to the Deputy for Science and Technology, who develops an overall funding strategy and presents it for approval by the Leadership Team, headed by the Laboratory Director. All projects selected for funding must also receive concurrence from DOE.

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 year, the Deputy for Science and Technology issues a call for proposals. In FY 2016, the call for proposals emphasized specific research priorities aligned with the Laboratory Agenda:

- Computer Science and Math for Exascale Computing,
- Integrated Energy Systems: Systems Integration & Cyber Security for Energy Infrastructure,
- Integrated Studies of Complex Biological and Environmental Systems,
- Materials Design and Innovation,
- Next Generation Science for Neutron Sources,
- Quantum Computing: Materials and Interfaces,
- Science and Informatics for Energy and Urban Infrastructure,
- Transformational Nuclear Science and Technology, and
- Discovery Science and Innovation.

The research priorities within the FY 2016 Director's R&D Fund initiatives are described in the following sections. The levels of investment in each focus area are summarized in Fig. 1.

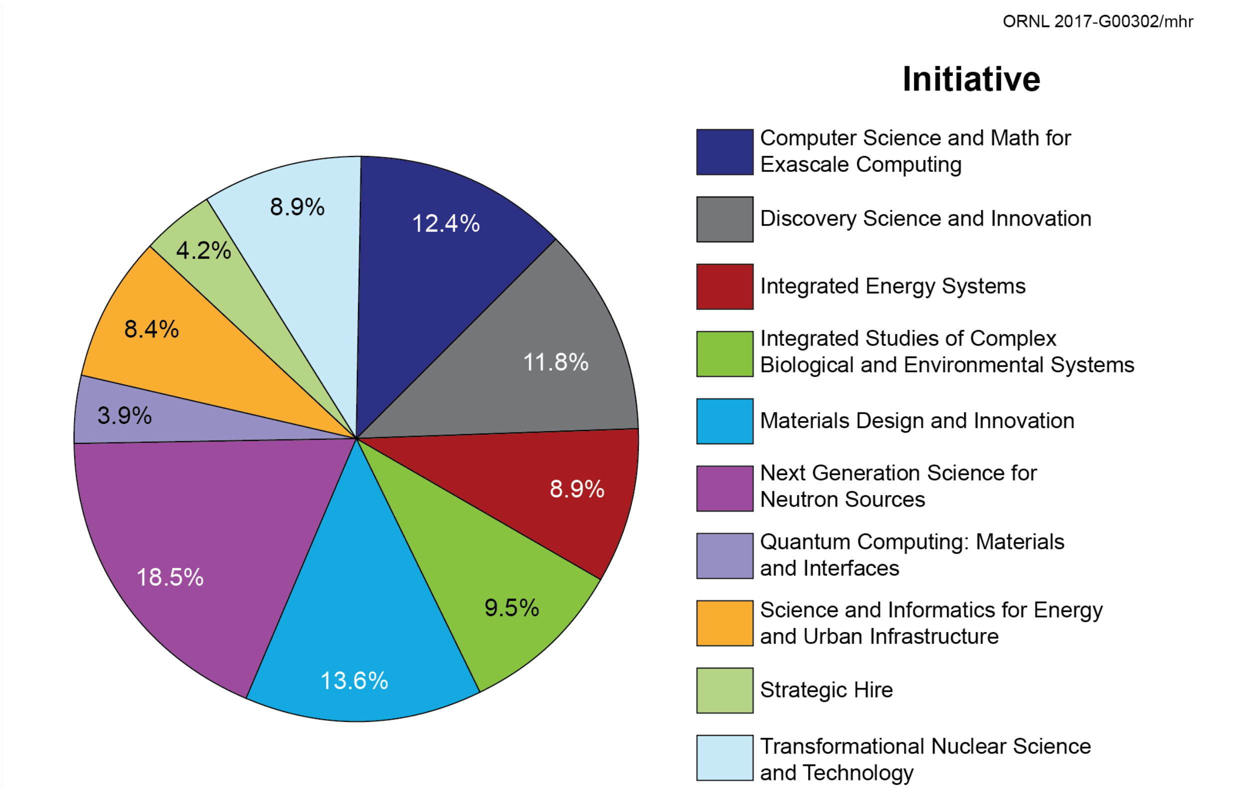

Fig. 1. Level of Director's R&D Fund investment in the Laboratory initiatives for FY 2016.

Computer Science and Math for Exascale Computing

Multidisciplinary efforts were solicited to use the nation's most capable high-performance computing (HPC) resources to (1) enable transformational research and scientific discovery and (2) advance HPC to the exascale and beyond. Proposals address exascale computing, advanced modeling and simulation, and data analytics.

Priorities include the following:

- computer science and mathematics,
- big data analytics algorithms and tools, and
- scalable co-design methods and tools.

Integrated Energy Systems

LDRD investments in this initiative are focused on the research necessary to revolutionize the way we currently produce, utilize, and distribute energy. Research priorities include the following:

- rational manufacturing;
- sensing, analysis, and control;
- cyber and cyber-physical security; and
- multi-objective generation/load/storage optimization.

Integrated Studies of Complex Biological and Environmental Systems

This initiative is focused on the research needed for the development and/or demonstration of tools and methods to facilitate studies of relevant systems from molecular to ecosystem response scales. Research is focused on the following:

- interactions between multicomponent systems (enzymes, microbes, plants, and communities) and their substrates or environments;
- biomembranes and their complexity and functions;
- bio-based or bio-inspired materials including but not limited to those from biomass; and
- complex environmental systems.

Materials Design and Innovation

This initiative is focused on understanding and controlling complex physical and chemical phenomena across broad time and length scales to predict, design, and deliver advanced materials for energy technologies. Priority is placed on research that takes advantage of ORNL's signature strengths in materials synthesis, advanced modeling and simulation, and advanced characterization techniques, especially neutron science. Research is focused on the following:

- combined experimental and theoretical/modeling approaches that focus on the control of materials structure and function at the atomic and molecular levels;
- demonstration of highly integrated approaches to materials design with a focus on model systems for a specific energy application;
- multi-scale computational approaches; and
- investigations of the structure of materials and dynamics of associated chemical and physical processes in situ and operando with multiple, simultaneous probes or with ultrahigh resolution/sensitivity.

Next Generation Science for Neutron Sources

The envisaged second target station (STS) at the Spallation Neutron Source (SNS) would provide the highest-brilliance beams of cold neutrons worldwide and therefore presents an outstanding opportunity for a leadership position in mesoscale science. LDRD investments in this initiative are focused on the R&D needed to engage in next-generation problems and to provide innovative applications of neutrons that will lead to increasing impact of user research scientific programs. Areas of emphasis include the following:

- the application of neutrons to quantum materials, including the fundamental understanding of quantum states in condensed matter to the application of these materials in devices;
- the use of HPC and simulation to model and design soft matter and biological systems, hierarchical materials, kinetics, and self-assembly; and
- measurement and modeling of chemical reactions and in situ processing, development of techniques for dealing with high-throughput measurement and modeling, and simultaneous use of spectroscopy and diffraction as well as other modalities to fully understand materials composition and behavior.

Science and Informatics for Energy and Urban Infrastructure

This initiative is focused on the research needed in critical infrastructure domain sciences, scalable data analytics and computing, unique data infrastructure, and modeling and simulation to address energy and urban dynamics. Focus areas include the following:

- data-driven modeling and simulation to facilitate discovery of emerging behavior of urban systems over large spatial and temporal scales with improved resolution;
- development and curation of unique data and knowledge resources; and
- development of technology measures that effectively address privacy, information security, and public trust.

Transformational Nuclear Science and Technology

This initiative is intended to strengthen ORNL's leadership role by supporting transformational research to develop nuclear fission and fusion energy. Proposals address the integration of ORNL's core scientific capabilities in nuclear, materials, and computational engineering and include the use of leadership science facilities for neutron irradiation and scattering research, nuclear material examination, radiochemistry, and HPC. Emphasis is on proposals that seek to effectively integrate experiments, operations experience, theory, and computational analysis for addressing key technical challenges in nuclear energy and security. Focus areas include the following:

- nuclear materials research and production technology;
- fusion technology development to address transients, whole device modeling, and plasma-materials interactions; and
- transformational fission power technologies.

Quantum Computing: Materials and Interfaces

The goal of this initiative is to develop a multi-qubit test bed for the investigation of qubit properties. This initiative is staged to include the following activities/ focus areas:

- qubit materials design,
- characterization and modeling of qubits,
- developing balance of system components, and
- initiating a programmable qubit test bed.

Discovery Science and Innovation

Scientific discovery and innovation are key elements of ORNL's science and technology mission. Research teams are encouraged to consolidate and leverage the unique capabilities and talents at ORNL to solve the most important science problems. Research is focused on scientific and technological breakthroughs that provide revolutionary advances in core ORNL basic science and technology program areas.

Strategic Hire

The Strategic Hire program was formed to add critical skills to the Laboratory by hiring individuals whose research is aligned with ORNL's strategic areas. Candidates for strategic hires are expected to be established investigators, well qualified for leading research programs, capable of developing substantial programs, and/or able to take organizational leadership roles. Promising individuals at earlier stages of their careers who bring expertise critical to major ORNL strategic initiatives may also be supported.

Strategic hire proposals are screened by the LDRD Manager for compliance with DOE Order 413.2C and are peer-reviewed by two or more Laboratory staff members. Recommendations are forwarded to the Director of the Office of Institutional Planning and the Deputy for Science and Technology for approval. The proposals also go through DOE concurrence.

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 SPP 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, 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, typically with the assistance of a technical reviewer. All Seed Money Fund proposals receiving favorable reviews and a funding recommendation are forwarded to the Deputy for Science and Technology for approval and to DOE for concurrence.

The distribution of Seed Money Fund support by research division is shown in Fig. 2.

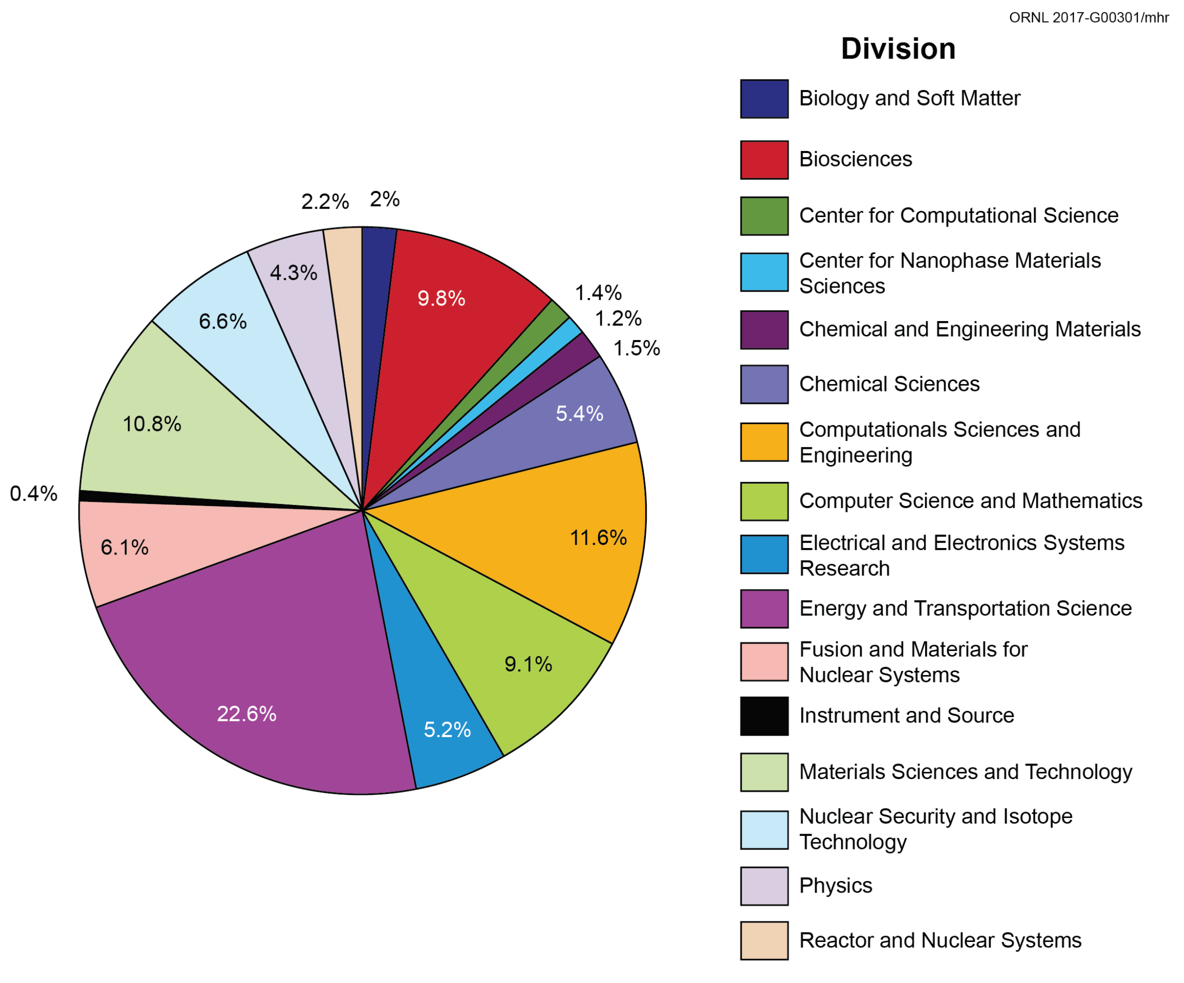

Fig. 2. Distribution of Seed Money Fund by research division for FY 2016.

Distinguished Fellowship Fund

In FY 2016, the awardees of the Laboratory's Distinguished Fellowship programs received funding through the LDRD Program. The fellowship programs were formed to provide research opportunities for exceptional early career scientists in honor of Dr. Alston Householder, founding director of the ORNL Mathematics Division; Dr. Liane Russell, ORNL's groundbreaking geneticist; Dr. Alvin Weinberg, former ORNL director; and Dr. Eugene Wigner, first Director of Research and Development at ORNL. The appointment of fellows at ORNL provides an opportunity for outstanding scientists and engineers in life, physical, computer, computational, and social sciences to pursue research in an area related to national energy problems and interests. 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 separate selection committees with a frequency depending on the Distinguished Fellowship.

Once the candidate is selected, a supervisor is assigned to help the appointed Fellow with the LDRD proposal that is aligned with the Fellow's research plan. Fellowship proposals are screened by the LDRD Manager for compliance with DOE Order 413.2C and are peer-reviewed by two or more Laboratory staff members. Recommendations are forwarded to the Director of the Office of Institutional Planning and the Deputy for Science and Technology for approval. The proposals also go through DOE concurrence.

Report Organization

This report, which provides a summary of all projects that were completed at the end of FY 2016 (September 30, 2016), is divided into 12 sections: one for each of the Director's R&D Fund initiatives, the Seed Money Fund, the Fellowship Fund, and Strategic Hire. 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 2016. Publications resulting from the project are also listed.

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

COMPUTER SCIENCE AND MATH FOR EXASCALE COMPUTING

06802

Predictive Soft Matter Materials Simulation

B.G. Sumpter , R. Kumar, M. Brown, J. Billings, S. Pannala, M. Eisenbach, B. Philip, B. Lokitz, J. Ankner

Project Description

The overarching goal of this proposal is to develop an integrated computational predictive framework for predicting and developing new or improved soft matter materials for energy science applications/technology with verification and feedback from experimental capabilities in precision synthesis and state-of-the-art characterization. Toward this end we will develop a leading research capability for multiscale-multiphysics soft matter simulation by implementing new algorithms that take advantage of data analytics, leadership and emergent computing architectures, and experimental verification. Specifically, we will develop a scalable simulation framework for studying end-anchored charged polymeric systems (e.g., brushes) and charged chiral-copolymeric materials. This requires development and implementation of mathematical algorithms for treating electrostatic interactions, heterogeneous time integration, efficient phase space sampling (featuring complex-Langevin and Wang-Landau schemes), and experimental verification. With these new developments our simulation framework will directly aid in the design of charged soft matter materials by targeting important use-based applications for enabling new functional materials relevant for separations, carbon capture, chemical purifications, and energy storage/conversion as well as the traditional domain applications of high-performance polymers and composites.

Mission Relevance

Given the importance of soft matter materials in securing our energy future, an integrated computational soft matter predictive tool/framework is a strategic and highly timely concept. We have developed an appropriate application software that can be used to guide the design of new soft matter materials and that can be readily tuned to directly help interpret experimental characterization techniques that probe morphology and its evolution over time (e.g., neutron scattering; high-resolution transmission and other electron microscopies; and x-ray, optical, dielectric, image, and atomic probe microscopies/spectroscopies).

Results and Accomplishments

Although we had a rather ambitious set of milestones, our progress has been on target and on time. Thus overall, this LDRD work has been very productive and has led to 13 very notable publications, several highlights, numerous invited presentations, and substantial program development for follow-on funding opportunities. For example, LDRD helped set the foundation for our participation in the Center for Understanding and Control of Acid Gas-induced Evolution of Materials for Energy, which is a new Energy Frontier Research Center. We took part in two DOE-BES computational materials science proposals (FOA-0001276), one led by ORNL the other by SNL, as well as an Exascale Computing Project applications proposal in 2016, and participated in the DOE Big Ideas Summit by contributing on the topic entitled "Beyond Moore's Law Computing."

In FY 2016, we demonstrated a full end-to-end theory/simulation prediction and validation from neutron scattering of d-spacing dependence on experimentally synthesized polymers with specific chain polydispersities; a key paper was published in *RSC Advances*, and several presentations were made on the topic, including two at meetings of the American Physical Society, three at the American Chemical Society, and two at math conferences. In another example, we used field theory simulations to develop and model charged and dipolar polymer brushes alongside molecular dynamics simulations of neutral polymers and brushes. As a result of the work, seven papers were published and three presentations were given. In addition, we developed and applied the Self-Consistent Field Theory to complex structure-transport processes in a novel way that resulted in six papers and two presentations, and we implemented Statistical-Temperature Monte Carlo Dynamics, a Monte Carlo Dynamics variant of Wang-Landau inside the Large-Scale Atomic/Molecular Massively Parallel Simulator at SNL.

Members of the research team have had the opportunity to interact in a number of ways with colleagues:

- Two LDRD principal investigators are now on the ORNL Soft Matter Council.
- One LDRD principal investigator has written a proposal for a DOE Early Career Award.
- Researchers have been invited to participate in the Controlled Structural Formation of Soft Matter Workshop at the Kavli Institute for Theoretical Physics, in China.
- Researchers have given invited keynote speeches at conferences of the Materials Research Society (November 2015); the American Chemical Society (August 2015, March 2016, October 2016); and the American Physical Society (March 2016).

Information Shared

Enhanced phase segregation induced by dipolar interactions in polymer blends, Rajeev Kumar, M. Muthukumar, Bobby G. Sumpter, *Macromolecules* **47**, 6491-6502 (2014). DOI: 10.1021/ma501067r

Understanding how processing additives tune nanoscale morphology of high efficiency organic photovoltaic blends: From casting solution to spun-cast thin film, Ming Shao, Jong Kahk Keum, Rajeev Kumar, Jihua Chen, James F. Browning, Wei Chen, Jianhui Hou, Changwoo Do, Kenneth C. Littrell, Sanjib Das, Adam Rondinone, David B. Geohegan, Bobby G. Sumpter, Kai Xiao, *Adv. Func. Mater.* **24**, 6647–6657 (2014). DOI: 10.1002/adfm.201401547

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06840

Pattern Discovery and Predictive Modeling on Heterogeneous Graphs Using Cray's Urika

S.-H. Lim, R. Vatsavai, Sukumar, S. Rangan, S. Powers, K. Ainsworth

Project Description

Pattern discovery and predictive modeling from seemingly related big data represented as massive, ad hoc, heterogeneous networks (e.g., extremely large graphs with complex, possibly unknown structure) is an outstanding problem in many application domains. To address this problem, we propose to design graph-mining algorithms capable of discovering relationship-patterns from such data and using those discovered patterns as features for classification and predictive modeling. Specifically, we propose to (1) explore the statistical properties, mechanics, and generative models of behavior patterns in heterogeneous information networks; (2) develop, implement, and demonstrate novel, automated, and scalable graph-pattern discovery algorithms on Cray's Urika; and (3) apply our relationship-analytics (data science + network science) expertise to a sponsor-advised use case for fraud prevention in the healthcare domain.

Mission Relevance

There is tremendous scientific and strategic potential to leveraging an ultrafast graph retrieval appliance such as Cray's Urika and transforming it into a graph-data inference engine that can be unleashed on terabytes of data hosted by federal departments and agencies such as DOD, DHS, NSF, DARPA, HHS, and NIH. Our federal sponsors in national security are expressing interest through calls for proposals, such as DOD - BAA-AFOSR-2013-0001 and DHS-DHSS-TLRBAA12-07 (RSD 1.1), that are open through 2014. Furthermore, the proposed healthcare use case specifically addresses the requirements of the senior technical advisor, Centers for Medicaid and Children's Health Insurance Program Services, and the acting director, Office of Enterprise Management, at the Center for Medicare and Medicaid Services. The principal investigator (PI) believes that a proof-of-principle demonstration on Urika can make a convincing case toward saving national resources in healthcare in the provider-screening and fraud/waste minimization grand challenges. The PI has also initiated conversations with the Division of Elections Office (Tennessee) toward assisting with data analysis and insights on voter identity fraud issues that surfaced during the election, a problem of national significance.

Results and Accomplishments

In Year 1, we presented benchmarking results that showed that our approach provides at least one order and, in some cases, two orders of magnitude speedup on Urika compared with the performance of modern cloud architectures for doing the same analysis. In Year 2, we extended the benchmarking to different aspects of graph databases, including data loading, pattern search, and pattern mining. In Year 3, we secured a $290 K of follow-on funding with PayPal aligning with this project. We will work with PayPal on distributed graph replication where the source data for the graph is geographically distributed across the globe.

We designed and demonstrated EAGLE (Algorithmic Library for Exploratory Analysis), for the Python programming language. EAGLE implements 25 popular graph-mining algorithms, such as degree distribution, PageRank, and Connected Components, at scale on Cray's Urika. EAGLE is currently being applied to different scientific domains of interest within BES, such as molecular biophysics, quantum computing, genomic-association studies, and to diverse issues in areas such as the electric grid and healthcare. We achieved significant advances to these sciences. (Parts of EAGLE are now available as open-source software at https://github.com/ssrangan/gm-sparql.) We also designed, implemented, and tested a methodology for approximate search using pairwise-similarity approximation on prioritized patterns, developed new algorithms for heterogeneous graph analysis ("diversity-degree" and "path-based-reasoning),"and visualized graphs hosted on Cray's Urika using a browser-based interface that works seamlessly on desktop computers, tablet computers and the ORNL EVEREST (Exploratory Visualization Environment for Research in Science and Technology) facility.

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06917

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

M. (Arjun) Shankar, J. Schryver, J. Nutaro, O. Ozmen, H. Park; S. Kieltyka, G. Weigand

Project Description

A fundamental shift in national healthcare from fee-for-service (FFS) to value-based-purchasing (VBP) is taking place over this and the next decade. The Patient Protection and Affordable Care Act 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. To address the dynamics of this change, we constructed a large-scale high-fidelity model for the constituent actors in the US healthcare ecosystem. The model supports scenario-driven and prospective investigations of cost and quality outcomes regionally and nationally and allows us to anticipate and respond to the challenges of VBP. The large-scale computational model is necessary to expose underlying system behaviors and unintended consequences resulting from new risk structures, and the complex and discontinuous nature of the interactions between the claimants and the providers (e.g., physicians, hospitals). By creating emulated datasets of patient-provider interaction data, we have created a first-in-the-nation large-scale 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 health outcomes, we are creating a valuable resource for tackling a leading national question of our time.

Mission Relevance

It is well known that a significant fraction of the national gross domestic product (about 18%) and a great part of the deficit going forward are attributed to healthcare expenditures. It is less widely recognized that little large-scale systematic computational modeling is done to understand the cost drivers before policies and procedures are put into law. We 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 and, crucially, our ability to do this analysis with healthcare claims situate 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 (HPC) system architecture itself is rapidly changing, with a single system lifetime of only about five years. The trajectories of the source data, computation data, and output data require combined analysis at multiple scales while at the same time accommodating a large, scenario-driven parameter space.

Results and Accomplishments

We have completed a baseline beneficiary property description dataset that acts as the basis for the simulation model. The dataset has 30 million individual beneficiaries represented with demographic characteristics and health characteristics. It has been created by disaggregating into a higher resolution the lower-resolution data obtained from the Health Indicators Warehouse (http://www.healthindicators.gov/).

The behaviors of the beneficiaries are simulated for different environmental parameters to evaluate the overall outcomes and costs of the system. These preliminary simulations in the DEVS (Discrete Event System Specification) simulation framework set the stage for scale-up. The development on scale has been implemented in Repast HPC; detailed modeling has been done in the Repast workstation version. Each of the beneficiaries created in the dataset has an associated behavioral model emulating the chronic disease condition of diabetes. The model is a novel formulation that combines Theory of Planned Behavior and Gene-Meme network message flows. The interventions required for the beneficiaries have been specifically modeled in collaboration with Summit Strategic Solutions.

The execution of the behaviors of simplified versions of the above interactions and the behaviors when simulated show that an agent-based exploration of the parameter space is a critical component of such healthcare simulations.

We have developed the above framework to explore and demonstrate the use of HPC for the healthcare-modeling domain. This is particularly relevant to the ORNL and DOE Exascale mission because it creates a new domain area of HPC simulation that drives a social-simulation-focused programming paradigm and an accompanying software architecture harness. To our knowledge, a design formulation like ours has not been developed for performing these system science computations on an HPC platform. No code with this formulation has run on Titan until now. We have filed associated invention disclosures.

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07339

Application Data Structure Layout and Access Pattern Port Planning for Exascale Memory Architectures

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Project Description

The purpose of this project is to devise a memory-architecture-centric co-design tool for determining how the data structures of parallel applications need to change in layout, redundancy, and distribution for future exascale systems. This will allow reasoning about the performance/energy gains and associated software reengineering costs that will enable the capability to determine which program data, either because of their structure or access pattern, are likely to cause problems or to benefit from a future system and to what extent. We will develop an integrated development environment (IDE) that will operate on three inputs: users' porting expertise, parallel applications' classifiable memory patterns, and memory architecture models. We will explore expressive models to characterize future memory architectures by leveraging GLEIPNIR, our current full-application OLCF memory/simulation tool, and the ORNL ASPEN performance modeling methodology. We will initially target the miniapplications set, which ORNL has recently developed for petascale-to-exascale performance portability studies.

Mission Relevance

It is broadly understood that transition to exascale computing paradigms will require rethinking of how program data are placed and structured on such systems. This has been proven extremely difficult for emergent technologies and is attributed to the coarseness of data modeling in the software engineering methodology. We simply lack the technology that would permit us to take a large piece of computation, often involving complex data structures spanning the entire program scope, and to analyze how these structures should be reorganized for a future memory architecture. We must begin to address this challenge today, while exascale memory architectures are being molded and in need of characteristic and reliable performance models. It is important that we develop the means for capturing, reusing, and revisiting the wealth of information that goes into performance porting so that ORNL applications can embrace the co-design paradigm during these times of ascension to exascale.

Results and Accomplishments

We have demonstrated the foundation of an ecosystem of interoperable tools for co-design specifically targeting memory systems for current and future (exascale) platforms. At the heart of this ecosystem are the ASPEN performance modeling tool and memory system simulators, such as DRAMsim2. Models for computational kernels can be specified in the ASPEN modeling language, and they can be composed into more complex models if desired. ASPEN can generate synthetic memory traces from the kernels that have been validated against actual memory traces from an equivalent "real" implementation of the kernel, written in C, for example. The validation is a notable result of this work. The validation methodology involved collecting memory traces by executing the real kernel implementation in a full-system simulator, such as GEM5. In addition to direct comparison of the actual and synthetic memory traces, we were able to analyze and compare certain statistics on the memory access patterns. In the actual memory traces, care must be taken to isolate those references belonging to variables of interest in the kernel. Real memory traces contain many additional references, such a loop indices and most scalar data, that are not generated by the ASPEN model.

The synthetic memory trace can then be run through one of the existing memory simulator tools, which provide the ability to simulate a variety of current and hypothetical memory systems. We are also working towards the capability to generate C code (or any other programming language) that can execute memory access patterns following the trace on real hardware. In order to generate and edit ASPEN kernels quickly and easily, we created an IDE for the ASPEN modeling language, based on the widely-used Eclipse platform. Additionally, other work (not part of this LDRD project) aims at being able to generate ASPEN kernel models automatically from real code, via a compiler-based tool. These capabilities contribute to the flexibility and extensibility of the developing ecosystem.

Once the appropriate tools are in place, users can easily manipulate ASPEN kernels representing key portions of their application, and they can use appropriate memory simulators to model their performance on different memory architectures. Users can easily alter kernels to carry out performance experiments on different memory architectures in order to understand how to obtain the most portable results and how to tune for specific architectures.

Information Shared

No information shared in FY 2016

07347

CloneX: Discrete Event Cloning at Exascale

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Project Description

To overcome the challenges with respect to concurrency and memory in achieving exascale computing, we have undertaken the design, development, and implementation of a novel technique of large-scale, transparent, and optimized "cloning," which efficiently and dynamically creates whole logical copies of simulations without full physical duplication. In this project we developed the conceptual framework, the algorithmic foundations, and a prototype interface with implementation of runtime system scaling to thousands of graphical processing units (GPUs) together containing hundreds of thousands of processor cores, and we tested the entire technology with example applications in which aggregate concurrency and memory needs are improved by two to three orders of magnitude. Our work (1) demonstrated a novel way to exploit exascale computing capability for a range of applications that fall short in scaling potential to exascale in the traditional sense, (2) showed a reduction of two to three orders of magnitude in aggregate memory requirement, (3) demonstrated a naturally effective fault-tolerant mode of cloning, and (4) delivered an optimized and scalable cloning runtime system suitable for multiple applications.

Mission Relevance

The CloneX effort directly advances DOE's current thrust in exascale computing. By dramatically improving the memory and speed gains of very large parallel simulations, the effort benefits multiple

DOE programs, including climate change science, material design, and biochemical sciences. The envisioned improvements in large-scale simulation technology can also cut down the total energy used by computations on the next generation of supercomputing machines by an order of magnitude.

Results and Accomplishments

We developed a runtime cloning engine for spawning clones in two-dimensional models; four application benchmark models; software implementation ported to Titan; a detailed performance study, which scales to 1,024 GPUs; and demonstration of scenarios in which computation and memory savings have delivered speedup and memory savings of more than two orders of magnitude (102.5×) compared to traditional ensembles.

The core runtime cloning engine, CloneX-GPU, can span a large number of GPUs and automatically redistribute clones across memories. The development of a full, multilevel, multibranching cloning interface and implementation has been completed. The code is written in CUDA and C++/MPI. We also successfully ported it to Titan, ran many-GPU experiments, and achieved speedup of more than two orders of magnitude. A new load-balancing algorithm synchronizes across all GPUs and assigns new clones to processors by taking into account the weights of the clones at each processor. Arbitrary levels of branching (k) and branching factors (m) are fully supported on the GPUs. Large values for k and m have been exercised (k up to 10, m up to 6, giving a few millions of ensemble scenarios) with the ability to simulate thousands of more simulations than possible by traditional ensembles.

We developed four different application kernels amenable to cloning: heat diffusion model, transportation network model, forest fire model, and earthquake model. We also developed a functional animation capability in an interactive cloning software tool that can be used for batch-driven simulations with animation and also for user-driven, "what-if" scenarios to clone instances on the fly.

To support looking up clones dynamically on the GPU for every logical to physical address mapping, we implemented one of the fastest index search algorithms published in the literature. This algorithm, called GART, for GPU-based Adaptive Radix Tree, has been integrated and used within the GPU kernel of the applications to pull data from ancestors within the clone tree. Our implementation is capable of 880 million lookup operations per second on a single GPU.

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07409

In Situ Multiscale Visual Analytics for Transformative Extreme-Scale Science

C.A. Steed, S. Atchley, D. Wang, J. Daniel, J. Beaver, Y. Pei, B. Hernandez Arreguin, W. Halsey

Project Description

The traditional approach to scientific simulation analysis is to store data to disk, initiate prolonged transfers, and analyze reduced samples later, disconnected from leadership-class platforms. This process can take years to yield scientific insight and thus can delay discoveries. When subjected to the data scales and energy efficiency constraints of future exascale platforms, the present approach will altogether fail and will paralyze scientific discovery. The goal of this project is to address these important issues by developing an extreme-scale visual analytics framework for interactive, multiscale, and energy-efficient computational science in situ. Novel analytics will execute in parallel with simulation processes, enabling real-time analysis via new asynchronous models of computation. By intelligently processing, monitoring, and indexing simulation results, the algorithms will extract and preserve salient features that characterize the simulated processes and that expose high-performance computing system status. New level-of-detail models will allow interactive, multiscale visualization and analysis for in situ and postprocess scenarios. The resulting framework will be evaluated with climate experts on leadership-class platforms. Successful completion of the proposed research will allow efficient and efficacious intervention in the simulation process by increasing efficiency, reducing knowledge discovery time cycles from months to weeks, and significantly increasing transformative scientific output.

Mission Relevance

The importance of this research project is confirmed by recent calls for in situ analysis capabilities and extreme-scale visual analytics in recent DOE future challenges reports. Despite these calls, recently initiated DOE ASCR in situ analysis and visualization research primarily focuses on data management and parallel performance, not exploratory data analysis and integrating human interactions. Furthermore, with ORNL leading the development of next-generation climate simulation software (e.g., the BER-funded ACME project) while preparing for the installation of new pre-exascale supercomputers (e.g., Summit), now is the time to begin developing the interactive analytic capabilities proposed in this project. This initial investment in extreme-scale visual analytics at ORNL has helped establish a highly marketable research program, which opens the door to new research funding from DOE, NOAA, DHS, DOD, NGA, and industry.

Results and Accomplishments

The research funded by this LDRD has resulted a new data management framework that harnesses the computational power of extreme-scale computing, distributed communication toolkits, and unique large-scale data analysis resources to provide dynamic memory access of simulation results on OLCF platforms—key capabilities for the future exascale computing era. We have developed a new in situ data management framework for efficiently transferring simulation memory to a remote target node for subsequent analysis. In addition, while developing this framework, we made fundamental algorithmic and policy contributions to the science of in situ data management. This framework has been connected to the DOE ACME Land Model on OLCF platforms and has been demonstrated in real climate science scenarios. New visual analytics tools were developed for both temporal and statistical multivariate data analyses. One visual analytics tool, called Falcon, was designed for human-centered exploratory data analysis of large and complex time series data streams. The other visual analytics tool, called EDENx, was developed to provide multiple views at different levels of detail for large multivariate datasets. These new algorithms and systems have become significant components in new DOE proposals and projects at ORNL. Both tools have been demonstrated in climate and additive-manufacturing data analysis scenarios. Two invention disclosures and one open source software license have been filed on the framework. Ten publications based on this LDRD research have been published or accepted for publication, and 2 other manuscripts are under review. Seven students have participated in the project.

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07417

Algorithms for Context-Specific Analysis of Heterogeneous Unstructured Big Health Data

G. Tourassi, R. Sukumar, A. Ramanathan, C. Steed

Project Description

High-dimensional, multimodal, unstructured data pose significant visual and computational analytic challenges. Data-driven knowledge discovery is impeded when domain experts limit their attention to data subsets because they are overwhelmed with data volume and complexity. In medicine, for example, mining heterogeneous data such as patients' genome sequences, images, and sensor data in context with prior history for clinical decision support is an outstanding problem. The problem is complex because of the volume (e.g., genome sequences are several gigabytes/person, image databases on the order of terabytes) and the variety of the data. For some emerging problems, data variety poses a greater challenge than data volume. To address those problems, we are proposing (1) a data-organizing framework to discover and store associations across transdisciplinary unstructured datasets; (2) scalable in-memory methods for multimodality similarity discovery; and (3) an informative, context-adaptive display to explore, prioritize, and visualize recommendations of relevant associations that would have otherwise overwhelmed the human perceptual and cognitive bandwidths. This framework will show proof of principle for health data, enabling an order-of-magnitude improvement in processing time and informative visualization while integrating and analyzing multimodal, complex health data. The underlying scientific principles for data organization, association, and knowledge discovery will extend to other application domains beyond medicine.

Mission Relevance

In 2012 the White House launched the Big Data R&D initiative with six federal departments and agencies (DOE, HHS/NIH, DOD/DARPA, NSF, USGS) committing $300 million for the development of tools and techniques to access, organize, and glean discoveries from huge volumes of data. The technology developed in this project addresses directly the integration, context-driven analysis, and informative visualization of complex big data in health. The capability supports the National Strategic Computing Initiative, announced by the White House in 2015; the Precision Medicine Initiative, announced by NIH; and the Cancer Moonshot Initiative, announced by the White House in January 2016. The proposal is directly relevant to ORNL's mission on exascale computing, data infrastructure, and analytics at scale for science missions.

Results and Accomplishments

The overarching objective of this proposal is to develop a scalable, interactive analytic and visualization platform for exascale data, integrating highly heterogeneous health data at multiple spatial and temporal scales (from genotype to phenotype). The proposal has four main tasks: (1) identify optimal query models for heterogeneous data; (2) develop a scalable data organization framework to make domain-specific associations; (3) develop inference algorithms for multimodal, multitask learning (MTL); and (4) develop visual analytics approaches to enable context-specific navigation. The FY 2016 focus is on tasks 3 and 4. First, we developed a scalable MTL framework for classification of heterogeneous biomedical data. Specifically, we implemented two scalable MTL algorithms, one version, which is specifically suited for distributed processing using the Apache Spark framework and the other version, which uses the Theano Deep Learning package for processing using general-purpose/graphical-processing-unit engines. We performed clinical validation and scalability benchmarking experiments using a large corpus of unstructured text data from pathology reports for two and three relevant information extraction tasks, namely inference of primary cancer site, laterality, and histological grade. For Task 4, we developed a data visualization and navigation framework for large-scale biomedical text data. We conducted interface-efficiency experiments for seamlessly navigating between the "feature" space and the "data" space using the same corpus of pathology text reports that were used for Task 3. The framework allows navigation, dynamic keyword statistics aggregation, and analysis of pathology reports and annotations based on conventional natural language concepts.

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07475

Extreme Scale Analytics for Near Real-Time Information Extraction in Multimodal Data

M. Shankar, R. Archibald, A. Belianinov, A. Borisevich, E. Endeve, S. Kalinin, E. Lingerfelt, O. Ovchinnikov, C. Symons

Project Description

We develop a framework composed of scalable mathematical algorithms, scalable machine learning algorithms, and simulation-based analysis for near real-time information extraction from data generated from multiple high-throughput modalities (multiple experiments and simulations). Near real-time information extraction from multimodal data is required for timely feedback to optimize experimental resources when researchers have a limited time window at a facility, as is often the case at DOE scientific facilities. Scalable algorithms that can utilize high performance computing platforms are required to efficiently analyze and explore the large complex datasets these facilities generate for timely feedback and to support high throughput experiments. This is currently not being done, only single source analysis is available and even in this case, it is often dependent on human visual inspection of the data, manual data processing, and manual fitting of the data to models for information extraction. To guide the development of this framework we partner with the Center for Nanophase Materials Science (CNMS) to provide high performance computational science discovery from multimodal data with an initial focus on high-veracity microscopic imaging of ferroic oxide materials. The work ties together for the first time

ORNL's strengths in computational and data science, high-resolution electron and probe microscopy imaging, and advanced atomistic theory, positioning it to take advantage of new materials genomic, imaging, and data science initiatives.

Mission Relevance

The advancement of high-resolution real-space imaging techniques such as (Scanning) Transmission Electron Microscopy (STEM), Scanning Tunneling Microscopy (STM), and Non-contact Atomic Force Microscopy has created a significant data challenge for scientists that wish to utilize these instruments to understand complex materials such as ferroics. These materials are key objects of study in condensed matter physics due to the wide range of properties they exhibit, which consequently make them difficult to analyze because of their inherit spatial complexity. This brings an opportunity to address this challenge through the creation of new mathematical algorithms for image processing, machine learning techniques suitable for feature extraction in high dimensional space, and analysis of complex physical dynamics via large-scale simulation. Effective analysis of this multimodal high dimensional data has the promise of answering DOE Grand Challenge Scientific questions concerning fundamental physical models describing ferroics. While initially targeted towards CNMS, the creation of the framework proposed holds the promise of enabling equally significant breakthroughs across DOE.

Results and Accomplishments

1. Image reconstruction and registration – Image reconstruction pipeline has been created on the STEM images. The conversion to HDF5 scripts for the large data sets has been performed.

2. Feature extraction and co-regularization – We have prototyped and performed a preliminary evaluation of scalable data analysis routines on ORNL's Compute and Data Environment for Science (CADES) infrastructure using Hadoop technologies. We have carried this out on CNMS input data and evaluated the preliminary performance improvements on CADES infrastructure. New scaling of analytics algorithms have been brought to the CNMS analytics suites.

3. Automation of Data Analysis Workflow & Management – *We have successfully automated cross-facility on-demand workflows that ingest data from the IFIM devices and processing them in the CADES environments.* We have demonstrated this capability through mapping the overall workflow to in-progress analytics. The data is being uploaded and transferred to CADES.

4. We have shown how to "burst" the analytics from CADES to the DOE HPC cloud. Specifically, we are able to run on Titan, thus instantiating an end-to-end workflow: STEM to CADES to Titan and other ASCR facilities and back to the end-users.

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08231

Deep-Learning-Enabled Clinical Cancer Surveillance for Exascale Computing

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Project Description

One of the key goals of the Precision Medicine Initiative (PMI), which was announced recently by President Obama, is to build reliable predictive models that can support specific treatment choices based on a patient's genetic, clinical, lifestyle, and/or environmental factors. Especially in the context of cancer, the need for such predictive models is urgent because, even with significant scientific discoveries in the last decade following the Human Genome Project, clinical translation of such discoveries to patient-specific treatment options remains challenging. A key stumbling block in building these predictive models is the lack of effective population-wide surveillance of cancer across the country. In particular, effective clinical surveillance of cancer requires integration of heterogeneous datasets, including multiple-source, panomics datasets (e.g., molecular/gene, cellular, tissue/organ-specific, patient-level), and deep analytic techniques that can identify complex genetic, lifestyle, and environmental factors that play a role in patient-specific cancer etiology. Our deep-learning enabled clinical cancer surveillance (DECCS) project will address this challenge. We will develop the essential algorithms and computational tools targeted at exascale computing to make PMI a reality within clinical cancer surveillance. In particular, we will (1) prototype a scalable deep-learning toolkit for automated text comprehension and analytics from a large sample of heterogeneous clinical reports and (2) develop scalable in-memory/in situ data analytic workflows for quantifying population-level cancer outcomes. Together, the two parts of our project will pave the way for the design and development of advanced computational and informatics solutions needed for a comprehensive, scalable, and cost-effective cancer surveillance program across the nation.

Mission Relevance

The National Strategic Computing Initiative promotes a "whole-of-government" approach to applying the unique national computing capabilities at DOE to transforming how a partner agency executes its mission. DOE is exploring a joint partnership with the NIH NCI to develop exascale-ready tools, algorithms, and capabilities to enable precision medicine for cancer in a program called "Predictive Oncology." This supports the PMI. DOE's efforts will focus on co-design research that will be coordinated with parallel efforts by the NCI to develop the field of predictive oncology. In data sciences, efforts will include work on scalable population health data integration and analysis to enable a large-scale, comprehensive cancer surveillance program in the United States.

Results and Accomplishments

DECCS is an off-cycle LDRD proposal whose overarching objective is to instantiate scalable deep-learning networks for deep comprehension and information extraction from unstructured text data. The proposal has two main objectives: (1) develop scalable deep-learning tools for automatic text comprehension and (2) benchmark the performance of these tools on the ORNL Titan supercomputer. Working toward these objectives, first we ported existing deep-learning packages such as Theano, Neon, and Torch on Titan. Then, we performed a series of benchmarked tests for various information extraction tasks from a large corpus of pathology reports provided by our collaborators at NCI. Specifically, we implemented convolutional neural networks and multiple-task deep neural networks for two and three information extraction tasks and benchmarked their classification accuracy by comparing it with the accuracy of conventional machine-learning algorithms (Naïve Bayes, Logistic Regression, Support Vector Machines, Random Forests) and text representation algorithms (n-grams, CHUNK, RAKE). To evaluate scalability, we performed experiments on Titan with the Torch Deep Learning package. The experiments demonstrated that the runs that we conducted were at least four times faster than would be possible on traditional computer clusters.

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DISCOVERY SCIENCE AND INNOVATION

07319

Quantum Key Distribution in Conventional Optical Fiber Networks Using Untrusted Devices

B. Qi, M. Bobrek, W. Grice, P. Lougovski, R. Pooser, C. Lim, P. Evans

Project Description

In principle, quantum key distribution (QKD) can provide unconditionally secure cryptographic keys and thus can greatly enhance cyber security. However, the high cost associated with conventional discrete-variable (DV) QKD, especially the requirement of a dedicated dark fiber, limits its applications in practice. Furthermore, imperfections in QKD implementations can lead to side-channel attacks and thus can compromise their security. We propose to remove the above roadblocks on the path to wide application of QKD by developing a continuous-variable (CV) QKD system based on a novel optical coherent detection scheme with a “locally” generated local oscillator, which can greatly simplify the QKD design and close security loopholes. This protocol will significantly reduce the cost of QKD by allowing multiple QKD channels to share the same optical fiber with classical communication channels, thereby removing the requirement for a dedicated dark fiber. It will also open the door to a CV version of the recently discovered measurement-device-independent (MDI) QKD, which allows secure QKD using untrusted measurement devices. To implement the proposed protocol, we will develop a novel shot-noise-limited optical coherent receiver, where the local oscillator and the signal to be measured are generated from independent laser sources. The output of this project is a highly secure, low-cost QKD system compatible with existing optical fiber networks. We expect that the technologies developed in this project will greatly improve the long-term cyber security of important utilities and infrastructures in the United States.

Mission Relevance

There is a growing interest within both government agencies and industry in secure communication based on quantum cryptography. The global quantum cryptography market is projected to reach $1.0 billion by 2018, driven by the need to secure the transmission of sensitive communications. The output of this project is a novel CV QKD system that is compatible with existing optical fiber networks. It will significantly reduce the cost of QKD by removing the requirement for dedicated dark fibers. In addition, it will open the door to a CV version of the recently discovered MDI QKD, which is automatically immune to all detector side-channel attacks (the most dangerous attacks in practice). The proposed project provides an economical solution for sustainable improvements in reliability and resiliency of cybersecurity for critical infrastructure. It is well aligned with primary missions of DOE OE and the DHS Cyber Security Division’s Control System Security Program.

Results and Accomplishments

One existing challenge in CV QKD is how to generate the local oscillator used in coherent detection locally using an independent laser source at the receiver's end. Such a scheme is highly desirable because it can significantly enhance the security and efficiency of CV QKD while greatly simplifying its implementation. In FY2015, we solved this long-standing problem in CV QKD by demonstrating a novel pilot-aided feed-forward data recovery scheme, which is in the heart of our LDRD proposal. Using two independent commercial laser sources operated in free-running mode and a 25 km spool of optical fiber, we constructed a coherent communication system and successfully demonstrated reliable coherent detection without transmitting a strong local oscillator. We also developed a broadband shot-noise-limited homodyne detector, a crucial component in CV QKD. The prototype that we developed has a bandwidth of 50 MHz and shows an extremely low noise level. We also studied commercial balanced photodetectors and explored methods to further improve their performance. We performed numerical simulations of various secret key reconciliation techniques and developed the reconciliation procedures for our project. A field-programmable-gate-array–based electronic system for sampling data, estimating phase, recovering data, and interfacing with a computer has been designed and is under development. We also conducted theoretical research on position-based quantum cryptography, a scheme that allows a legitimate party to use its geographical location as its only credential to implement various cryptographic protocols. We also investigated security loopholes in the detector-device-independent QKD, which had been proposed recently as a simplified implementation of MDI QKD. In FY2016, we developed a rigorous security proof of CV QKD based on the locally generated local oscillator idea and built a protocol-type CV QKD system. The whole system is built upon commercially available telecom devices. We investigated various practical issues, including polarization feedback control and high-extinction-ratio laser pulse generation. One unexpected discovery is a novel coherent communication protocol, which could allow us to do deterministic classical communication and QKD on the same communication system. This protocol opens the door to repurpose a classical coherent communication system for QKD, thus significantly reducing the corresponding cost. We also conducted theoretical studies on both the CV MDI QKD and the DV MDI QKD. Our conclusion is that the DV MDI QKD provides an ideal solution for building up a local QKD network.

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07329

National Extreme Events Data and Research Center (NEED) – Transforming the National Capability for Resilience to Extreme Weather and Climate Events

D. Kaiser, T. Wilbanks, T. Karnowski, S. Ostro, R. Devarakonda, R. Vatsavai, T. Jiang, S.-C. Kao, M. Allen, M. Ashfaq, K. Evans, T. Boden, J. Gulledge

Project Description

The ORNL Climate Change Science Institute (CCSI) will implement the National Extreme Events Data and Research Center (NEED), a novel concept to transform how the United States studies and prepares for extreme weather events in the context of a changing climate—with the goal of positioning ORNL-NEED as the home within DOE and the federal government for integrated research and tool development for resilience to climate- and weather-related extreme events. The two main components of the project are (1) development of the Weather and Climate Extremes Portal (climate-extremes.ornl.gov) to enable discovery and application of scientific knowledge on historical and projected extreme weather and climate events of all types for a wide range of stakeholders and (2) characterization of relationships between extreme upper-atmospheric ridges (poleward excursions of the jet stream) and extremes at the surface (such as heat waves) through basic and applied research that leverages ORNL's climate analysis, modeling, and computing expertise, coupled with the expertise in weather extremes of colleagues in the operational weather-forecasting field.

Mission Relevance

This project advances ORNL's strategy in basic sciences and thrust areas (earth and atmospheric sciences, high-performance computing, energy, and national security) by using an interdisciplinary approach to address a scientific problem of national and global importance—the prediction and management of extreme weather events and the impact of climate change on them. The unusual series of climate- and weather-related disasters in the United States in the early 2000s has focused attention on improving the nation's capacity to predict and cope with such events, and DOE has devoted significant attention to their impacts on energy systems. Presently, data, assessments, and research findings for weather and climate extremes are found across many federal, intergovernmental, and university web sites. The Extremes Portal will consolidate critical historical and projected extremes data and information in one place, enabling easier discovery and application. It will also provide a means for a focused and sustained assessment process that would be an asset as a component of the US Global Change Research Program (USGCRP).

Results and Accomplishments

We developed and launched the ORNL Weather and Climate Extremes Portal (climate-extremes.ornl.gov), a valuable resource for many types of stakeholders that will also serve as home for climate extremes data and research assembled by the CCSI. Through collaboration with NOAA, DOE, and USGCRP extremes scientists, we are exploring the possibility that the portal can play an important role in a sustained assessment process on extremes under the National Climate Assessment. In the extremes research area, we conducted a detailed analysis of how extreme upper-atmosphere ridges have been changing over recent decades, and we developed the ridge anomaly index (RAI), a new metric that captures several features of ridges that weather forecasters use to estimate chances of extreme weather events. The RAI has been trending upward over the past few decades. Our formal detection and attribution analysis indicates that this trend results from anthropogenic greenhouse gas emissions, and future work in this area needs to look for possible causative relationships between RAI and various extremes at the surface. An interesting aspect of this research effort is that it brought together an interdisciplinary team: ORNL climate scientists, ORNL signal-processing engineers, and a senior meteorologist from The Weather Channel, with one of the main goals being to bridge gaps in the perception of climate change between climate scientists and weather forecasters.

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07393

Quantum-Enhanced Plasmonic Ultra-Trace Sensors

R. Pooser, B. Lawrie, P. Evans, C. Britton, A. Marino

Project Description

Surface plasmon resonance (SPR) devices are currently used as sensors used as sensors by governmental agencies for the detection of chemicals (e.g., for nuclear nonproliferation) and biological agents. SPR sensors based on extraordinary optical transmission measure small changes in the optical transmission through nanohole arrays when a substance binds to probe molecules on the surface. State-of-the-art SPR sensors demonstrate a detection limit (determined by the combined sensitivity and noise floor) of 10^{-9} refractive index units (attomolar concentrations), but nonproliferation agencies have identified the need for smaller detectable concentrations and faster acquisition times. Unfortunately, no further improvement to the noise floor is possible using classical readout light sources. We propose to improve the fundamental limits of detection by at least two orders of magnitude for SPR sensors by (1) utilizing quantum-noise reduction in the readout light source and (2) designing and fabricating nanostructures that exhibit highly efficient optical coupling, exceeding 90%. This two-pronged approach will result in sensors with detection limits of zepto-molar concentrations, at least two orders of magnitude higher sensitivity than the state of the art. This work will yield a new capability for ORNL: a quantum sensor program meeting global security needs for advanced sensors with unprecedented detection capabilities.

Mission Relevance

This work supports the ORNL national security mission through counterproliferation. Advanced sensors are needed for future arms control and treaty verification, and this project provides such sensors. Further, a national need has been identified in the area of coupling optical modes carrying quantum information into nanostructures. This project directly addresses that need by improving the efficiency of coupling of quantum light sources to nanoscale structures.

Results and Accomplishments

We achieved the first goal with our collaborator at the University of Oklahoma. Our quantum noise reduction deliverable was 9 dB below the shot noise. To meet our second goal, we undertook a multipart effort in nanoscale fabrication: to model nanostructure geometries, determine suitable commercial coatings, and fabricate plasmonic devices that exhibit extraordinary optical transmission. We developed a new approach to nanofabrication at the Center for Nanophase Materials Sciences (CNMS) in which free-standing nanostructures are fabricated that have most of the substrate below the patterned metallic films removed. We also modeled several candidate nanostructures with increased transmission and narrowed features. Using nanohole arrays fabricated at CNMS, we demonstrated transmission of entangled states of light into multimode plasmons that were located on completely independent substrates, separated by tens of centimeters, producing the first long-range, continuous variable quantum plasmonic network. The device can be used for subdiffraction imaging of analytes.

Continuing work with the SPR sensor, we demonstrated the first quantum sensor that beats the state of the art in ubiquitous classical sensors. We applied calibrated optical oils to the SPR sensor to directly detect a local shift in index of refraction using a modulation format to eliminate low-frequency noise, followed by quantum noise reduction to reduce the noise floor to a point below the shot noise for every measurement. The sensor is highly responsive in the low-index-shift regime, precisely the area of interest for trace detection. This sensor improves drastically on our previous device because it provides a true quantum-noise-limited signal with sub-shot-noise resolution at all points, a first for any plasmonic sensor. We also implemented an interferometric plasmonic sensor, which has a higher signal-to-noise ratio (SNR) than intensity-based devices. Our implementation used a nonlinear interferometer, which uses nonlinear amplification to achieve a higher SNR on the phase shift signal than classical interferometers. We applied this interferometer to a sensor employing extraordinary optical transmission to detect shifts in index of refraction as a function of glycerin concentration. We also added an additional innovation that includes a naturally stable implementation and radio-frequency modulation to serve as the signal field.

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07398

Nonlinear Nanophotonics with Ultrastrong Plasmonic Coupling

B.J. Lawrie, R.C. Pooser, Y. Ma, P. Lougovski

Project Description

Broadband, ultrahigh-efficiency optical nonlinearities enabling frequency conversion, squeezed-state generation, and the optical Kerr effect are critical to applications in quantum information science, solar energy conversion, and optical information processing. In cavity quantum electrodynamics (CQED), strong coupling between quantum emitters such as quantum dots and dye molecules and microcavities enables high-efficiency nonlinearities, even at single-photon levels, that are unobtainable with nonlinear crystals. Unfortunately, their nonlinearities cannot be frequency-tuned, they require ultrahigh vacuum and low temperatures, and the small microcavity line widths necessary to achieve strong coupling result in long interaction times, making practical microcavity nonlinearities difficult to implement. Plasmonic structures confine light in nanoscale mode volumes that dramatically increase atomic coupling efficiencies and enable CQED-like effects when hybridized with quantum emitters. By deterministically placing quantum emitters in plasmonic structures exhibiting nanoscale field confinement, we propose to demonstrate optical nonlinearities that enable next-generation quantum information processing, telecommunications, and solar energy conversion with (1) nonlinear efficiency that is four orders of magnitude greater than that of nonlinear crystals (quantum-limited efficiency is possible in principle), (2) frequency tuning that exceeds 100 THz (typical microcavities operate in the range of megahertz to gigahertz), and (3) a nanoscale footprint and operability at room temperature and ambient pressure.

Mission Relevance

Research in quantum computation and quantum key distribution directly addresses ORNL's strong interests in cyber security. Both fields rely on efficient nonlinearities to support quantum repeaters and quantum gates, but traditional nonlinear materials demonstrate nonlinear efficiencies at 5 to 10 orders of magnitude below unity at the single-photon level. The high-impact fundamental science described in this proposal would culminate with the demonstration of nanostructures demonstrating near-unity nonlinear efficiency at the single-photon level, an enabling technology for next-generation integrated quantum information science. This research would support the training of a graduate student in nanofabrication and nonlinear optics and would provide the framework for follow-on funding from a program on nanoscale coupling to quantum emitters that is expected from the intelligence community in the near future. In addition, these efforts toward harnessing coherence in light and matter constitute a BES grand challenge topic.

Results and Accomplishments

A quantum master equation developed in conjunction with finite difference time domain (FDTD) models of plasmonic resonators fabricated at the Center for Nanophase Materials Sciences (CNMS) was used to describe the viability of strong plasmon emitter coupling in the single-emitter regime. The FDTD simulations were used to classically describe the local density of states of the plasmonic nanoresonator as the imaginary part of the Green's function, and the mode volume was calculated with quasinormal mode techniques. By integrating these classical electromagnetic simulations into the quantum master equation, we demonstrated that experimentally accessible plasmonic heterostructures are capable of exhibiting strong coupling at room temperature at the single-emitter scale.

A CNMS user proposal written to enable the nanofabrication of plasmonic resonators and metasurfaces for this LDRD is supported for the period of February 1, 2015, through January 31, 2017. Nanoresonators designed to achieve a maximal ratio of quality factor to mode volume were patterned at CNMS with designs guided by finite difference time domain simulations. After strong coupling was demonstrated between aluminum split-ring resonators and CdS quantum dots, it was determined that cathodoluminescence spectroscopy in a scanning transmission electron microscope (STEM-CL) offered the most direct route to probing single-emitter/single-plasmon coupling energetics. To that end, a VG601 STEM was used to characterize the cathodoluminescence of nitrogen vacancy (NV) centers in diamond nanoparticles deposited on single-crystal Ag nanopillars. The coupled nanostructures were patterned on freestanding SiN_x membranes developed via a multilayer lithography process at CNMS. In order to understand the quantum coherent dynamics of the coupled diamond/Ag heterostructure, Hanbury Brown Twiss interferometry was performed on the cathodoluminescence collected after electron-beam excitation in the VG601. The photon statistics of the coupled system demonstrated electron shelving in a dark state that is inaccessible to optical driving fields. Furthermore, these results provided the first evidence of plasmonic control over photon statistics in CL spectroscopy. Notably, this response was maintained in a phonon-broadened emission over a bandwidth spanning more than 100 nm. These results were the cornerstone of Roderick Davidson's PhD defense at Vanderbilt University on October 24, 2016, after two years of work on the LDRD through the Graduate Opportunities program. Multiple manuscripts are currently in preparation describing the effects described above.

Serrated Au metasurfaces were also developed in order to demonstrate the viability of cross-polarized ultrafast pulses for ultrafast switching of nonlinear plasmonic materials. Those results were published in *ACS Photonics*.

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08488

High-Purity, Enriched-Isotope, Chemistry, Purification and Characterization of Semiconductor Gases

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Project Description

The goal of this project is to address chemical transformation and purification challenges associated with fluorinated chemicals used as feed gases in gas centrifuges that enrich selected isotopes relative to their natural isotopic abundance. The chemicals of interest are used in R&D projects to fabricate electronic devices with novel properties and improved performance. The first challenge addressed by this project included the chemistry and reaction parameters needed to convert the enriched fluorinated feedstock material (e.g., silicon tetrafluoride [SiF_4]), to an equivalent hydride (e.g., silane [SiH_4]) with high yield while avoiding production of undesirable by-products such as methane. This project task produced approximately. 100 g of crude silane enriched in the ^{28}Si isotope. The next challenge addressed by this project was to develop a prototype purification system based on chemically selective, gas-permeable membranes and to make measurements of relative permeability of a number of contaminant gases (e.g., methane) vs. the major gas (silane).

Mission Relevance

Interest in utilizing materials enriched in the ^{28}Si isotope for specialized electronics development has increased over the last several years. The results of this project will enable ORNL to leverage its expertise in isotope enrichment technology funded by DOE-NP to address production of R&D materials (e.g., isotopically enriched silane) for a variety of electronics development projects. The data, methods, and equipment produced by this project may also be used for purification of feed gas for germanium isotope enrichment, which is of interest to other DOE–SC programs, such as the MAJORANA project, which will require large quantities of ultrapure and isotopically enriched ^{76}Ge for use in detectors. Germanium tetrafluoride (GeF_4) is the feed gas used to enrich germanium isotopes in gas centrifuges, so much of the effort devoted to silane purification will also be applicable to conversion of GeF_4 to germane (GeH_4) and to germane purification.

Results and Accomplishments

The conversion chemistry task successfully converted approximately 100 g of crude silane from an isotopically enriched $^{28}SiF_4$ sample; methane contamination was reduced to part-per-million levels in the conversion reactor sample. The second task, to build and test an ORNL-designed membrane-based purification system prototype, was successful, and data from several gas mixtures, including silane and methane as components, was produced. Two membrane materials in particular were studied, PDMS and a fluorinated membrane obtained from a commercial vendor. The proof-of-concept results obtained from the prototype included permeability measurement for silane and methane. The separation factor calculated from results obtained for one membrane, polydimethylsiloxane (PDMS), compared well with a previously published result, thus validating the membrane cell design, process methodology, and measurements. This prototype and associated data established proof of concept for this gas purification approach.

The data, along with a mathematical model for the separation based on analytical analysis, will provide the basis for a system capable of depleting contamination in silane to "electronics grade" levels. A third task included in this project resulted in significant improvements to ORNL's analytical gas characterization capability, including an improved gas-chromatography method for analytical measurement of silane, methane, and SiF_4 gases; the procurement of a high-resolution Fourier transform infrared spectrometer and long-path-length gas cells capable of part-per-billion detection of contaminant gases in silane; and a round-robin validation study with an external laboratory to validate the ability of the ORNL analytical laboratory to issue certificates of analysis for trace metal impurities in silane.

Three significant advantages of the ORNL-designed system are (1) a small-dead-volume closed-loop system to minimize losses of highly expensive, isotopically enriched, feed gas; (2) a higher separation factor for a methane/silane mixture compared to other published work for the PDMS membrane; and (3) an easily interchangeable membrane design that enables several different membranes with different properties to be studied and incorporated into a scaled-up production system.

Information Shared

Valmor de Almeida, et. al. 2016, "Analysis of Gas Membrane Ultra-High Purification of Small Quantities of Mono-Isotopic Silane", J. Membrane Sci., submitted.

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Briefings with DOE Office of Nuclear Physics during August and September have resulted in a $100K FY17 project to continue investigation of membrane materials for electronics gas purification.

INTEGRATED ENERGY SYSTEMS

07457

Off-Grid Building Management Systems

R. Jackson, S. Curran, A.M. Momen, I. V. Vlassiouk, I. Sharma

Project Description

Three primary physical systems must be integrated to achieve an effective and resilient off-grid building (OGB): energy generation, energy storage, and building energy demand. In addition, to achieve cost competitiveness, ensure required performance criteria, and maintain system constraints, the three physical systems must be optimally integrated and dynamically managed. The optimal solution must consider uncertainty while meeting occupant demand on hourly, daily, monthly, and yearly bases. An integrated approach was taken in this project to meet the challenge of developing a resilient OGB. The project was broken down into three tasks that were addresses by four subtasks:

- Develop advanced generation and storage systems to demonstrate new technologies that can enable cost-effective OGBs.
  - Subtask 1: Determine the best choice for flexible energy generation.
  - Subtask 2: Optimize ground-level integrated diverse energy storage (GLIDES) for buildings.
- Utilize a use-inspired approach to understand the science needed to make transformative breakthroughs in energy storage.
  - Subtask 3: Develop atomically thin, two-dimensional capacitors based on graphene and hexagonal boron nitride (hBN) monolayers.
- Develop an OGB management system to optimally integrate and manage the building load, distributed generation, and required energy storage.
  - Subtask 4: Develop an integrated management system for OGBs.

Mission Relevance

This research is aligned with the DOE EERE mission to develop and deliver market-driven solutions for energy-saving homes, buildings, and manufacturing; sustainable transportation; and renewable electricity generation. The proposed research will enable the optimal performance of a built environment that requires less energy to operate while efficiently integrating advanced generation and storage technologies. By also enabling cost-competitive OGBs, this research could be leveraged by other governmental agencies (e.g., DOD, DOT, EPA). For example, DOD could apply the research results to microgrid applications for off-grid environments at mission-critical locations.

Results and Accomplishments

Under subtask 1, the team successfully installed and characterized the efficiency of a small natural gas feed free-piston sterling heat engine generator (HEG) and performed experiments to determine the potential of the Stirling HEG as a range extender for ORNL's Printed Utility Vehicle in the NTRC's chassis dynamotor laboratory. Additional experiments were performed to evaluate the potential for the HEG to act as the hot-side source for subtask 2.

The results of subtask 2 showed that GLIDES could achieve round-trip efficiency ranging from 66% to 82%, depending on system configuration. This study demonstrates that additional efficiency gains can be realized by using heat transfer enhancement strategies, such as liquid spraying, using condensable gases, or leveraging any available waste heat to counter the expansion cooling and provide a thermal boost. A cost analysis showed that GLIDES is amenable to modular design and that it is a scalable technology; the installation cost could be half of the cost of the lead acid batteries.

Under subtask 3, we fabricated a nanoscale 2D dielectric capacitor by sandwiching hBN dielectric material between monolayer graphene electrodes. As fabricated, it is highly flexible and transparent. The 2D capacitor opens a path to the development of fundamentally new energy storage devices. It shows promising electrochemical performance (e.g., specific capacitance, specific power, specific energy) as well as increased stability. A layer-dependent dielectric constant was observed for hBN; it rises as the number of layers increases from three to nine and approaches the bulk value beyond nine layers.

Under subtask 4, we developed a building energy management system model that optimally integrates and manages the building load, distributed generation, solar photovoltaic (PV) generation, and energy storage. The model predictive control approach used in the current framework captures the future behavior of the system and compensates for the uncertainty associated with forecasts of demand and solar PV generation. A short sampling time (15 min, suitable for real-time applications) was used to compute more accurate and effective controls for the operation of the building. The system will be deployed as part of a project on Advanced Manufacturing and Integrated Energy demonstration project.

Information Shared

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Yijing Stehle, Panos Datskos, Sergei Smirnov, Ivan Vlassiouk, Controllable Synthesis of Mono-Layer Hexagonal Boron Nitride Thin Film by Atmospheric Pressure Chemical Vapor Deposition, MRS 2016 Mar, Abstract # 2408655

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08219

Additive Manufacturing Science of Multiphase Metallic Hybrid Materials

A. Shyam, Y. Yamamoto, T.R. Watkins, K. Unocic, R. Dehoff, S. Gorti, S.Simunovic, S. Babu

Project Description

In the last decade, metal additive manufacturing (AM) processing has shown the potential to make complex components of homogenous materials. Relatively few efforts focus on using the inherent site-specific building process of AM. Recently, ORNL researchers have shown the proof of principle for manipulating the face-centered-cubic (FCC) crystallographic texture in a homogeneous alloy (alloy 718). However, the general applicability of this scientific methodology for a wide range of compositions and phases has not been proven. Our overarching scientific interest is to determine whether is it possible to induce tailored properties by dispersing materials with different crystal structures, such as FCC, body-centered cubic (BCC), and hexagonal close packed (HCP) structures, in precise geometric locations at length scales ranging from nanometers to millimeters while maintaining stability of the structures during long-term cyclic loading or thermal exposure. Such precise overall control of metallic phases with varying crystal structure within a component has not been attempted but could be applied to obtain unprecedented functionalities by applying basic physical metallurgy principles to extend the science of AM.

Mission Relevance

AM allows for unprecedented geometries and properties for multiple energy systems such as those for power generation or transportation.

Results and Accomplishments

This was a four-month effort. Progress was hampered by lack of readily available alloy powders for the multiphase builds, whose designs were based on physical metallurgy principles. Three methods were applied to make multiphase metallic hybrid materials: alloy multilayers with laser melting, thermal cycling of diffusion couples fabricated with e-beam welding, and direct build of multiphase hybrids with two powder hoppers in a DM103D directed-energy deposition system. Although the available source powders were not ideal, out of the three methods, our team was able to make multiphase builds of a Co-Cr alloy mixed with a Ni-based alloy (Inconel) and with Ni (FCC) and Ti_6Al_4V (BCC+HCP). Extensive characterization was performed on the structures. It was found that multiphase structures with stable interfaces can be built with the above technique. Several ideas have been generated to make improved multiphase builds as custom alloy powders become available. Multiple applications will be enabled with this approach where a balance of structural and functional properties is needed.

Information Shared

No information shared in FY 2016

INTEGRATED STUDIES OF COMPLEX BIOLOGICAL AND ENVIRONMENTAL SYSTEMS

06826

Direct Catalytic Conversion of Methane to Methanol

C.K. Narula, M.M. DeBusk, M. Kidder, S. Overbury

Project Description

The goal of this project is to demonstrate an economical path to conversion of natural gas (methane) into liquid fuel for transportation. The key step is to directly convert natural gas to methanol or hydrocarbons using a novel catalytic process. The urgency of the proposal is driven by the rapid increase in the abundance of domestically produced natural gas, which provides a new opportunity for national energy independence. This project will generate the underpinning intellectual property and publications that will establish expertise at ORNL in catalysis for natural gas conversion to hydrocarbons and will provide a foundation for future work in efficient natural gas utilization. Because of the importance of this work, there are multiple opportunities for follow-on funding. We will pursue financial support from DOE SC for mechanistic studies while exploring financial support from FE, ARPA-E, DOD, and industrial collaborators for scale-up and techno-economic studies. The optimization of the catalytic process and process development for commercialization of technology will be carried out under follow-on funding from those offices as well as from industry under SPP arrangements.

Mission Relevance

The 40 year effort to reduce our dependence on foreign oil has stimulated research on a variety of alternative technologies (e.g., production of gasoline from coal or biomass, alternative fuels such as biodiesel or ethanol and methanol mixed with gasoline, and H_2 with solar or nuclear power). Since the nineties, oil prices have tripled, and the US supply of natural gas has increased tremendously. In the current climate, the ratio of the cost of petroleum to that of natural gas is high, favoring substitution of natural gas for oil. Thus there is a major opportunity for development of lower-cost, efficient processes that convert natural gas into methanol, which can then be converted to liquid hydrocarbon fuel.

Results and Accomplishments

Nonoxidative methane conversion to aromatics. Our results confirm our proposal that heterometallic zeolites exhibit superior methane conversion over monometallic species. This is illustrated by the activity of *m*In/*n*Mo/ZSM-5 (*n* and *m* indicate the weight percentage of metals) catalysts, which were prepared by indium impregnation of Mo/ZSM-5. While the benzene and C2 hydrocarbons selectivity over these catalysts remained comparable to that of Mo/ZSM-5, we observed dramatic reductions in coke formation (about half that of Mo/ZSM-5) and ~20% improvements in hydrocarbon selectivity.

Based on decreased coke formation, the catalysts are ranked as follows:

1In/2Mo/ZSM-5 (optimal) > 2In/2Mo/ZSM-5 > 3In/2Mo/ZSM-5 > 2Mo/ZSM-5.

Standard characterization of catalysts (e.g., elemental analysis, x-ray diffraction; Brunauer-Emmett-Teller surface area analysis; ultraviolet, visible-light, Fourier transform infrared, and Raman spectroscopy) suggests a high dispersion of metal oxides on the ZSM-5 substrate. The catalysts remain intact after several hours under operating conditions and multiple regenerations. Although the role of indium in coke suppression is not understood at this time, the indirect evidence for its participation comes from the fact that In/ZSM-5, Mo/ZSM-5, or their mechanical mixtures did not exhibit coke suppression. Thus it is likely that coke suppression is a function of In-Mo interaction by either In-O-Mo–type bonds or spatial proximity between In and Mo.

Oxidative methane conversion to methanol. We initiated this work by reproducing literature reports on Fe/ZSM-5–catalyzed methane oxidation to methanol and scaling up the reaction 15 times. A variety of other catalysts, such as H-ZSM-5 (Al : Si = 11.5), and Mn, Co, Ni, or Ru supported on H-ZSM-5, were prepared and were found to be inactive toward methane oxidation. A small amount of Fe in the framework of commercial ZSM-5 probably accounted for the trace conversion (< 0.002%) of methane to methanol during the catalytic runs. We found that, in contrast to the results in published reports, Cu-ZSM-5 showed ~5% methane conversion to methanol. Our results clearly show that the activity of Cu for methane conversion is dependent on the bonding modes of Cu in zeolites.

Information Shared

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06984

A Genome-Enabled Approach for Predicting Plant Functional Traits in Dynamic Vegetation Models

D. Weston, A.P. Walker, L. Gu, W. Muchero, G.A. Tuskan, J.M. Warren, S.D. Wullschleger

Project Description

Our inability to accurately represent plant functional traits (e.g., those traits governing photosynthesis and production) for a wide array of taxa and the interaction of those traits with variable environmental conditions are considered key uncertainties in land-surface models, including the DOE-BER–funded Community Land Model. Given the importance of this issue, it is imperative that the scientific community leverage advances in genomics and genetics to better predict plant traits that govern the performance of species under various climatic conditions. We designed a laboratory system and an instrumented field plot to develop advanced genomic modeling approaches to predict trait distributions for species such as peat moss (*Sphagnum*) that are critical to carbon cycling, deploy this model as an open source service within the KBase knowledgebase project that is interfaced with climate models, and test the output of model runs with laboratory and field-based manipulations within a critical ecosystem. This project will eliminate the current disconnection between the genomics-based research carried out by the BER Biological Systems Science Division (BSSD) and the climate-based research carried out by the BER Climate and Environmental Sciences Division (CESD) and will thereby set a precedent where advances from biological system research are brought to bear in climate system research.

Mission Relevance

Integration of systems biology and ecological modeling promises to usher in a new era of understanding in community compositional shifts to future climate through genome-predicted plant functional traits. This work will allow us to classify plants into trait distribution types at the species and population levels and to infer mechanisms driving susceptibility and tolerance to changing climatic conditions. The need for such an understanding was emphasized in the DOE Carbon Cycling and Biosequestration workshop, which resulted in a funding initiative for the inclusion of microbial communities and metagenomics data in carbon-cycling models. The inclusion of plant genomics in carbon-cycling models was recently addressed in the BER Advisory Committee report on virtual grand challenges and will be addressed again in an anticipated DOE-BER workshop to be cosponsored by program managers from BSSD and CESD. The proposed research sets the stage for ORNL, as the premier plant biology lab in the DOE system, to address a key uncertainty in carbon-cycle predictions through the integration of genomics, climate, and advanced computational modeling.

Results and Accomplishments

The major objective of this project is to develop the genomic resources and analytical capabilities necessary to link genomic predictions to trait functioning relevant to carbon cycling. The experimental component of this work is over. The small fraction of funding budgeted for FY 2016 was for the salary of a postdoctoral researcher, who is assisting with manuscript writing. Therefore, the focus in this reporting year is on dissemination of results and information through manuscript publication, proposal writing for follow-on funding, and workshop organization. To that end, we have had an extremely successful year, with four publications, including articles in *New Phytologist* and *PNA*S; three funded user facility proposals to the Environmental Molecular Sciences Laboratory (EMSL at PNNL) and the Center for Nanophase Materials Sciences (CNMS at ORNL); five invited talks; and the co-organization of an international workshop.

Information Shared

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Additional User-Facility Proposals from this work

The metabolite exchange within a tri-partite plant – fungus – cyanobacterium interaction system using a Maldi FT-ICR Mass Spectrometry imaging To EMSL, PI Weston

Determining the elemental and small molecule signatures of a plant - cyanobacteria symbiosis using TOF-SIMS, PI Weston - funds for one week of CNMS user facility time

Nanometer studies of both detrimental and beneficial interfaces between plants and microbes. PI David Allison to CNMS

Invited Talks Related to This Work

EMSL: Plenary speaker for Multiscale Ecosystem Analysis and Design Sept 2016.

Plant and Animal Genome Conference: The metabolic modeling of plant-microbe interactions. Jan. 2016

Ecological Society of America: From plot scale experimental manipulations to constructed communities: insights into the Sphagnum microbiome

Brookhaven National Lab: Defining a diazotroph and plant interaction from ecosystem to individual scale

American Society of Botany: Characterizing the *Sphagnum*-microbiome: From natural surveys to manipulation studies.

Workshops and Leadership

Co - organized the International 'The Sphagnum genome project' workshop for the New Phytologist Trust. March 2016, Duke University.

Leading an International team for the Sphagnum genome sequencing project.

06988

Revealing the Structural Organization of Membranes in Living Cells by Small-Angle Neutron Scattering

J.G. Elkins, J.D. Nickels, F.A. Heberle, S. Chatterjee, R.F. Standaert, D.A.A. Myles, J. Katsaras

Project Description

Neutron scattering has been widely applied to the study of isolated biomolecules and model biological systems. However, it has found limited application to the study of intact, living cells. In particular, the potential of neutrons to characterize nano- to mesoscopic structural features that do not give rise to Bragg scattering remains practically unexploited. Using a unique approach, we will demonstrate this potential by determining whether membrane domains (lipid rafts) exist *in vivo*, a question that has vexed biologists and confounded experimentalists for over 30 years. In neutron-scattering experiments, the prerequisite for detecting domains is the contrast between domains and the surrounding regions of the membrane. We will initially exploit the inherent neutron contrast that exists between the major classes of biomolecules (i.e., lipids, nucleic acids, and proteins). Subsequently, specific neutron contrast will be generated in genetically manipulated cells, for example, by selectively incorporating H-labeled lipids into substantially deuterated cell membranes. Live cells grown under differing H/D conditions will be characterized using small-angle neutron scattering (SANS) to provide neutron "fingerprints" that correlate with cellular composition. The presence or absence of nano- and mesoscopic domains will be assessed by SANS under conditions designed to cause and to prevent their formation. The detection of domains in living cells would be a landmark in contemporary biology, and the development of the toolsets described here will propel neutron-scattering analysis to the forefront of structural cellular biology.

Mission Relevance

The results from this work will be of high scientific impact and of key strategic importance to the development of bioscience research at ORNL and its user facilities. The ability to study membrane structure, composition, and organization in living cells would influence programs in environmental, bioenergy, and biomedical sciences, including (1) DOE programs involving recognition and transport at microbial cell membranes; stress responses of plant and microbial membranes; and the communication, organization, and structure of microbial colonies and (2) NIH programs involving cell biology, transport, signaling, communication, biosensing, drug delivery, and the design and discovery of new diagnostics and therapeutics of disease.

Results and Accomplishments

We have made substantial progress in applying SANS techniques to study the lateral structure of intact bacterial membranes in viable cells. An essential component of our approach is to control the fatty acid composition of *B. subtilis* cells during growth by blocking *de novo* synthesis of membrane fatty acids while preventing the catabolism of fatty acid mixtures added to the medium. Establishing this capability has allowed us to produce a cellular membrane that is largely proteated (H-lipid) while the other cell components (e.g., protein, nucleic acid, cell wall) are highly deuterated, which provides isotopic contrast. Our system relies on a small-molecule inhibitor of type-II fatty acid synthases (cerulenin) to block fatty acid production in a mutant strain of *B. subtilis* (Δ*yusL*), which is unable to break down exogenous fatty acids. Gas chromatography mass spectroscopic analysis was used to verify that we were able to construct functional membranes by feeding *n*-16:0 and *ai*-15:0 fatty acids to *B. subtilis* cultures growing under defined conditions. The ability to control the composition of the membrane enabled us to apply SANS using both the Bio-SANS and EQ-SANS instruments to resolve the lamellar form factor of a lipid bilayer in a living cell and to determine membrane thickness. Also, by controlling the isotopic (H/D) composition of low- and high-melting-point lipids, we are now able to use neutrons to probe for lateral structure and organization within the membrane of living cells, which is a significant advancement over the use of model membrane systems. Additional methods, including protocols to preserve cell viability over long collection periods, were developed to improve on-beam analysis of intact bacterial cells. Taken together, our methods constitute a leading-edge program that leverages advanced capabilities unique to ORNL to better understand important aspects of structural membrane biology, especially as they are implicated in human health and disease, as well as microbial responses to advanced fuels and other chemicals.

Information Shared

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07443

Interrogating Monolignol Transport Using a Multimodal Imaging Approach

J. Morrell-Falvey, R. Standaert, J. Chen, T. Calhoun, D. Joy, A. Ragauskas, M. Doktycz, D. Roberts

Project Description

Predicting and manipulating molecular-scale processes to influence responses on the organism and community levels are fundamental goals of DOE missions in bioenergy, plant-microbe interactions, carbon cycling, and remediation. To achieve these goals, a detailed understanding of the function of biological molecules and cellular networks is needed. Elucidating the process of lignification of plant cell walls will enable strategies to manipulate lignin content and composition for downstream applications in bioenergy and materials development. This project aims to interrogate transport of monolignols across the plasma membrane, a key step in lignin deposition. We will study monolignol transport using a multimodal imaging approach to visualize distribution of the transporter within the plant and deposition of monolignol analogs in the cell wall. We will establish an experimental system to study the monolignol transporter in *Arabidopsis* and will identify monolignol transporters in *Populus*. This research involves genetics, biochemistry, probe synthesis, and refinement of imaging methods to promote a detailed understanding of monolignol transport. We will employ common experimental samples that will facilitate correlation of results from the imaging modalities described to afford insight into the biology and chemistry of lignification.

Mission Relevance

This research will advance the methodology and the science that connect genomics to the solution of practical problems. Our target biological process, lignification, is the core of DOE's bioenergy and biomaterials programs targeting biomass deconstruction, renewable materials, and bio-inspired processes. USDA has many congruent interests, and DOD (DARPA) is interested in novel materials such as those that could be developed from engineered lignin. We are establishing an integrated program to study monolignol transport using customized probes and reagents that are compatible with multiple imaging platforms. Moreover, the expertise acquired by our team in multipurpose sample preparation and the integration of multiple analytical methods can be applied to other biological challenges.

Results and Accomplishments

We have identified two AtABCG29 sequence homologs in *Populus* that display different patterns of tissue and organ expression as determined by semiquantitative reverse transcription-polymerase chain reaction analysis. Potri.001G189500 is expressed in root, xylem, phloem, stems, and leaves, whereas Potri.003G049600 expression is only detected in roots. The expression pattern of Potri.001G189500 is consistent with a possible role in monolignol transport. The sequence-verified *PtABCG29a* (Potri.001G189500) has been transformed into the *A. thaliana abcg29* mutant line to determine complementation. We expect that expression of Potri.003G049600 or Potri.001G189500 will rescue the growth defect of *abcg29-1* plants if the candidate *Populus* gene encodes a functional *p*-coumaryl alcohol transporter. It is possible, however, that these proteins may be involved in transport of other monolignols or related compounds, which would be an exciting finding as well. Thus we are testing the functional properties of these poplar genes, including their transport mechanism and substrate selectivity, in a *Xenopus* oocyte expression system. Because of the flexibility of the *Xenopus* system, the transport selectivity of the poplar proteins can be assessed for *p*-coumaryl alcohol substrates as well as other monolignols (e.g., sinapyl alcohol, and conferyl alcohol) and related compounds (*p*-coumaryl alcohol glucosides, caffeic acid, and ferulic acid), which may be involved in lignin and extracellular polysaccharide biosynthesis. We have also succeeded in preparing a fluorescently tagged version of coniferyl alcohol (G lignol) suitable for fluorescence imaging. We developed several important modifications to the published approach that eliminate the need to isolate labile intermediates and allow stockpiling of the modified fluorophore in a stable, convenient form (hydrochloride salt) that simplifies production of the final products. The fluorescent G-monolignol was fed to wildtype *Arabidopsis* seedlings for imaging studies. Our data show that the fluorescent G-monolignol analog is found localized to the cell walls of *Arabidopsis* seedlings. We can now extend these experiments to look at patterns of monolignol uptake at higher spatial resolution, with other imaging methods, and in various *Arabidopsis* and poplar strains.

Information Shared

No information shared in FY 2016

MATERIALS DESIGN AND INNOVATION

06813

New Paradigms in Passive Polymer Membranes for Carbon Dioxide Separation

T. Saito, S. Mahurin, J. Mays, A. Sokolov

Project Description

The vast majority of the world's energy is presently derived from the burning of fossil fuels, which releases vast quantities of carbon dioxide (CO_2) into the environment and contributes to climate change. Practical and cost-efficient methods of CO_2 separation and capture would thus solve one of the most challenging problems facing humanity today. The challenge to practical CO_2 separation is to produce a material that has very high permeability to passively separate CO_2 from a flue gas, because of the large volumes of gas coming out of power plants. This project focuses on fundamental understanding of molecular transport through polymer membranes with the goal of achieving high permeability combined with good selectivity in separating CO_2 from nitrogen (N_2). Our specific target is to develop highly CO_2-permeable polymer membranes via precise synthesis of novel polymers containing CO_2-philic functional groups with design guided by simulation. Various characterization methods, including a membrane test system, a gravimetric microbalance, and broadband dielectric spectroscopy as well as computational simulation will elucidate the relationships of the polymer structure to its physical properties upon CO_2 separation.

Mission Relevance

On August 3, 2015, President Obama announced the Clean Power Plan, a goal of which is to cut greenhouse gas emissions from existing power plants by 32% from 2005 levels by 2030. Passive polymer membranes that have high flux and good selectivity for CO_2, that are robust enough for use at elevated temperatures in an oxidizing environment, and that are economical to produce are extremely attractive targets for carbon separation and are high on DOE's list of basic research needs to reduce our human footprint on the ecology and to combat global warming. Successful completion of the work proposed herein will place ORNL in a favorable position in this critical area. Moreover, the fundamental understanding gained during the project on transport of gases through polymer membranes will be used to create novel high-permeance polymer membranes for many other applications.

Results and Accomplishments

Novel functionalized polymers were successfully synthesized, and novel membranes were characterized. Among our major achievements was the development of one of the best permeable polymers reported; its performance is above the Robeson upper bound. This upper bound represents the current limit for selectivity at a given permeability of a membrane. One of the novel high-permeability polymers is crosslinked polydimethylsiloxane-polynorbornene (PDMSPNB). Our approach to preparing crosslinked

PDMS revealed that tuning crosslink densities of PDMS using macromonomers can improve CO_2/N_2 separation significantly. The peak performance at a cross-link density of 1.19×10^{-5} mol/cm^3 is approximately a factor-of-two improvement in CO_2 permeability and CO_2/N_2 selectivity over the well-studied conventional crosslinked PDMS.

The unprecedented performance achieved by a careful design of the macromolecular architecture and crosslink mechanism reveals the hidden potential of PDMS, a rubbery polymer, for gas separation. This new finding can open up a new approach to enhancing its performance for gas separation and could help to elucidate additional factors for the gas separation mechanisms in rubbery polymers. Moreover, our approach provides a platform for synthesis of various functional membranes. In particular, a series of the PDMSPNB copolymers with CO_2-philic monomers were successfully synthesized, and their gas-permeability properties were evaluated. Among them, we identified the CO_2-philic groups, which enhance CO_2/N_2 selectivity. The membranes having the CO_2-philic groups showed excellent CO_2 permeability with good selectivity, and fine-tuning the degree of CO_2-philic functionalization achieved the performance above the Robeson upper bound line (e.g., CO_2 permeability ~8000 barrer; CO_2/N_2 selectivity~18). The enhanced performance with incorporation of CO_2-philic groups proves the validity of our hypothesis, and the excellent permeability of the copolymer provides great potential for practical applications.

We also conducted systematic studies that identified several parameters crucial for design of passive polymer membranes: polymer dynamics; packing; intra- and intermolecular interaction (e.g., hydrogen bonding); rigidity (glassy vs. rubbery); and degree of crosslinking. Further studies, including investigation of these parameters, are needed to develop a deep fundamental understanding of what controls the CO_2/N_2 permeability and selectivity. The membranes synthesized for this study could offer permeance of about 6,000 to 9,000 gpu if a 1 µm layer could be coated over a gas-separation substrate such as a hollow-fiber membrane. Thus thin layers (1 µm or less) of our membranes could readily meet the DOE cost targets that are based on cost assessments of CO_2 capture from power plant exhaust.

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06895

Sustainable Energy Through Complex Oxide Materials: Multivalent Oxygen Sponges for Efficient, Low-Temperature Catalysts

H. Nyung Lee, V.R. Cooper, D.A. Lutterman, A.A. Savara

Project Description

This LDRD project will identify key descriptors that determine the catalytic performance in multivalent oxygen sponges made of transition metal oxides (TMOs) and materials architectures that effectively enhance catalysis. By combining synthesis, theory, and characterization of catalytic gas conversion and electrochemical reactions, we will focus on addressing the following scientific questions: How can complex *d*-band orbital occupation be manipulated to facilitate surface catalytic reactions? Can the catalytic activity be controlled by modifying the physical constraints? What are the structural, chemical, or electrical processes that influence the surface catalytic reactions [i.e., the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER)]? Therefore, the outcome of this work will ultimately help (1) identify routes to producing low-temperature catalysts by controlling and understanding the role of the physical constraints, (2) discover key descriptors for efficient catalysts in multivalent oxides, and (3) bridge the gap between materials physics and catalytic applications. We envision that our approach of utilizing oxide physics to address key fundamental issues in energy materials is the first step toward achieving sustainable energy through the development of TMO-based high-performance catalysts.

Mission Relevance

The materials to be investigated are highly relevant to DOE science and energy missions because of their potential usefulness for energy applications. The success of this proposal can ultimately provide a foundation for inventing new parts for existing catalysts and for developing new directions in future BES-funded field work proposal programs, energy-related projects, and Energy Frontier Research Centers at the Lab. Since the physics and chemistry of TMOs have a direct connection with the performance of catalysts and energy-generation/storage devices, the work proposed here provides a scientific basis for identifying both ways and materials to better understand the interface and surface behaviors and properties that critically influence the performance of advanced heterogeneous catalysts. Thus the outcome of this project would be to provide a valuable asset to ORNL to pursue future BES funding opportunities and to contribute to seeking funding from DOE EERE and other technology programs.

Results and Accomplishments

The focus in FY 2016 (the third year of the project) is on developing bifunctional oxide-based thin film catalysts and controlling catalysis by epitaxial strain. A particular focus was on the control of orbital polarization by epitaxial strain and its role on ORRs and OERs. To demonstrate the advantages of using strain to control oxide catalytic activity, we grew strained films of the conducting perovskite $LaNiO_3$ by pulsed laser epitaxy onto substrates with varying lattice spacings. Using a custom-built rotating-disk electrode setup, we showed that compressive strain increased the activity of the oxide to catalyze both the ORRs and the OERs, enhancing its bifunctionality in excess of a Pt reference. A combination of materials characterization and computer modeling determined that the underlying rationale was due to a strain-induced tailoring of the orbital asymmetry, a technique that could easily be expandable to other oxides. At a critical juncture in oxide catalysis, where doping with other ions is proving increasingly complicated, the introduction of a new method to increase electrochemical activity should prove to be of immediate benefit.

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07004

Untangling the Role of Boundaries, Defects, and Interfaces in Two-Dimensional Inorganic Materials: A Combined Theoretical and Experimental Approach

M. Yoon, A.-P. Li, B. Sumpter, M. Chi, K. Xiao, D. Geohegan

Project Description

The goal of this proposal is to theoretically and experimentally investigate and develop a fundamental understanding of the structural and electronic properties of boundaries, defects, and interfaces of two-dimensional (2D) materials and their impact on key properties, such as electronic transport. Such a study is only possible with an integrated application of state-of-art experimental and theoretical approaches. We will use atomic-spatial-resolution microscopes to identify the atomic arrangement of defects and boundaries and for electronic potential mapping. Scanning tunneling spectroscopy will be employed to identify interface effects and the in-plane electronic and transport properties. These experimental studies will be used to consolidate trustable (validated and verified) and efficient (scalable) theoretical approaches for accurately describing the fundamental properties of large-scale systems to enable characterizing defects, boundaries, and interface properties. Such characterizations are critically important for further progress in the field. In this regard, we will build on our very recent work for optimized first-principles functionals by minimizing many-electron quasi-particle corrections to the Kohn- Sham energy spectra for extended systems. Such a theoretical approach can be utilized for fast and efficient data mining and identification of structures with desired properties.

Mission Relevance

A theoretical tool for an efficient and accurate description of electronic and structural properties of materials, which fixes some problematic behaviors and shortcomings of density functional theory in describing low-dimensional systems, will be a significant boost to any ORNL materials research proposal to BES under the Materials Genome Initiative, the Mesoscale Initiative, and Energy Frontier Research Centers as well as other funding agencies, such as the NSF for the "2D beyond graphene" proposal call. The success of our proposal will advance our understanding of fundamental physical and chemical processes related to energy materials, potentially providing breakthroughs that address today's technology barrier.

Results and Accomplishments

Thermal properties at the low-D interfaces. Our theoretical calculations reveal that the interface of monolayer MoS_2 and metal substrates have a strong electron-phonon coupling that can change the interfacial thermal conductivity by more than two orders of magnitude. The strong interfacial effect on thermal transport was confirmed at the stacked graphene and hexagonal boron nitride heterostructure.

0D defects (vacancies and alloys). The roles of defects and alloys in controlling the electronic properties of 2D systems were studied. We found that defect densities of $MoSe_{2-x}$ can greatly tune their intriguing optical and electric properties. We theoretically demonstrated that alloying can be utilized to suppress deep levels in 2D transition-metal dichalcogenides in an unexpected manner.

1D interfaces. We demonstrated that one-dimensional interfaces of the 2D lateral heterostructures can be utilized by strain. In particular, their energy band gaps and band offsets can be greatly tuned by strain with high power conversion efficiency.

2D interfaces. We revealed the strong coupling of interlayer stacking in the bilayer graphenes and their electronic properties depending on external electric field and investigated the interlayer coupling of WSe_2/WS_2 bilayer heterostructures in their optoelectronic properties. Our theory shows that interface interaction between h-BN and Cu(100) plays a key role in tuning oxygen superstructures. We explained the mechanism of growth of metal phthalocyanine on deactivated semiconducting surfaces steered by selective orbital coupling. We demonstrated that ideal Rashba states can be formed on layered semiconductor surfaces by strain engineering.

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07019

Rational Design of Novel Polymeric Organic Framework Materials

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Project Description

The goal of this research is to demonstrate a design approach for novel amorphous, hierarchical, micro- to mesoporous polymeric organic framework (POF) materials with superior capacity and binding strength, and sorption dynamics that are chemically, thermally, and mechanically stable for economic use in transport processes. This combination of properties, which is not found in any existing material, is called for in several critical applications in separations, storage, and energy technologies. Emerging POF materials combine disordered porous properties with organic functionalities, but pore size control and enhanced surface functionalization remain challenges. The key to improved transport performance is to customize the POF pores for specific functionality. This can be achieved by (1) controlling the effects of synthesis parameters on polycondensation kinetics and molecular structure, (2) functionalizing and extending the topology of the POFs for material tunability, and (3) understanding how the porous structure influences the effective transport of adsorbates. We will construct POF materials through condensation reactions of inexpensive, readily available building blocks that will provide flexibility for material design. Currently, no rational, systematic design strategy exists for realizing the potential of POF materials. Therefore, our approach is based on integrating the various tools from computational and experimental techniques necessary to close the "synthesis → characterization → transport" design cycle. The closure of this cycle depends on the ability to understand material transport performance and to establish a feedback loop for chemical synthesis. To this end, we propose to combine neutron-scattering measurements, nuclear magnetic resonance (NMR), and complementary atomistic simulations to characterize POF materials, to predict their transport performance, and to guide synthesis strategies.

Mission Relevance

The focus of this proposal is the rational synthetic design of tunable POF materials through the integration of computational and neutron-scattering techniques to predict transport performance that will guide synthetic strategies. Preliminary results generated in this project are relevant to areas within DOE EERE, BES, FE, and NE. Follow-on funding will be targeted for anticipated programs such as Mesoscale Science, the Materials Genome Initiative, and national security. Since the preparation of this proposal, reports have emerged indicating that ordering materials into crystalline and semicrystalline structures has begun to be utilized in biological applications, and a paramagnetic POF material synthesized with a precursor that gives semiconductor-like properties has been prepared. Both show the diversity of POF materials.

Results and Accomplishments

We studied the tunability of the POF framework (i.e., control of pore size, structure, and surface area) through incorporation of rigid, bent, extended, and rotationally free aromatic precursors. In parallel with this, we explored the functionalization properties that will enhance the CO_2 uptake through the use of targeted precursors. We formed our base model POF material from pholoroglucinol and terepthalaldehyde precursors, each a one-benzene unit structure containing three hydroxyls per oligomer unit. As we enhanced the structure's surface area and pore dimensions, it was clear that we could take advantage of resorcinol-based precursors that would double the amount of available hydroxyls per oligomer. We observed that this increase in hydroxyls would increase the amount of CO_2 uptake almost twofold. We deliberately chose these hydroxyl-functionalized POF structures because they can be postfunctionalized with amines and ethers, which increase the amount of captured CO_2. We explored the Burcherer reaction and the ethoxylation reaction, which successfully postfunctionalized approximately 25% of the structure while enhancing the uptake of CO_2 by three times that in the amine-functionalized POF material. We are currently exploring how to enhance the conversion of the hydroxyls.

As part of understanding the kinetics and formation of the POF frameworks, we have applied NMR, dynamic light scattering, and small-angle neutron scattering (SANS) as well as molecular dynamics simulations to help understand the early two-step preformation process in which condensation of the precursors occurs. The significant amount of insight gained in this study helps to guide the choice of solvent, precursors, and concentration of monomer units and solvent systems to direct the structural formation of the POF systems.

Our research in FY 2016 involved neutron scattering carried out on the Spallation Neutron Source (SNS) EQ-SANS instrument. Data obtained from neutron scattering induced by hydrogen in a deuterated liquid was interpreted through molecular dynamics simulations (*J. Phys Chem. B,* 2016). We also looked at the CO_2-enhanced uptake associated with postsynthetic modifications of POF materials and a publication is in progress. Neutrons were also used to describe the preformation step of POF materials while in situ using EQ-SANS at SNS and molecular dynamic simulations are underway. We also successfully synthesized a deuterated POF system to examine the dynamic interaction of CO_2 and methane on its surface through quasi-elastic neutron scattering using the SNS BaSiS instrument. In addition, neutron vibrational spectroscopy experiments are under way on the SNS VISION instrument to probe the chemical/physical interaction of CO_2 with chemical moieties on the POF framework.

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07476

Exploring Structure and Functionality of Oxides in Real Space: "Deep Data" in Atomic Resolution Imaging

S. Jesse, R.K. Archibald, S.V. Kalinin, A.R. Lupini, E. Lingerfelt

Project Description

Progress in imaging technologies since the beginning of the 21st century has opened the floodgates of high-veracity information in the form of multidimensional datasets. This LDRD project aims to use the power of big data to uncover and control the physics of strongly correlated ferroic oxides hitherto concealed in details of high-resolution imaging. We aim to mine experimental data for a variety of physically and chemically relevant information and to synergistically link the results to atomistic theories through the microscopic degrees of freedom, an approach we refer to as "deep data." We will establish a new paradigm for direct mapping of structure-property relationships in strongly correlated oxides on single-unit cell and defect levels. Locally extracted structures with explicitly deconvolved contribution to functional response will enable theoretical models to be constructed to give materials scientists and engineers accurate guidance to improve materials properties and to allow for direct verification of fundamental physical models. The proposed work will tie together the ORNL strengths in high-resolution electron and probe microscopy imaging, advanced atomistic theory, and large-scale computation and will position ORNL to take advantage of new materials genomic, imaging, and data center initiatives.

Mission Relevance

This LDRD project will bring ORNL's imaging effort into an entirely new era, greatly accelerating and effectively merging experimental and theoretical study and offering a critical competitive edge in the electron and probe microscopy communities. It will also position ORNL for success in an anticipated upcoming call for data science centers across the DOE SC complex. This single award could provide $10M to $20M per year for a data science center at ORNL. Similarly, it will provide a unique counterpart to Materials Genome–type initiatives. It will also provide a critical experimental link to Oak Ridge Compute and Data Environment for Science to provide scalable computing and data infrastructure as a service to scientific and engineering communities via a software-as-a-service delivery paradigm.

Results and Accomplishments

We have built a computational environment to enable data-driven material science discovery from otherwise intractable datasets based on the co-development of a data and compute infrastructure, standardized data structure, a set of critical scalable algorithms for analysis, and a user-friendly deployable interface. This approach provides the flexibility to choose and combine various high-performance computing (HPC) optimized algorithms to distil and reveal patterns within "big data." In terms of infrastructure, we have built a high-speed, secure, direct connection of instruments to HPC; a big data storage, curation, and analysis system; and multiple HPC platforms and algorithms to choose from, combined with user-friendly web access from anywhere in the world. The developed data structure conforms to or leads DOE requirements for data management; records full analysis workflow and intermediate results; and enables communication across multiple platforms and uses Hierarchical Data Format (HDF5) to allow parallel read and write, data organized as folder-tree, and multiple-language compatibility.

Our approach is based on having a few core algorithms that can be strung together at the user's discretion to form complex analysis workflows. Where appropriate, algorithms are made scalable and are optimized for HPC on multiple platforms. Core algorithms implemented so far include functional fitting, principal component analysis, and K-means clustering. The user interface, a lightweight Java environment that can run on a laptop or small desktop and that can be installed on a Windows, Mac, or Linux platform, gives easy access to cloud-based data storage, navigation within data, push-button execution of supercomputing jobs, and data and results visualization.

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Open-Source Code

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Data Analytics Applied to Chemical Transformations in Liquids RR Unocic, AV Ievlev, S Jesse, X Sang, KL More, SV Kalinin Microscopy and Microanalysis 22 (S3), 740-741

Fast Aberration Measurement in Multi-Dimensional STEM AR Lupini, M Chi, SV Kalinin, AY Borisevich, JC Idrobo, S Jesse Microscopy and Microanalysis 22 (S3), 252-253

Distortion Correction in Scanning Transmission Electron Microcopy with Controllable Scanning Pathways X Sang, AR Lupini, RR Unocic, TL Meyer, TZ Ward, HN Lee, E Endeve, Microscopy and Microanalysis 22 (S3), 900-901

Atomic-level sculpting in STEM for studies of thickness dependent structural behavior in oxide thin films A Borisevich, Q He, S Jesse, A Akbashev, J Spanier, M Fuentes-Cabrera, APS Meeting Abstracts

Ptychographic Imaging in an Aberration Corrected STEM AR Lupini, M Chi, SV Kalinin, AY Borisevich, JC Idrobo, S Jesse Microscopy and Microanalysis 21 (S3), 1219-1220

Moving atomic-resolution imaging into the age of deep data OS Ovchinnikov, S Jesse, A Belianinov, ST Pantelides, SV Kalinin, Microscopy and Microanalysis 21 (S3), 1607-1608

Automated and Shaped-Controlled Liquid STEM Nanolithography RR Unocic, AR Lupini, AY Borisevich, SV Kalinin, S Jesse Microscopy and Microanalysis 21 (S3), 1127-1128

Atomic-Level Fabrication of Crystalline Oxides in STEM Q He, S Jesse, AR Lupini, DN Leonard, MP Oxley, O Ovchinnikov, Microscopy and Microanalysis 21 (S3), 939-940

STEM in 4 Dimensions: Using Multivariate Analysis of Ptychographic Data to Reveal Material Functionality S Jesse, M Chi, AY Borisevich, A Belianinov, RR Unocic, CT Symons, Microscopy and Microanalysis 21 (S3), 1863-1864

E. Lingerfelt et al. "A New Computational Infrastructure for the Advanced Analysis of Materials Imaging", Joint NSRC Workshop 2015: Big, Deep, and Smart Data Analytics in Materials Imaging, June 9, 2015. Contributed Talk.
E. Lingerfelt. "Bellerophon: A Computational Infrastructure for HPC Workflows and Experimental Data Analysis", ORNL CSED Computational Data Analytics (CDA) Group Meeting, June 22, 2015. Invited Talk.
E. Lingerfelt et al. "Bellerophon Environment for Analysis of Materials", 2015 ORNL Software Expo, Aug. 5, 2015. Contributed poster presented by Eirik Endeve.
E. Lingerfelt et al. "Unifying In Silico and Empirical Experiments in CADES: Scalable Analysis of High-Dimensional Nanophase Materials Imaging Data with BEAM", Smoky Mountains Computational Sciences and Engineering Conference: Integration of Computing and Data Into Instruments of Science and Engineering, Sept. 2, 2015. Invited Poster. Only 20 posters were invited.
E. Lingerfelt. "Unifying In Silico and Empirical Experiments in CADES: Scalable Analysis of High-Dimensional Nanophase Materials Imaging Data with BEAM", ORNL CSMD Computational and Applied Mathematics Group (CAM) Seminar Series, Sept. 10, 2015. Invited Talk.
E. Lingerfelt et al. "Near Real-time Scalable Analysis of High-dimensional Nanophase Materials Imaging and Neutron Science Data in the DOE HPC Cloud with BEAM", 2015 International Conference for High Performance Computing, Networking, Storage and Analysis, Nov. 18, Austin, TX.
E. Lingerfelt. "BEAM: A Computational Workflow System Enabling Scalable In Silico & Empirical Exploration of Materials Science Data in the DOE HPC Cloud", ORNL NDAV Seminar Series, Jan. 13, 2015. Invited Talk.

07555

Enhanced piezoelectric response near the morphotropic phase-boundary in lead-free (Na,Bi)TiO_3-$BaTiO_3$ investigated with neutron scattering and piezo-force microscopy

O. Delaire, C. Luo, D. Viehland

Project Description

This project investigates the underlying microscopic mechanisms leading to enhanced piezoelectric properties in lead-free (Na,Bi)TiO_3-$BaTiO_3$ (NBT-BT), through a combination of neutron scattering experiments, electron microscopy, piezo-force microscopy (PFM), and characterization on high-quality single-crystal samples. Lead-free $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) piezoelectrics have received much attention due to environmental concerns associated with traditional lead-containing piezoelectric compounds [1-5]. Structural investigations by x-ray diffraction (XRD) and neutron diffraction have revealed a morphotropic phase boundary (MPB) in the NBT-x%BaTiO3 (NBT-x %BT) solid solution for $6<x<7$, where piezoelectric coefficients as high as 480 pC/N have been reported [6]. The overall composition-temperature phase-diagram is reminiscent of lead-containing compounds $Pb(Mg_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PMN-PT) and $Pb(Zn_{1/3}Nb_{2/3})O_3 - PbTiO_3$ (PZN-PT), which have been thoroughly studied owing to their good piezoelectric properties. However, the properties and microscopic mechanisms leading to the large piezoelectric response of NBT-BT have been much less studied. This project provides insights into atomic origins of piezoelectric performance enhancement near the morphotropic phase boundary in lead-free materials. This understanding of novel advanced materials will lead to the design of better materials for more efficient, more environment-friendly piezoelectric devices, for either actuators or sensors, and harvesting of mechanical vibrational energy.

Mission Relevance

The project will provide insights into fundamental atomic origins of piezoelectric performance enhancement near the morphotropic phase boundary in lead-free materials. This understanding of novel advanced materials will lead to the design of better materials for more efficient, more environment-friendly piezoelectric devices, for either actuators or sensors, and harvesting of mechanical vibrational energy. We anticipate that future funding could be obtained from DOE BES, DOE EERE, or possibly Office of Naval Research.

Results and Accomplishments

We have prepared single-crystals of NBT-x %BT at compositions x=0, 4, 5, 6.5%, and we have performed inelastic neutron scattering measurements at the SNS using the HYSPEC spectrometer. We have started to perform diffuse x-ray scattering studies (SNS single-crystal x-ray difractometer). We have obtained further beamtime at SNS (Hyspec) and at the APS synchrotron (ID-11) for inelastic and diffuse scattering measurements. Our neutron measurements revealed important characteristics of these lead-free relaxors: 1) We observed "Columns" of inelastic scattering at M-points in reciprocal space, similar to prior observations in PMN systems and supporting proposals, which is a signature of the relaxor state (first observation in a lead-free system). 2) We identified extinct superlattice peaks at some of the M-points, previously unidentified, and we are currently correlating this finding with x-ray data to determine the tilt pattern responsible for this behavior. 3) We mapped phonon dispersions for two compositions of NBT-BT (x=5, 6.5%) using the HYSPEC spectrometer at SNS.

The ferroelectric domain and local structures of NBT-xKBT single crystals have been investigated with TEM. We find the presence of a unique hierarchical domain structure. Small polar lamellar sub-domains exist that are oriented/stacked along the (001) and that correspond to the R (R3c) phase. Similar to NBT-xBT, the NBT-xKBT system has a polar order parameter with a coherence length on the order of 10-100nm, and has both R- and M-type nonpolar rotational order parameters with a coherence length of a few nanometers. These ferroelectric polarization and oxygen rotational order parameters are known to be coupled through rotostriction. Thus, domain frustration over multi-scales plays an important role in the hierarchical arrangement, resulting in similar quadrant-like domains. In turn, following the adaptive phase theory, this may restrict the piezoelectricity in NBT-type systems, due to an increased difficulty in redistributing the domain distribution under electric field.

Information Shared

Chengtao Luo, Olivier Delaire, Barry Winn, Dwight Viehland, "Dynamical mechanism of enhanced piezoelectric response near the MPB in lead-free (Na,Bi)TiO_3 - $BaTiO_3$", Fundamental Physics of Ferroelectrics Workshop 2015, Knoxville TN (poster presentation).

Chengtao Luo, Yaojin Wang, Wenwei Ge, Jiefang Li and D. Viehland, O. Delaire, Xiaobin Li, Haosu Luo, "Hierarchial domain structure of lead-free piezoelectric $(Na_{1/2}Bi_{1/2})TiO_3$-$(K_{1/2}Bi_{1/2})TiO_3$ single crystals", *(to be submitted to Jounal of Applied Physics)*

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08180

Development of Multimodal Spatially Resolved Imaging on a Combined AFM/FIB-TOF-SIMS Platform

O.S. Ovchinnikova

Project Description

The global need for more efficient and sustainable energy sources requires the development of better materials and systems for production and storage of energy. The functionality of materials for energy is determined largely by the mechanisms that take place at submicron length scales and at interfaces. In order to understand these complex material systems and to further improve them, it is necessary to measure and map variations in properties and functionality at those length scales and to determine their local relationships. Particularly of interest are tools that can combine high spatial resolution and chemical information such as multimodal imaging approaches incorporating scanning probe microscopy with chemically sensitive spectroscopies. ORNL recently purchased a groundbreaking tool that aims to achieve this in a new and largely unproven combination of high spatial resolution secondary ion mass spectrometry with in situ atomic force microscopy (AFM). The work proposed here is to demonstrate and test the capabilities of correlative microscopy using the AFM combined with a focused ion beam time-of-flight secondary ion mass spectrometer (AFM/FIB-TOF-SIMS) instrument on samples relevant to the ORNL's science mission. To achieve this goal we will (1) implement co-registered multimodal imaging for the AFM/FIB-TOF-SIMS, (2) demonstrate high-resolution correlative imaging using the FIB-SIMS ion guns, and (3) demonstrate advanced data analytics for multidimensional data from the AFM/FIB-TOF-SIMS instrument. These achievements will clearly demonstrate and enable the new AFM/FIB-TOF-SIMS instrument.

Mission Relevance

We propose to demonstrate multimodal imaging capabilities for the AFM/FIB-TOF-SIMS instrument that will be utilized by the ORNL research community in support of the ORNL science mission. This basic knowledge and capabilities will then be available at ORNL for current and future research projects focused on chemical functionality at the nanoscale. These developments will position ORNL to take full advantage of multimodal chemical imaging capabilities of the AFM/FIB-TOF-SIMS instrument.

Results and Accomplishments

The work in this LDRD project centered on demonstrating and testing the capabilities of the AFM/FIB-TOF-SIMS instrument newly acquired by ORNL for mission-related science research and getting the tool ready for launch in the newly created Instrumentation Characterization Core Service Center. To achieve this goal, we worked with multiple ORNL users across divisions and directorates. Users included projects sponsored by BES, BER, EERE-VTO, and NNSA. These collaborations enabled scientific research in the wide variety of systems and materials, including nanoscale functional materials (ferroelectrics, oxides, photovoltaics); biological systems; polymers; geochemicals; metallic alloys; and glasses.

Additionally, we worked to develop a universal advanced data analytics tool kit to be used in conjunction with multidimensional AFM/FIB-TOF-SIMS data. The data analysis represents a nontrivial problem because it produces large amounts of multidimensional data. To resolve this issue, advanced statistical and mathematical tools of multivariate data analysis have been developed for the AFM/FIB-TOF-SIMS instrument through its incorporation into the Bellerophon Environment for the Analysis of Materials (BEAM) platform and development of user-friendly multivariate analysis tools on BEAM for TOF-SIMS data. This allowed us to develop a workflow for comprehensive TOF SIMS data interpretation and to develop a universal technique of the topo-induced TOF shift correction (submitted to *Scientific Reports*).

The techniques that were developed for data characterization have been implemented as a part of the BEAM project, allowing fast multivariate data analysis of microscopic and spectroscopic data through the web interface, using supercomputer capabilities of ORNL.

Information Shared

Authored Article

Hopf J., Eskelsen J.R., Chiu M, Ievlev A.V. Ovchinnikova O.S., Leonard D, Pierce E.M., Toward an understanding of surface layer formation, growth, and transformation at the glass-fluid interface *in preparation*.

Ievlev, A.V., Kannan, R., Jesse, S., Sukumar, S.R., Doktycz, M., Retterer, S., Kalinin, S.V., and Ovchinnikova, O.S. "Automated Approach for Comprehensive Interpretation of ToF SIMS data Based on Data Analytics" Scientific Reports, 2016, *submitted*.

Pudasaini, P.R., Noh, J.H., Wong, A.T., Ovchinnikova, O.S., Haglund, A.V., Dai, S. Ward, T.Z., Mandrus, D., Rack, P.D. "Ionic Liquid Activation of Amorphous Metal-Oxide Semiconductors for Flexible Transparent Electronic Devices." *Adv. Func. Mat.* (2016), **26**, 2774.

Invited Talk:

"Multimodal Chemical Imaging of Nanoscale Transformations using Scanning Probe Microscopy and TOF-SIMS." SIMS Europe 2016, September 18-20, 2016, Munster, Germany.

08474

Elucidating the Role of Interfacial Water on Material Structure and Function Through a Novel Multiscale-Measurement Approach

O.S. Ovchinnikova, I. Ivanov, B. Doughty

Project Description

The formation and structure of water layers on spatially heterogeneous surfaces play a critical role in a broad spectrum of phenomena, including surface ionic/electronic conductivity, friction, and chemical reactivity, but surprisingly, they remain poorly understood. In this LDRD project we aim to establish a sustainable workflow for multiresolution studies of these molecular-scale processes to elucidate the impact of water on material surfaces and overall function. This will be achieved through correlating ultrafast time-resolved and spatially resolved optical microscopies that report on electronic and molecular processes at intrinsic time and length scales, ellipsometry and impedance measurements that describe the spatially averaged properties of the water layer with scanning probe microscopy (SPM) techniques to resolve local electrical transport phenomena. We will explore assemblies of NiO particles as a model system. Such assemblies have shown a remarkable chemiresistive response that is dependent on the local humidity, yet the mesoscale phenomena surrounding this property are not well understood. The success of this short-term project will establish a universal workflow for characterization of spatially heterogeneous surfaces via a unique combination of ultrafast optical microscopies, ensemble measurements, and SPM, thus opening up new opportunities for the study of increasingly complex materials and interfaces on intrinsic time and length scales.

Mission Relevance

The DOE Grand Challenge science questions emphasize the critical need to understand and control matter at the electronic and molecular levels to ultimately drive new and efficient energy technologies. Among the many approaches to meet these needs exists the major challenge of characterizing molecular structure and dynamics in complex and heterogeneous media. To address these challenges, new combinations of techniques, each with inherent advantages and complementary data streams, are required to interrogate the range of possible molecular and dynamic phenomena taking place on intrinsic time and length scales. Through the combination of experimental approaches making use of highly specialized instrumentation and novel data analytics, we aim to develop a cohesive physical picture of the role that water plays on material function. This work will position ORNL as a leader in novel materials and chemical-imaging applications, allowing for the pursuit of follow-on funding from multiple agencies (e.g., BES, BER, EERE, NSF, NIH), the Materials Genome Initiative, and mesoscale science opportunities.

Results and Accomplishments

This work developed a universal workflow for co-registration and subsequent data analysis measurements made on radically different instrumentation probing distinctly different properties and dynamics for the study of spatially heterogeneous materials. This approach utilized linear and nonlinear microscopy, optical spectroscopy, and scanning probe measurements to probe novel materials with the potential to sidestep limitations of conventional photovoltaics while creating a basis for the automated analysis of large and complex datasets. Part of this work resulted in a sustainable workflow for data collection and automated analysis using the Bellerophon Enviroment for the Analysis of Materials (BEAM) environment, where it was possible to carry out cross-correlation and multivariate analysis of co-registered data from multiple instruments and multiple measurements . Additionally, we started work to develop G-Spec Ultrafast Imaging, which allows us to circumvent limitations in data collection for time-resolved measurements.

Information Shared

Submitted manuscripts:

Low temperature operation of UV-activated ZnO films on flexible substrate for O2 and H2O sensing" to (ACS Sensors)

Jacobs C. B Wang K. , Ievlev A., Collins L. F, Muckley E. S., Ivanov, I. N Functional 2D/3D assembly of nickel oxide and monolayer WS2 J. (Photonics for Energy) PTS 69995

Conference presentation:

PTS 69102: Jacobs C. B Wang K. , Ievlev A., Collins L. F, Muckley E. S., Ivanov, I. N Towards functional assembly of 3D and 2D nanomaterials SPIE Optics + Photonics August 28-September 01, 2016 Proc. SPIE 9929, Nanostructured Thin Films IX, 99290C (26 September 2016); doi: 10.1117/12.2238211

Follow on funding:

150K CRADA SMALL BUSINESS VOUCHER PROGRAM COOPERATIVE RESEARCH AND DEVELOPMENT AGREEMENT NO. NFE-16-06392 Scalable Processing of High Efficiency ZnS Quantum Dots with Nano Elements Source, LLC

NEXT GENERATION SCIENCE FOR NEUTRON SOURCES

06789

Thermomechanical Integrity of Critical Engineering Structures by High Spatial Resolution Neutron Diffraction

K. An, A. Stoica, E. Iverson, P. Peterson, Z. Feng, J. Carpenter

Project Description

Measurements obtained by nondestructive deeply penetrating neutron diffraction provide essential information for understanding mechanical integrity and predicting the life of critical engineering structures such as dissimilar metal welds in nuclear power systems. The complex inhomogeneous chemical composition and microstructure in such systems require high-spatial-resolution (HSR) measurement to accurately resolve the stress/strain and microstructure for benchmark modeling results. The objective of this proposal is to develop new collimation techniques to enable unprecedented HSR (down to 200 μm) for diffraction measurements of lattice strain, phase, and microstructure for the material in complex engineering structures. New collimation techniques and novel data acquisition algorithms will be developed by making use of the high-flux white spectrum and the advanced detector systems of the VULCAN diffractometer at the ORNL Spallation Neutron Source (SNS). The one-order-of-magnitude improvement of spatial resolution at VULCAN will enhance the current engineering neutron diffraction capability and will enable fine profiling of stress/strain, texture, and phases in critical structural materials as well as monitoring of phase transformation and energy-conversion processes in functional materials.

Mission Relevance

The new and unique capabilities developed from this LDRD project will strongly position the DOE-funded SNS to pursue scientific and engineering problems that cannot be handled at other neutron-scattering facilities. It will strengthen the in-house scientific capability and will attract high-quality collaborative research projects. It will benefit scientific and applied programs related to in situ HSR materials studies funded by DOE BES and EERE; DOD (Army, Navy, Air Force); and industries.

Results and Accomplishments

We have demonstrated the HSR neutron diffraction mapping capability by pinhole diffraction with a high-resolution He-3 detector module that matches the proposed HSR pinhole diffraction. The spatial resolution was improved from 2 mm to 1, 0.5, and 0.2 mm configurations by implementing the single-channel slit systems in front of a shifted collimator. A 2D HSR grain texture measurement was also demonstrated. A lamellar mockup sample validated the spatial resolution in both 1D and 2D, and a scientific engineering application demonstration was taken on Mg alloys under in situ bending and in situ torsion, in which a different amount of twinning varies through the sample thickness due to the strain gradient. In situ thermomechanical deformation strain across the material interface of a dissimilar weld was measured by the new capability. A pseudorandom multichannel slit diffraction configuration has been designed and measured with the developed collimation boxes to increase the diffraction intensity while maintaining the HSR. The capability will be funded and implemented in the VULCAN user program as part of instrument upgrade project with He-3 detector expansion. The new capability will directly enhance the neutron-scattering user program at SNS by providing a new tool with which to tackle issues in fundamental and applied research of the mechanical integrity of critical engineering structures.

Information Shared

Wu, W. et al. 2016, "Intragranular twinning, detwinning, and twinning-like lattice reorientation in magnesium alloys", Acta Materialia, **121**, 15-23.

Wu, W. et al, 2016, "Investigation of deformation twinning under complex stress states in a rolled magnesium alloy", Journal of Alloys and Compounds, **683**, 619-633.

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Invited, Stoica A. D. and An, K. 2014, 63rd Annual Conference on Applications of X-ray Analysis, Big Sky, Montana.

Invited, An, K. et al, 2015 MECASENS 8, Grenoble, France.

07331

Development of a Wide-Angle Neutron Velocity Selector for the Neutrons Scattered at the Sample Position at Inverted-Geometry Spectrometers

E. Mamontov, W.M. McHargue, A.F.M. dos Santos, J.C. Neuefeind, A.J. Ramirez-Cuesta, C.A. Tulk

Project Description

We propose to design and build a novel device that will enable inelastic neutron-scattering experiments using wide-angle velocity selection (WAVES) of broad-energy-band incident neutrons scattered from the sample. The device will be implemented first at the existing time-of-flight diffractometers at the ORNL Spallation Neutron Source (SNS). Implementation on NOMAD and SNAP, the most immediate candidates, would enable, respectively, simultaneous measurement of inelastic excitations and pair-distribution function and inelastic experiments at extremely high pressures. The ultimate goal is to gain experience with the design, construction, and operation of these devices to implement them at two new spectrometers at the SNS Second Target Station: a very high-resolution backscattering spectrometer and a high-resolution broad-band inverted geometry spectrometer. These spectrometers will feature a small-incident-beam cross section optimized for studying small samples, such as proteins, that are available only in limited quantities. They will share the optimized sample holders and together will provide coverage over about six to seven orders of magnitude in the relaxation times, which is essential for biological and soft-matter systems. Both spectrometers will require implementation of the WAVES devices that we are going to prototype and test at the existing instruments in the course of the proposed LDRD effort.

Mission Relevance

The proposed project directly addresses the call for a new generation of neutron instrumentation. The novel device, WAVES, to be built and tested in the course of the proposed effort, will enable new capabilities at existing instruments at the first SNS target station and, importantly, will make possible the construction of the two new spectrometers at the SNS Second Target Station. This will provide unprecedented opportunities for neutron-scattering studies of microscopic dynamics in soft matter and biological systems. The operation and development of neutron-scattering facilities at SNS is supported by the BES Scientific User Facilities Division.

Results and Accomplishments

We have received the assembled WAVES device from Astrium GMBH (Airbus), the principal project vendor, along with the detailed calculations of the stresses and strains anticipated in the course of WAVES operation. We have procured necessary auxiliary parts from SKF, another project vendor. The chamber for off-line WAVES testing has been manufactured. The vacuum pumping system has been procured. The parts for the chiller system have been procured. All machine protection sensors (such as an infrared thermocouple sensor) and cables have been purchased. A rack and chassis for WAVES operation have been purchased. The design of the NOMAD housing for WAVES has been finalized. Two novel concepts of neutron spectrometers utilizing WAVES and sandwich-type WAVES (SANDWAVES) for SNS Second Target Station and a reactor-based source, respectively, have been proposed and published.

Information Shared

“A novel approach to neutron scattering instrumentation for probing multiscale dynamics in soft and biological matter”. E. Mamontov. Journal of Physics: Condensed Matter 28, 345201 (2016).
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07374

Development of Novel Neutron Spin-Echo Methods for Ultrahigh-Resolution Spectroscopy at ORNL

J. Fernandez-Baca, R. Pynn, F. Li, S. Parnell, W.A. Hamilton, A.D. Christianson, G. Ehlers

Project Description

The purpose of this project is to develop the expertise and capabilities to implement novel neutron spin-echo (NSE) techniques for ultrahigh-resolution neutron spectroscopy at ORNL. NSEs, in combination with triple-axis spectroscopy at a high-flux reactor, can be used to determine lifetimes of dispersive excitations over the entire Brillouin zone with microelectron-volt resolution. Such measurements are the most direct way to unlock the relationship between the fundamental interactions and couplings in complex materials. Currently this ultrahigh-resolution spectroscopy can be achieved by a technique called neutron resonance spin echo (NRSE), which was developed in Europe and is only available at the high-flux reactors in Munich and Berlin, Germany, and at the Institut Laue Langevin, in France. The goal of this project is to develop the expertise and capabilities in NSE techniques that are not available in the United States. The effort will be based on the newly developed superconducting magnetic Wollaston prisms (WPs), which will be used instead of the radio frequency (RF) coils used in the NRSE technique to encode the neutron spins. This development will enable science in the United States that now can only be pursued in Europe.

Mission Relevance

This project is directly relevant to the mission of the DOE SC scientific user facilities to provide the most advanced tools of modern science to perform scientific research. The combination of NSE and triple-axis spectroscopy provides unique microelectron-volt resolution at a wide range of energy transfers, which is otherwise inaccessible to neutron or x-ray spectroscopies or any other method. The development of expertise and capabilities in these techniques that fully utilize the unique properties of neutrons is essential to providing the US scientific user community with modern techniques for ultrahigh-resolution neutron spectroscopy. It is anticipated that these types of measurements, which enable the understanding of the interplay of various subsystems, will become increasingly important in the study of strongly correlated systems in the years to come.

Results and Accomplishments

Completion of the construction and tests of two WP pairs and associated vacuum vessels. The team designed, constructed and tested two WP pairs (WPPs) and associated vacuum vessels to perform ultrahigh-resolution spectroscopy (single- or double-arm Larmor diffraction and phonon-focusing applications). Each WPP consists of two WPs separated by a guide field unit. The four coils of each WP are wound separately to better protect the integrity of the high-temperature superconducting (HTS) tape and to achieve a better control of the different magnetic field intensities. The HTS coils have been designed to hold currents of at least 30 A and to provide a magnetic field of 35 G/A. It was found out that the operation of the WPP requires very stable power supplies that can be operated in a controlled temperature range.

Demonstration of the tilting of magnetic field boundaries using WPPs. The main accomplishment of this project was the demonstration that the WPPs can be used to tilt magnetic field boundaries in a manner that is equivalent to that of the RF coils in the NRSE technique, and thus they can be used for ultrahigh-resolution neutron spectroscopy applications. Unlike the RF coils in the NRSE technique, where the tilting of the magnetic field boundaries is accomplished by the physical rotation of the RF coils, the tilting of the magnetic field boundaries is accomplished by the manipulation of the magnetic fields in the HTS coils. This demonstration involved the measurement of the lattice parameter of a silicon crystal using a single-arm WPP Larmor diffraction.

Demonstration of high-resolution spectroscopy. Single- and double-arm WPP setups were used to measure the lattice expansion of a perfect copper single crystal using Larmor diffraction. The measured lattice expansion of copper using the double-arm WPP setup was within 0.5×10^{-4} of the published value. This precision can be improved by achieving a better temperature stability of the power supplies. A mu-metal shield was fabricated for the sample and the closed-cycle refrigerator to provide a zero-field environment suitable for phonon-focusing measurements in an isotopic germanium single crystal. The first attempt to measure the linewidth of the germanium acoustic phonons was not successful, but an understanding of the experimental issues that prevented this measurement was achieved.

Information Shared

No information shared in FY 2016

07406

High Resolution Solid State Neutron Detectors for Second Target Station

R. Riedel, J.P. Hodges, Z.W. Bell, D.J. Singh, C.A. Bridges, M.P. Paranthaman, A. Burger

Project Description

This project seeks to couple the search for a new high-brightness scintillator with the search for a new sensor based on a silicon photomultiplier (SiPM) detector. Theory based on first-principles calculations is used to obtain the electronic structures of $Li_2Se(Te)$ and to predict scintillation and optical properties. These results are then used in selecting compounds most suited to experimental investigation, helping guide optimization of the materials and in interpreting experimental results. Different growth parameters using Bridgeman growth under a variety of conditions will be used to synthesize the most promising compounds. To obtain large-area scintillators, experiments will be made involving the sintering of single-crystal precursor materials as well as other promising compounds. A test platform using SiPM sensors will then be constructed.

Mission Relevance

The Anger Camera Neutron detector developed at ORNL and its use on three instruments at the Spallation Neutron Source (SNS) have the potential for greatly expanded use at the Second Target Station and by the larger scientific community if the current resolution of 1 × 1 mm can be increased. To achieve resolutions in the range of 100 to 300 µm, a new high-light-yield neutron-sensitive scintillator must be found, and the use of a new class of optical sensors will be required.

Results and Accomplishments

Three very exciting accomplishments occurred as a result of research directed by this LDRD project.

Discovery of $Li_2Se(Ag)$, a new neutron-sensitive scintillator. A new neutron scintillator, Li_2Se doped with silver, was discovered. The original first-principles calculations made during the first LDRD year led to the first growth of the intrinsic material, which did not scintillate. The successful growths of Li_2Se via the flux melt method at Fisk University led to an additional set of growths containing Ag as a dopant. A distinct scintillation response was observed when the transparent (slightly brownish) crystals were first measured using alpha excitation at Fisk. Measurements were subsequently done at ORNL for neutron, radio-luminescent, and photo-luminescent responses. A light yield spectrum for neutron response is about one-third that of GS20 lithium glass. The response to neutrons was quite strong in spite of the use of natural Li in the crystal growth. Additional oxidation of the sample was noted during the transport from Fisk to ORNL. The sample measured at ORNL was a deep red, indicating, at a minimum, additional surface oxidation that was not present immediately after growth. The effect of the oxidation to the light yield or other properties could not be determined. However, it did not completely suppress the scintillation from the material. Measurement of the sample in a fluorimeter failed to produce a photo-luminescence peak. A radio-luminescence peak centered near 410 nm was measured during exposure to gamma rays.

Development of a very high-resolution SiPM-based Anger Camera detector. A 50 × 50 mm test platform using an 8 × 8 array of SiPM 6 × 6 mm sensors, GS20 as a scintillator, and standard Anger Camera electronics was completed. We measured the resolution of the test system using a modulation mask, which consists of line pairs of various widths from 0.5 to 1.5 mm. Using the calculated modulation, we measured a resolution of 650 µm, which is a significant improvement over the current production

Anger Camera value of 1.2 mm. We found the noise current associated with the SiPM to be acceptable at room temperature, so a Peltier cooler was not needed to provide a functional prototype.

Synthesis and characterization of LiF/CaF_2:EuF_2 scintillators. Significant progress was made toward development of a LiF/CaF_2 eutectic scintillator that could provide an alternative to the slow LiF/ZnS scintillator screen currently in use at the POWGEN powder diffractometer at SNS. We have shown reproducible growth of eutectic material that has three times the light yield of commercial GS20. Addition of a small amount of AlF (1%) to the melt was found to stabilize the Eu in the material and is believed to be responsible for improvement in scintillation uniformity and reproducibility. Examination of the various growths with inductively coupled plasma (ICP) spectroscopy shows a dramatic difference in distribution of the elements between LiF/CaF_2 and LiF/CaF_2 having 1% AlF. Without the AlF we find that Eu is not associated with the location of CaF_2 crystals. With the addition of AlF, the Eu is well located near the CaF_2 grains, and the segregation of LiF and CaF_2 is less severe. The grain separation of LiF and CaF_2 seen in the ICP data can also be seen visibly and is of the order of 1 mm.

A very exciting discovery was made during the measurement of thin films of the eutectic material. We find that there is a pulse shape difference between gammas and neutrons in the thin films. This discovery is the first known indication of neutron/gamma pulse shape difference in the eutectic material.

Information Shared

No information shared in FY 2016

07739

Virtual Experiments in Neutron Spectroscopy (VirtuES)

A.J. Ramirez-Cuesta, L.L. Daemen, S. Campbell, Y. Cheng

Project Description

For the first time in the history of neutron scattering, an inelastic neutron-scattering spectrometer will be able to effectively perform spectroscopy on large, complex systems. The VISION spectrometer at the Spallation Neutron Source (SNS) is unique and extremely powerful. It is the world's only high-throughput broadband inelastic neutron-scattering (INS) spectrometer and has the world's highest-energy resolution. The instrument has two complementary medium-resolution, high-count-rate diffraction banks, which give it unparalleled capabilities to determine simultaneously the structure and dynamics of materials. At the moment we are designing and building a sample changer that will allow the measurement of tens of samples on a daily basis. With this high throughput, VISION is facing the challenge of timely data analysis and interpretation. Its extraordinary sensitivity allows the measurement of extremely small signals in large backgrounds, making the study of subtle effects in chemistry and catalysis apparent to neutron studies. Ultimately, we want to establish that computer clusters dedicated to data interpretation and experiment steering on high-throughput beamlines will become the norm at high-power, advanced neutron sources.

Mission Relevance

Successful completion of this LDRD project will establish a US leadership position in chemical spectroscopy with neutrons by developing the next-generation approach to data collection, reduction, and analysis. There is no equivalent instrumentation in the world. The bottleneck to scientific production is data interpretation. With the unparalleled data throughput of VISION, a dedicated computer cluster is required for delivering high-impact science. The experience developed in the proposed work will then be extended to other high-throughput beamlines worldwide and to the SNS Second Target Station instruments. Linking ORNL's advanced neutron facilities with its world-leading computational expertise will create a new model for understanding and predicting material properties. Our data and modeling methodology integrates neutron scattering with ORNL strengths in high-performance computing and materials theory. Successful completion of this LDRD project represents a significant step toward establishing ORNL as a leader in the integration of world-class computational capabilities and world-class experimental facilities, thus providing the foundation for a paradigm shift in materials research.

Results and Accomplishments

The cluster was installed in February and March 2016. During the installation, we got access through the ORNL Compute and Data Environment for Science to temporary computational resources (2 Cray XK7 cabinets containing 184 compute nodes, each with 16 cores). The cluster was commissioned, and software was purchased and compiled.

We organized and ran a workshop with Dr. Greg Schenter from PNNL on the use of CP2K to perform molecular and lattice dynamics and to train users on the software.

We studied the gate-opening effects on metal organic frameworks (MOFs), using INS experiments and DFT lattice dynamics collaborations. We determined the mechanism that produces the gate opening thorough the interaction of the adsorbed molecule and the methyl groups on the organic linkers. A paper was published in *Chemical Communications* (impact factor of 6.6). A second paper, which describes how the study was extended to include other gases to determine the nature of the interaction upon the dipolar moment of molecules, has been submitted, also to *Chemical Communications*.

We studied SO_2 adsorption in a MOF to understand the mechanism of the highly selective adsorption. The adsorption sites and orientations as well as the vibrational properties of the SO_2 molecules were determined by DFT calculation, and the results were compared with neutron powder diffraction and INS experiments. The paper was published in *Advanced Materials*. Following a similar strategy, we performed simulations on CO_2 adsorption in a different MOF, in which the hydrogen bonding is known to play a key role in the interaction between the gas molecules and the host. The calculated INS difference spectra match experiment perfectly, confirming the finding that the macroscopic packing of CO_2 in the pores is directly influenced by the primary binding sites. This study was published in *Nature Communications*.

We also used VirtuES to study hydrides. For example, we studied a series of alanates to understand their vibrational spectra. Combining the experimental data collected at VISION, we were able to understand the roles of different vibrational modes on hydrogen release, which is important for their potential applications in hydrogen storage. This paper was published in *Chemical Communications*.

Information Shared

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6. Y. C. Li, et al. "Neutron vibrational spectroscopic studies of novel tire-derived carbon materials" to be submitted
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SCIENCE AND INFORMATICS FOR ENERGY AND URBAN INFRASTRUCTURE

07365

A High-Performance, Data-Driven Simulator of the American Population for Modeling Urban Dynamics

R. Stewart, H. Aziz, A. Morton, H.B. Park, S. Duchscherer, J. Piburn, M. Hilliard, M. Maness, N. Nagle

Project Description

Major areas of urban dynamics research, such as energy, water, transportation, and health, are closely linked to the demographic composition of populations. By forging links between energy, demography, and household size, demographically rich agent-based transportation modeling exemplifies important connections between dynamics and population data. Traditional reliance on census data is no longer possible due to spatial coarseness of the data. Contemporary high-resolution population count models (e.g., LandScan) offer no estimates of demographic composition. The lack of a high-resolution, diurnal (day/night) demographic population model is a substantial obstacle in advancing urban dynamics. To address this, we developed a customizable diurnal demographic model with unprecedented resolution and geographic coverage by extending the recently developed Penalized Maximum Entropy Model to include nighttime demography and daytime worker demography and to demonstrate the use of this data within an urban transportation case study. The result represents an unprecedented advance in the population sciences, enhances ORNL's leadership position in urban demography, and provides crosscutting support to major DOE focus areas in energy and environment.

Mission Relevance

Because population and population dynamics underpin water and energy consumption, transportation, and environmental impacts, high-resolution demographic data of the kind developed in this LDRD project and the use of the data within spatiotemporal modeling systems will influence nearly every mission area of DOE, EPA, NIH, and NRC. The work has been used by a DOE Energy Policy and Systems Analysis project, in which households that have adopted distributed solar generation are characterized. In another LDRD project at ORNL, "Fine-Resolution Modeling of Urban-Energy System's Water Footprint in River Networks," it has been used to create high-resolution demographic data for energy consumption modeling. These activities clearly demonstrate at an early stage the impact that this research can have in characterizing, modeling, and planning in energy, water, and transportation missions.

Results and Accomplishments

Population as a service (PaaS). The P-MEDM algorithm, which simulates the American population at the block group level and is critical for downscaling and reconstructing rich demographic detail, was situated with a user interface for selecting areas to create synthetic populations within a computational environment for rapid data ingestion, computation, and delivery. Users can now easily choose the areas in which they wish to simulate real populations with high spatial and demographic detail.

Worker Simulated Flow origin-destination demography model. The novel Worker Simulated Flow probabilistically moves workers, with rich demographic detail from the PaaS model, from their nighttime block group to daytime block group locales, thus creating an industry-specific worker flow model under uncertainty. Because demographic detail remains attached to workers during model flow, scientists can simulate the kind of workers (race, gender, income, education), where they might live, and where they might work. The implications are substantial for transportation models.

High-performance computing (HPC) agent-based non-motorized commuter model. As a proof of concept for transportation theorists, ORNL implemented an HPC agent-based modeling and simulation model that probabilistically simulates the commute modes of millions of commuters in New York City, given each worker's demographic characteristics, community infrastructure, and social influences. The simulation exercise was used to demonstrate how the PaaS and Worker Simulated Flow models scale, how theorists could use the demographic data, and how urban planners could investigate "what-if" scenarios.

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07396

Scalable Data and Informatics for Connected Vehicles Leveraged to Enhance Efficiency

A.A. Malikopoulos, J. Carter, S. Hong, W. Lu, J. Rios-Torres

Project Description

Recognition of the necessity for connecting vehicles to their surroundings is gaining momentum. In this "new world" of massive amounts of data from vehicles and infrastructure, what we used to model as uncertainty (noise or disturbance) for traffic becomes additional state information in a much higher-dimensional vector. Connected and automated vehicles (CAVs) provide the most intriguing opportunity for enabling users to better monitor transportation network conditions and make better operating decisions to improve safety and reduce pollution, energy consumption, and travel delays. Progress has been made, especially in the area of safety and how accidents could be prevented, but the extent to which we can improve fuel consumption if we assume that the vehicles are connected and can exchange information with each other and with infrastructure remains to be determined. This project directly addresses the appropriate conceptual approaches for control and optimization to achieve a smooth traffic flow by coordinating CAVs at different transportation segments (e.g., intersections, merging roadways, speed reduction zones. The long-term potential benefits of the outcome of this research are substantial. Overall operation of vehicles can be improved in terms of fuel economy and greenhouse gas emissions. Coordination of vehicles will help in avoiding congestion, eliminating stop-and-go driving, and reducing engine idling, thus enabling additional fuel savings and improving comfort.

Mission Relevance

In the approach that we take in our LDRD project, vehicles do not operate in isolation. They can integrate external data and are understood to function as part of a whole. The direct implication of our approach is that it changes the mathematical framework of how traffic flow is optimized by converting noise-based models into almost entirely deterministic ones with larger state spaces. The outcome of this project 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 and that decrease the dependence on foreign energy sources. The results of this project would also be of great importance and interest to DARPA, and thus could generate further funding opportunities, because it can be used for military CAVs.

Results and Accomplishments

The overarching goal of this project is to establish a rigorous optimization framework and to develop the decentralized control algorithms for online coordination of vehicles within an environment where vehicles are wirelessly connected to each other and to an infrastructure. The underlying concept hinges on the idea that, because of the massive amounts of data available from vehicles and infrastructure, what we used to model as uncertainty (noise or disturbance) becomes additional input or additional state information in a much higher-dimensional vector. In that context, we modeled mathematically vehicle interactions in different transportation segments (e.g., intersections, merging roadways, speed reduction zones), and we Formulated a centralized optimal control problem and established that the safety constraints dictate the time for each vehicle to cross an intersection or merge into another roadway, by forming a first-in-first-out (FIFO) queue with the time dependent only on the preceding vehicle's state. Once the time for each vehicle is determined, the centralized problem becomes, under certain conditions, equivalent to a decentralized framework over all CAVs in the FIFO queue.

We also showed that, under certain conditions, the centralized problem becomes, equivalent to a decentralized framework whereby the extent to which each CAV minimizes its energy consumption is subject to the throughput-maximizing timing constraints. We presented a complete analytical solution of these decentralized problems and derived conditions under which feasible solutions satisfying all safety constraints always exist. We conducted several simulation studies to quantify the impact of having vehicles coordinated in these transportation scenarios and compared them to the state of the art (e.g., intersections with traffic lights, merging roads with stop signs to prove the concepts and to evaluate the effectiveness of the efficiency of the optimal solution. We quantified the impact of these concepts in terms of fuel consumption and travel time. The studies indicated that fuel consumption can be improved by up to 65% and that travel time can be improved by up to 35%.

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07399

Fine-Resolution Modeling of Urban-Energy Systems' Water Footprint in River Networks

R.A. McManamay, S. Surendran Nair, R.N. Stewart, A. Morton, C.R. DeRolph, S.-C. Kao, B.T. Smith

Project Description

Characterizing the interplay between urbanization, energy production, and water resources is essential for ensuring sustainable population growth. Water is a critical resource, supporting infrastructure, societal needs, and ecosystem services upon which humans depend. In order to balance limited water supplies, competing users must account for their realized and virtual water footprint (i.e., the total direct and indirect net amount of water consumed, respectively). Unfortunately, publicly reported US water use estimates are spatially coarse and temporally static, and they completely ignore returns of water to rivers after use. These estimates are insufficient to account for water budgets in urbanizing systems characterized by high spatial and temporal heterogeneity in infrastructure, population demographics, and subsequent water use. Likewise, urbanizing areas are supported by competing sources of energy production, which also have heterogeneous water footprints. Hence, a fundamental challenge of planning for sustainable urban growth (and decision making across disparate policy sectors) lies in characterizing interdependencies among urban systems, energy producers, and water resources. As a result of this LDRD project, we will present a modeling framework at an unprecedented scale that provides a novel approach to integrating urban-energy infrastructure into a spatial accounting network that accurately measures water footprints as changes in the quantity and quality of river flows. River networks (i.e., networks of branching tributaries nested within larger rivers) provide a spatial structure to measure water budgets by modeling hydrology and by accounting for use and returns from urbanizing areas and energy producers.

Mission Relevance

This LDRD project will contribute to the scientific and technical vitality of ORNL by exploring the dynamics of water consumption in urban energy systems at an unprecedented scale. This proposal specifically addresses a DOE initiative, the Energy-Water Nexus, a research agenda for the national laboratories to better understand linkages among energy demands and water resources. By measuring spatially and temporally dynamic water footprints and by integrating urban and energy systems, this project is creative and stimulates new exploration in science and technology. The proposed research would be a proof of concept for accurate water budgeting and multifaceted decision making. The proposed research is high risk, in that the concept is a novel and unproven, but also highly valuable in that it provides a tractable concept for DOE funding. ORNL is well positioned for this research as it integrates and strengthens existing capabilities in the geographic data sciences, population distribution modeling, energy network and infrastructure modeling, future land use and population projection models, and ecological systems models.

Results and Accomplishments

We accomplished our objective to provide a futuristic decision support tool to sustainably plan and minimize the impacts of urban expansion on the water cycle. We used Atlanta, Georgia, and Knoxville, Tennessee, as case studies. We evaluated direct future impacts of urban expansion on the water cycle by evaluating population growth, increased impervious land surfaces, and future water intakes to meet public water consumption. We also evaluated indirect changes to the water cycle through elevated energy demands requiring increases in surrounding energy producers, including those relying on water to generate electricity (e.g., thermoelectric facilities, hydropower). We developed more than 40 scenarios of future urban expansion through 2030 and 2050 that include various configurations of future land cover, future water supply intakes, future energy demand, and divergent future energy portfolios with varied goals of being carbon-neutral or water-neutral. In each scenario, we evaluated impacts to the water cycle and subsequent impacts to aquatic biodiversity. Urban and regional planners can evaluate urban expansion within the context of holistic impacts to water.

To accomplish building this framework, we first used the Soil and Water Assessment Tool (SWAT) to develop a dynamic river network modeling framework that accounts for water budgets from the urban-energy interface as changes in water quantity and quality to river systems. We also modeled energy and water demand at very high resolutions (block groups) in the landscape to link urban dynamics with water and energy consumption. Doing so provided a mechanism with which to identify the water intakes and energy producers that supported each metropolitan area. LANDCAST provides grounds to estimate future water footprints. We used it to model future urban expansion, including population growth, urban footprint, and land cover.

We estimated future energy and water demands based on population growth. Optimization procedures were used to identify locations of optimal water intakes and power plants under a series of contrasting future goals that range in water-neutral versus carbon-neutral future strategies. We generated more than 40 scenarios that included future landcover, water intakes, and energy demands. Each scenario was modeled in SWAT to examine changes in the water cycle and subsequent impacts to biodiversity.

Information Shared

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07451

Integrated Framework for Urban Climate Adaptation Tool (Urban-CAT)

O.A. Omitaomu, E.S. Parish, P.J. Nugent, R. Mei, L.M. Sylvester, K.M. Ernst, M. Absar, T. Carvalhaes

Project Description

The president has asked "America's top-sector innovators to leverage open government data resources and other datasets to build tools that will make America's communities more resilient to climate change and to forge cross-sector partnerships to make those tools as useful as possible." Through collaboration with the City of Knoxville, Tennessee, we are developing the Integrated Framework for Urban Climate Adaptation Tool (Urban-CAT) to help urban governments understand climate change impacts on water infrastructure; identify and prioritize adaptation options (e.g., green infrastructure emplacement) for minimizing projected impacts; and explore potential benefits of the adaptation options under different scenarios related to urban growth and infrastructure evolution. Integration of climate model outputs with infrastructure and population data will help local governments understand potential tradeoffs between urban-planning objectives and risks due to climate change. Collaborating with decision makers throughout the project will improve the understanding within the climate-modeling community of the data and tools needed by US cities. The impacts of this project include adaptation of the tool to other urban areas in the United States within 3 years and in other countries within 10 years, enhancement of community-based adaptation planning process to water-related climate-induced impacts, and successful translation of science to solutions.

Mission Relevance

Cities have an opportunity to become more resilient to future climate change through investments made in urban infrastructure today. Provision of scientifically based tools for evaluating local climate change impacts will be critical to the development of adaptation strategies. In particular, mid-sized cities, which are home to nearly half the world's urban dwellers, lack access to the credible high-resolution climate change projection information needed to assess and address key vulnerabilities arising from future climate variability in conjunction with a growing population. The capabilitie*s* developed in Urban-CAT will provide a platform to facilitate communication among urban policy decision makers; promote science-driven policies and regulations for updating urban infrastructure; help to quickly identify, adapt for, and mitigate emerging environmental problems; and provide guidance for planning judicious urban development. These capabilities target DOE's five-year objectives recently proposed in the energy-water nexus and climate change "Big Ideas."

Results and Accomplishments

To ensure credibility and local relevance of the developed framework, we established collaboration with key stakeholders from City of Knoxville and exchanged datasets for co-production of knowledge. We met quarterly and brought them to ORNL at various times over the two-year period. In spring 2017, we will discuss our final results to with our City of Knoxville collaborators and meet with Mayor Rogero. We extended the collaboration to the Knox County Storm Water Association in FY 2016 following an invitation to speak at its East Tennessee Regional Meeting in March 2016. The association provided us with several datasets for integration into Urban-CAT, and we have shared climate data and information with them in return.

To understand climate impacts at different spatial resolution, we have implemented novel bias-correction and statistical techniques to downscale the original 18 km climate data to 1 km and 4 km over Knoxville using DayMet historical data. Using the downscaled climate data for 1 km and 4 km, we completed statistical analysis to assist in determining the similarities and differences among the model scenarios. The results are used to provide monthly summary data to decision makers. A technical report based on these results is made available to the collaborating stakeholders.

We analyzed the implications of climate data on the rainfall frequency spectrum in Knoxville and the surrounding region. The daily precipitation values are used to determine changes in percentile rainfall event depths for planning and mitigation of storm water runoff over the past (1980–2005) and future (2025–2050) periods. A technical report based on these results is made available to the collaborating stakeholders.

We analyzed the implications of climate data on plant hardiness zones for green infrastructure planning using the City of Knoxville and the surrounding region as a case study. The modeled climate data for the past are daily data from 1980 to 2005; the future data are projected for 2025 to 2050. The average was calculated of all the modeled annual extreme minimums for each time period of interest. Each raster cell was placed into zone categories based on temperature, using the same criteria and categories suggested by the USDA. Overall, the outputs suggest that the region of interest is moving into the next warmer zone, which indicates that some of the current tree species may not survive in this region in the future. A technical report based on these results was made available to the collaborating stakeholders.

We developed a theoretical framework for Urban-CAT to explicitly define and integrate sustainability and resilience objectives needed for robust indicator selection and measurement, both for the immediate task of helping Knoxville with green infrastructure placement and as a means to extend our work to other cities and climate adaptation concerns. We also developed computational data services that will help local planners process and analyze all the available climate data in a more efficient manner. The services allow users to select the climate data of interest, select the statistics of interest and year, and initiate the data processing. The outputs are available as a downloadable data in geographic information system formats. This helps local planner have access to the appropriate method for processing climate data.

In consultation with the stakeholders, we developed some key underlying questions for evaluating urban-scale green infrastructure placement decisions. Using these questions as guidelines, we developed a list of relevant resilience indicators and collected related datasets. We processed the datasets and developed a framework for identifying suitable areas for placing green infrastructure of different types in conjunction with cost-benefit considerations and several climate change scenarios. The framework is formalized as an if-then scenario capability and integrated into Urban-CAT.

To disseminate the developed framework, we designed the technology stack for a web application. The framework is built to be deployable to various cloud environments and to possess a service-oriented architecture for interoperability with multiple data sources and geo-processing tasks. The framework also is highly configurable in that the stack may be rebranded per stakeholder organization and configured with a predefined area of interest and relevant datasets and processes. The tool is divided into two major areas, the Mayors Corner and the Planners Corner. The Mayors Corner contains the various data outputs obtained as part of this project. These outputs are available for visualization. The Mayors corner is meant for decision makers who want to see and use the model outputs but who are not interested in the details of the data modeling. The Planners Corner, on the other hand, is meant for planners or users that may want to develop their own scenarios and run our models.

We established collaboration with an interdisciplinary team at the University of Tennessee to submit a Joint Directed Research and Development Program proposal in FY 2016. The proposal was selected for funding. We also collaborated with a larger team to submit a proposal to the NSF. The NSF proposal was also selected for funding. The NSF project will begin in FY 2017.

This project was integral to a recent $100M proposal submitted by ORNL's Climate Change Science Institute and Urban Dynamics Institute to the MacArthur Foundation in collaboration with Resilient Cities on October 5, 2016.

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STRATEGIC HIRE

07285

Chemical- and Radiation-Induced Volumetric Expansion of Mineral Composite Interaction with Cement-Like Materials

Y. Le Pape, K. Field, E. Tajuelo Rodriguez, Y. Yang

Project Description

The objective of this LDRD project is to provide a comprehensive understanding of the mechanisms and effects of combined radiation-induced and alkali-silica reaction (ASR)–induced swelling of silicate-based aggregate on the mechanical behavior of concrete used by the nuclear industry. The mechanisms of the ASR are fairly well understood, but those of concrete irradiation are, to a great extent, limited to the characterization of residual macroscopic use properties after exposure to neutron and gamma radiation. Although several degradation mechanisms may be involved during the radiation of concrete, a relationship has been identified between neutron radiation–induced swelling of the silicate-based aggregate and a decrease in the strength and elastic properties of concrete. A preliminary micromechanical model confirms that aggregate volumetric expansion plays a dominant role in an increasing amount concrete damage and swelling. Although radiation-induced volumetric expansion requires further investigation, it is strongly suspected that amorphization of silicate-based minerals is primarily responsible for the aggregate swelling. No systematic study of the postirradiation mechanical properties of concrete is currently available, and therefore it is the subject of the first part of the proposed research. The second part deals with the possible synergies of irradiation combined with ASR. This project will investigate in detail the effects of different interactions resulting from various irradiation conditions (i.e., temperature, loss of moisture, gamma-induced radiolysis, and neutron-induced amorphization) on the formation of alkali-silica gels. The collected data will serve as the basis for developing a comprehensive model of concrete degraded by chemical- and radiation-induced volumetric expansion (CRIVE) and for determining acceptable service lifetimes of commercial reactors.

Mission Relevance

The electric power industry manages some of the most important concrete infrastructures in the nation. Although some knowledge and best practices from the hydroelectric industry and the transportation sector may apply, the nuclear industry operates under unique conditions and is subject to a more stringent regulatory environment. The DOE Light Water Reactor Sustainability (LWRS) Program aims to investigate most prominent causes of concrete degradation in nuclear structures. The Expanded Materials Degradation Assessment panel of experts identified radiation and ASR as being among the program's top three priorities in terms of structural significance and knowledge gaps for two main reasons. First, the concrete biological shield and the reactor pressure vessel support structure are exposed to high levels of radiation that may affect the mechanical properties of the concrete. Second, several occurrences of the ASR have been reported in nuclear power plants in Canada, France, and Japan, and one more recently in the United States. Although no case of ASR in the biological shield has been reported at this time, such a reaction is possible due to the nature of the concrete mix (similar to other structural concrete) and the high moisture-retention capability of such thick structures. The possibility of a coupling mechanism may increase the volumetric expansion of the aggregate and thus may increase the damage to the surrounding hardened cement paste. A preliminary qualitative analysis showed that if any damage were to occur, it would appear as surface cracking (and hence would be detectable by visual inspection), but it would induce damage beyond the passive steel reinforcement layer because of the formation of temperature, moisture, and irradiation gradients. Existing structural models of the effects of irradiation on nuclear structures ignore the possible implications of induced volumetric expansion. Hence, the current lack of knowledge of the potential impact of CRIVE of concrete on the performance of concrete structures in nuclear reactors requires a specific research plan not being addressed or sponsored by the LWRS Program.

Results and Accomplishments

Objective 1. Irradiation-induced swelling of silicate. A proof-of-principle experiment was conducted using the University of Michigan Ion Beam Laboratory low-energy ion implanter at a total fluence of 10^{+14} Ar^{+}/cm^{2} at 400 keV and room temperature. Based on the Stopping and Range of Ions in Matter (SRIM) code, the implantation depth should be 500 nm for quartz. It was found that quartz attains a metamict state following ion implantation but that calcite remains resistant to radiation damage for the same implantation dose. Molecular dynamics (MD) simulations highlight that quartz is nearly completely disordered by radiation and that calcite is far less affected. Using a confocal microscopy technique, we obtained the differential uniaxial dimensional change (step-height measurement) between an ion-implanted layer and control pristine quartz. The measured change was well aligned with the volumetric and density changes in the literature.

Objective 2. Investigation of the possibility of an irradiation-assisted alkali-silica reaction. *Pristine and ion-implanted samples of synthetic quartz, mica, and calcite as well as natural opal were analyzed with different techniques, including x-ray diffraction and scanning electron microscopy coupled with energy dispersive x-ray spectroscopy and vertical scanning (laser) interferometry. Special focus was placed on ascertaining structural changes induced by ion implantation and its effects on the aqueous reactivity (dissolution rate) of the minerals.* Direct evidence acquired on Ar^{+}-ion-irradiated calcite and quartz indicates that such minerals, which constitute aggregates in concrete, may be significantly altered by irradiation. Specifically, irradiated quartz shows a reduction in density of around 15% and an increase in chemical reactivity, described by its dissolution rate, attaining near equivalence to the dissolution rate of fused (glassy) silica for the same solvent compositions (an increase of about three orders of magnitude). Calcite however, shows little change in dissolution rates although its density is reduced by ≈9%.

Mineral dissolution rates are strongly correlated with a parameter known as "the number of atomic constraints," which describes the rigidity of a network of atoms. The number of atomic constraints is derived from MD simulations. The simulated system consists of a supercell of pristine quartz or calcite containing between 4,500 and 21,000 atoms, depending on the incident irradiation energy. Special focus is placed on quantifying the type and nature of damage, including amorphization, and on evaluating structural rigidity by analysis of atomic trajectories.

This model offers a novel a quantitative means of linking the state of atomic order of a given mineral to its chemical reactivity (i.e., dissolution rate). The research demonstrates a general basis by which chemical composition-structure-property relations can be elucidated for pristine minerals and for minerals that have been exposed to heat, pressure, or radiation and have thus experienced irreversible alterations of their atomic structures. These results clearly confirm the possibility of an irradiation-assisted ASR as a potential degradation mechanism that needs to be considered in license renewal for nuclear power plants.

A new set of experiments has been launched to study the effects of gamma-irradiation of the nanostructure changes of calcium-silicate hydrates.

Information Shared

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07542

Multiscale Model for Plant-Soil Hydraulic Coupling at the Watershed Scale

S.L. Painter, N. Collier, C.M. Iversen, A. Jan, G. Tang, A.P. Walker, J. Warren

Project Description

This LDRD project addressed selected gaps in the simulation capability needed to reliably project the hydrologic response of watersheds to changing climate. The focus was on extending PFLOTRAN, the highly parallel subsurface flow and reactive transport code, to improve its representation of combined soil-plant hydrology in watershed-scale applications. A new subgrid model for root water uptake was developed and was shown to successfully reproduce soil water content measurements from previous ORNL experiments. A fine scale modeling capability that merges an explicit representation of coarse-root architecture with a finely discretized soil volume was also demonstrated. Those new capabilities enable more mechanistic representations of plant-soil coupling at site and watershed scales. In addition, a new, more robust representation of integrated surface/subsurface hydrology, an essential capability for emerging process-rich models of watershed dynamics, was developed, successfully benchmarked, and demonstrated. Taken together, the new capabilities are designed to support improved assessments of how climate stresses, including changes in the timing and magnitude of extreme climate and weather events, affect critical watersheds.

Mission Relevance

The results from this LDRD project contribute to a more reliable capability to project watershed response in future climates, which supports the DOE BER mission to develop understanding of the Earth and its climate as a coupled system. The results are also anticipated to be of interest to DOE's applied energy programs because they can be used to improve the capability to analyze climate impacts on the water supplied to support energy production. The capability under development in the proposed project as well as the longer-term capability enabled by it are also expected to have significant appeal outside DOE; energy utilities, municipalities, and states also need to understand water supply for long-term planning under a changing climate. The integrated surface/subsurface modeling capability developed as part of this project is also relevant to ORNL's Mercury Science Focus Area and thus supports the environmental stewardship mission.

Results and Accomplishments

A multicontinuum model for coupled soil-root hydrology was developed and tested in PFLOTRAN. The approach conceptualizes four interacting continua representing roots, bulk soil, the rhizosphere, and a transition zone between the rhizosphere and the bulk soil. Water contents in the four continua are then solved for simultaneously. In this approach, gradients in water potential within and near roots are explicitly represented and develop dynamically, resulting in root water uptake profiles that respond dynamically to local soil water content and transpiration demand. This dynamic adjustment is in contrast to traditional approaches, which specify a vertical profile for root water uptake. The multicontinuum approach was used to model soil water content measured previously at ORNL's Free-Air Carbon Dioxide Enrichment experiment (run from 1998 to 2009). Using existing meteorological data and previously measured fine-root densities and specific surface area profiles as input, the model was able to successfully reproduce water content measurements with minimal calibration of soil properties. The approach is intended as a subgrid model for use in watershed-scale simulations. It was implemented as a preprocessing step using PFLOTRAN's explicitly defined unstructured mesh capability.

A complementary capability to model hydraulics in an explicitly defined root architecture coupled to a detailed representation of soil was also developed and demonstrated using PFLOTRAN. In the approach, a fully unstructured mesh is used to represent the coarse root architecture, which is then merged with a mesh representing a finely discretized soil volume; fine roots are represented implicitly as connections (possibly nonlocal) between the coarse roots and soil. This fine-scale modeling capability has potential applications in developing and refining hypotheses about root functional architectures and for testing and parameterizing the multicontinuum model.

A new, more robust representation of integrated surface-subsurface hydrology was also implemented in PFLOTRAN. Integrated surface-subsurface models couple three-dimensional solutions for variably saturated flow in the subsurface with the kinematic- or diffusion-wave equation for surface flows. The computational scheme for coupling the surface and subsurface systems is key to the robustness, computational performance, and ease of implementation of the integrated system. A new, robust approach for coupling the subsurface and surface systems was developed from the assumption that the vertical gradient in hydraulic head is negligible at the surface. This tight-coupling assumption allows the surface flow system to be incorporated directly into the subsurface system; effects of surface flow and surface water accumulation are represented as modifications to the subsurface flow and accumulation terms but are not triggered until the subsurface pressure reaches a threshold value corresponding to the appearance of water on the surface. The implementation was successfully compared to published benchmark results. Three-dimensional examples from the Walker Branch and East Fork Poplar Creek Watersheds, at or near ORNL, demonstrate the utility and robustness of the new approach using unstructured computational meshes.

A new model for hydrological effects of a leaf litter layer was also developed. Litter layers are hydrologically important features of forested watersheds because they slow runoff, enhance infiltration, and reduce evaporation from the underlying soil. We developed a dual-porosity macropore/micropore model for water dynamics in leaf litter that qualitatively represents two time-scale dynamics observed from infiltration experiments. Reliable representations of these hydrological effects are important for modeling effects of wildfire on watershed hydrology because wildfire removes or reduces the litter layer.

Information Shared

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07757

Quantum Communications Networks, Scaling Laws and Resource Requirements

N.A. Peters

Project Description

Quantum communications concerns the transmission of quantum states. A great challenge in quantum communications is to overcome the effects of transmission loss, which limits the rate at which quantum protocols may be carried out. Although yet to be fully realized, the standard approach to solving the challenges posed by loss is to use quantum teleportation over a quantum repeater link. However, for such an approach to be widely applicable, it must move beyond single links into large-scale networks, leveraging conventional networking techniques so that users in many locations can be connected. The goal of the proposed project is to derive the scaling laws for quantum communications networks and their resource requirements.

Mission Relevance

The proposed project is relevant to ORNL's mission to deliver basic and applied research to enabling transformative solutions to important problems in energy and security. In particular, the proposed project seeks to gain insight into the costs of building long-distance quantum communications networks, which would be needed to widely deploy quantum-guaranteed security solutions. This directly supports DOE's security mission to develop and deploy first-of-a-kind science-based security technologies to make the world a safer place. In addition, the proposed work bolsters ORNL's leadership in computing, one of its four major science and technology focus areas. In this case, this work supports the development of quantum networks to connect future quantum computers. In particular, quantum computing promises to efficiently simulate many-body quantum systems, an important class of problems in scientific computing.

Results and Accomplishments

We have considered several proposed repeater architectures to conceptualize a design for a backbone fiber-optic quantum network connecting dense mesh networks in large metropolitan areas. For the continental United States, a backbone network would need to consist of thousands of kilometers of optical fiber. For such applications, we determined that purification-based repeater architectures are not feasible because they are prohibitively slow at such distances. We identified one possible solution that encodes a single photonic quantum bit in a larger multiphoton quantum error-correcting code. Although not deterministic and requiring many more nodes than purification-based repeaters, this approach can correct for some photon loss. At each repeater node, quantum gates perform teleportation-based quantum error correction to transfer the incoming photonic state onto newly created photons. In the limit that each repeater node functions perfectly, such repeaters could be spaced by up to ~16 km of optical fiber. However, if one considers optimistic realistic device parameters, fiber spacing can drop dramatically (estimated at 1.0 km in one published document). Using the developed repeater scaling rules, we can estimate the number of repeater nodes that are required to form a backbone network of the 10 largest US cities, where each city is covered by a densely connected quantum mesh network. For this example, the number ranges from 450 repeater nodes in the ideal case to a little over 17,000 nodes in the more realistic case. We considered using multiplexing to reduce the required resources as well as beginning an investigation into alternate quantum error-correcting codes to reduce the required resources.

Information Shared

Results contributed to briefing materials for DOE on a potential future quantum network ultimately briefed to Secretary of Energy Moniz.

CLEO Conference, paper FM1N.8.

07758

Correlotypes: Determining Complex Genotypic Profiles Responsible for Complex Phenotypes

D. Jacobson

Project Description

Genome-wide association studies have focused on the analysis of individual single-nucleotide polymorphisms in an attempt to find single alleles responsible for a phenotype. Although it has proven useful, that approach does not account for the fact that many phenotypes are the result of a combination of a broad range of genomic variants and cannot be simply described or controlled by a single gene or variant. We propose to develop a method with which to find the complex, heterogeneous collections of genomic variants responsible for many phenotypes.

Mission Relevance

DOE and the USDA have independently launched ambitious research agendas to accelerate the development of domestic, renewable alternatives to liquid fuels and products. Fuels converted from cellulosic biomass offer one alternative to conventional energy sources, and supplementing fossil fuels with ethanol or other biofuels derived from bioenergy crops would benefit the economic growth and energy security of the United States. However, biological and technological barriers need to be overcome as DOE and industry develop cost-effective bioenergy crops. Biomass yield (dry tons per hectare), recalcitrance (i.e., the resistance of plant cell walls to degradation or deconstruction, which ultimately enables access to a plant's sugars), and sustainability (including plant-microbiome associations and responses to biotic and abiotic stress) are some of the most important factors controlling the cost of biomass production and utilization for biofuels. Short-rotation woody crops, such as *Populus* species and hybrids, are expected to be an important renewable feedstock for bioethanol production in the future due to their relatively low delivered cost. Biomass yield and recalcitrance and phenotypes associated with sustainability are complex polygenic phenotypes of high importance to DOE's biofuels programs.

Eukaryotic organisms such as *Populus* and switchgrass are derived from complex genetic systems that are composed of pleiotropic functional networks of interacting molecules and macromolecules. The subsequent phenotypes are the result of orchestrated, hierarchal, heterogeneous collections of expressed genomic variants regulated by and related to biotic and abiotic signals. However, the effects of these variants can be viewed as the result of historic selective pressure and current environmental as well as epigenetic interactions, and, as such, their co-occurrence can be seen as genome-wide associations in a number of different manners. In that context, a plant's association with its microbiome is a complex set of interactions involving many genes, peptides, and metabolites. Understanding these types of plant-microbiome associations is important to the DOE-funded Plant Microbial Interface Scientific Focus Area as well as other DOE-funded projects. Similarly, biomass yield and recalcitrance are complex polygenic phenotypes of high importance to DOE's biofuels programs.

Results and Accomplishments

We calculated 1.24×10^{14} allele-specific correlations among all pairs of 8 million bi-allelic single nucleotide polymorphisms (SNPs) across a population of ~1,000 *Populus trichocarpa* genotypes. A stringent threshold was applied, and the resulting 367 million correlations were modeled as an SNP correlation network. A Map/Reduce Hadoop approach has been taken to analyze the resulting network and to extract the connected components. The connected components and/or breadth first searches have been used to create sets of SNPs to be used for set-based genome-wide association studies (GWASs). Set-based GWAS methods are under development in order to use these SNP sets with a range of phenotype data.

The correlated SNPs have been mapped to genes in order to create gene coevolution networks. Plant phenotypes (including metabolomics phenotypes) have been associated to SNPs and genes with traditional (one SNP at a time) GWAS analysis, and the results have been used to create GWAS networks that model the multiple associations among 42,000 phenotypes and genes. RNA expression data from the *Plant Gene Atlas* as well as from 60 different genotypes have been used to create coexpression networks. Intersections between coevolution networks, GWAS networks, and coexpression networks have been created and are proving to be very useful in hypothesis generation and results interpretation. Futhermore, this work has led to the development of several new methods, including GWAS profile networks and pleiotropic decomposition.

The ability to identify the complex genomic underpinnings for plant phenotypes is of crucial importance to a number of areas of focus for DOE BER, including biofuels and plant-microbial interactions. ORNL has created the largest genome sequence dataset for a single plant species (*Populus trichocarpa*) in the world. The combination of the methods developed from this LDRD project on this dataset with one of the world's largest high-performance computing environments is allowing ORNL to analyze plant systems in a way that other institutions are unable to do at present. The results of this project have already played a key part of the Plant Microbial Interfaces (PMI) programs renewal proposal and have been a significant feature in the recent Bioenergy Research

Center application. We have had very good feedback from BER and have now taken a very active role in developing exascale applications for systems biology analysis.

This work has led to the creation of many networks focused around different research topics relevant to BioEnergy Science Center, PMI, CAM, and other DOE areas of interest. This has led the development of collaborations with researchers at ORNL, the University of Georgia, the Noble Foundation, NREL, the University of Nevada, Dartmouth University, LBNL, and the University of Newcastle.

Information Shared

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07776

Magnetoelectric Multiferroic Nanocomposites—Going Beyond Complex Oxide Perovskites

M.R. Fitzsimmons, E. Guo, R. Desautels

Project Description

Composite materials have long been important constituents of commercial products. Advances in materials science have enabled breakthroughs in sports, for example golf, kite surfing, skiing, snowboarding, and extreme sports, as most recently realized by the America's Cup AC72 class of hydrofoiling catamarans. The composites featured in these examples consist of different materials that vary over micron+ length scales. With improvements in materials synthesis, we have opportunities to synthesize nanocomposite materials (i.e., materials with chemical constituents that vary over nanometer length scales). Indeed, the interfaces between the different constituents play a prominent role in determining the behavior of the composite over even longer (i.e., mesoscale) length scales. This LDRD project will establish a competency in synthesis, characterization, and computational modeling of magnetoelectric multiferroic nanocomposites. Success will enable us to learn how to select and arrange interfaces in hierarchical structures exhibiting multifunctional behavior. We will develop magnetoelectric multiferroics whose functionality arises from coupling of properties of dissimilar materials across interfaces. We will use insight from computational modeling, validated by studies of parent compounds, to guide selection of inorganic perovskites and metal organic frameworks to prepare our mesoscale materials.

Mission Relevance

Understanding and controlling the properties of functional materials play critically important roles in innovative technologies for the energy and information technology sectors. Not surprisingly, a key goal of DOE is to enable scientific research in the synthesis, characterization, and predictive modeling of functional materials. The hierarchical arrangement of mixed-phase materials at the mesoscale (i.e., in the range that spans the atomic and micrometer length scales) is an important theme in the DOE BES Mesoscale Science Initiative report. Neutron scattering's ability to probe buried structures is crucially important to the DOE and is a key mission for ORNL. An outcome of the project will be development of tools and techniques to characterize static and time-dependent functional behavior of interfaces in real-life (in situ, operando) conditions—a transformative change for neutron scattering. Our success will address the mesoscale science goals of BES.

Results and Accomplishments

Postdoctoral fellows Er-Jia Guo and Ryan Desautels fabricated and characterized several multiferroic heterostructure systems, including ones involving $La_{1-x}Sr_xMnO_3$ (LSMO), $BiFeO_3$ (BFO), $SrRuO_3$, $SrTiO_3$, $LaNiO_3$, $NdNiO_3$, and $PbZr_xTi_{1-x}O_3$ (PZT) in the lab of Dr. H. N. Lee (ORNL Materials Science and Technology Division). Heterostructures were grown in order to develop synthetic magnetoelectric coupled multiferroics. Our interest in combining ferroelectric and ferromagnetic materials is to demonstrate control of magnetization using an electric field. In these systems magnetoelectric coupling occurs across an interface.

The first system consisted of a superlattice of 10 repeats of the bilayer sequence 5 unit cell (u.c.) BFO layer on 20 u.c. LSMO layer. The superlattice was epitaxially grown with the first LSMO layer in contact with the (001) single-crystal $SrTiO_3$. Using polarized neutron reflectivity (PNR), we were able to quantify the depth dependence of the BFO/LSMO magnetization in absolute units. We identified Curie temperatures for BFO and LSMO of 200 and 315 K, respectively. We found that the superlattice architecture exhibits a novel form of ferromagnetism in BFO and is simultaneously a ferroelectric for temperatures up to 200 K.

We performed PNR experiments to measure the response of magnetization to electric polarization from a ferroelectric PZT layer and a ferromagnetic $La_{0.8}Sr_{0.2}MnO_3$ layer grown on an $SrTiO_3$ substrate. The interfacial magnetism could be flipped by switching the polarization of PZT with the aid of an ionic liquid. Our work presents unambiguous evidence of control of the interfacial magnetic moment through electrostatic doping via ferroelectric gating. Moreover, our novel approach enables polarization switching of large samples suitable for neutron scattering.

Information Shared

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TRANSFORMATIONAL NUCLEAR SCIENCE AND TECHNOLOGY

06837

Neutron Scattering Studies of Select Uranium Compounds

B. Anderson, A. Huq, K. Herwig, E. Mamontov, A. Rondinone, A. Miskowiec

Project Description

This LDRD project applies neutron-scattering techniques to study the structure of select uranium compounds under a variety of environmental conditions. Neutron diffraction is used to follow the crystal structure evolution over the course of weeks and months of fixed-humidity exposure of uranyl fluoride hydrates. The influence of vapor-phase water on the decomposition of uranyl fluoride is further studied by quasielastic neutron scattering, which probes the motion of water on picosecond timescales. Application of these two techniques over the course of the aging process has the potential to establish a detailed relationship between the microscopic structure and the chemical influence of water on that structure. In addition, the capability to measure the effect of humidity on the dynamics of water in situ during the quasielastic neutron scattering measurements is also under development to support this project. This experimental research effort is only made possible by the unique capability of instrumentation at the ORNL Spallation Neutron Source (BASIS and POWGEN in particular) to probe the motion of water on the relevant timescales and the powder diffraction capabilities that provide sensitivity to light elements, especially in the presence of uranium.

Mission Relevance

This effort is relevant to the following DOE missions and/or missions related to nuclear science: sourcing minerals and raw materials for fuel production, performance of uranium oxide and composite fuels in reactor environments, environmental transport and fate of uranium-bearing nuclear waste, and the environmental impact of production and cleanup activities related to uranium fuel cycle operations. Characterization work has mostly focused on the oxides and metallic forms, with some work focused on oxyfluorides as the structures relate to fate and transport in the environment. Of particular relevance is the application of the ORNL Spallation Neutron Source (SNS) to a new mission space and the expansion of its scientific capabilities with the development of an in situ humidity-generation unit for quasielastic scattering measurements.

Further, the study of uranium compounds as critical materials used in the nuclear fuel cycle falls within the DOE’s scope. For instance, at very high humidity levels, uranyl salts (fluorides) deliquesce and enter a solute state, greatly increasing their environmental mobility. The chemical and structural pathway of uranyl salt decomposition under environmentally relevant conditions is foundational scientific knowledge for assessing and mitigating potential impacts of uranyl compound chemistry in the environment.

Results and Accomplishments

Neutron-scattering experiments in FY 2015 and FY 2016 identified water-induced phase transitions in uranyl fluoride and demonstrated the use of an in situ humidity-generation unit for the BASIS neutron spectrometer at the SNS. Three distinct physical phases of uranyl fluoride have been discovered based on the neutron-scattering experiments: an anhydrous UO_2F_2 crystal; partially hydrated $UO_2F_2 + x(H_2O)$, where $x < 1$; and a crystal hydrate of nominal chemical formula UO_2F_2+1.57(H_2O) as well as chemical and physical pathways between them.

Using in situ humidity control during quasielastic neutron-scattering measurements at BASIS allowed us to observe water intercalation directly into the structure and to observe the phase transition from $UO_2F_2 + x(H_2O)$ to UO_2F_2+1.57(H_2O).

We identified a novel production method of UO_2F_2+1.57(H_2O) involving application of controlled humidity and temperature. The original crystal structure was solved with x-ray diffraction, but the use of neutron diffraction provided some information about the hydrogen locations. Furthermore, quasielastic neutron scattering measurements indicated that the motion of water in UO_2F_2+1.57(H_2O) is substantially different from the motion of water in UO_2F_2 + x(H_2O).

Experience working with UO_2F_2 at has shown that $UO_2F_2 + x(H_2O)$ is the most common phase at ambient conditions. As such, an experiment was proposed for the higher-energy ARCS neutron spectrometer, also at SNS, in order to measure vibrational modes of water in that system. Several distinct modes related to water coupling to vibrations in the underlying structure were identified. The modes were later identified in Raman scattering measurements. Temperature-dependent Raman measurements showed that the hydrated-to-anhydrous phase transition occurs at 125°C. The identification was made based on the vibrational modes of the anhydrous structure, which were calculated using density functional theory and a follow-up experiment with anhydrous UO_2F_2 on ARCS.

Information Shared

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DOE and other interested sponsors have been briefed on results from FY16 experiments.

07325

Optimizing HFIR Isotope Production Through the Development of a Sensitivity-Informed Target Design Process Using High-Fidelity Modeling and Simulation Capabilities

B.T. Rearden, T.M. Evans, S.L. Hogle, S.R. Johnson, C.M. Perfetti

Project Description

The goal of this project is the investigation and demonstration of an integrated high-performance computing (HPC) toolset for optimizing isotope production in the ORNL High Flux Isotope Reactor (HFIR) by applying recent breakthroughs in sensitivity and uncertainty analysis to high-fidelity modeling and simulation (M&S) tools. Specific aims of this work include (1) investigation of state-of-the-art sensitivity and uncertainty analysis algorithms for use in ORNL HPC and high-fidelity M&S tools, (2) development of a prototypic isotope production optimization technique using sensitivity analysis to guide changes in HFIR target and shield design parameters, and (3) ensuring HFIR facility safety by quantifying the sources and impact of uncertainty in design-limiting irradiation target heat generation calculations.

Completion of these tasks will enable analysts to develop a sensitivity-informed irradiation target design process, and the success of this work will position ORNL with a unique capability for performing state-of-the-art sensitivity analysis using cutting-edge high-performance computing tools.

Mission Relevance

ORNL has a strong historical sponsor base for isotope production using HFIR. Opportunities exist for rapid business growth in this area with current and emerging programs such as ^{14}C, ^{229}Th, ^{238}Pu, ^{252}Cf, and ^{245}Es. Currently, isotope production targets are designed with simplified calculations and rely heavily on physical testing of small-scale irradiation experiments in the HFIR core. The experiments are expensive and time-consuming to perform, limiting the number of trials and optimizations that can be performed before a campaign must begin. The availability of advanced M&S tools for optimizing target designs using HPC platforms will enable increased efficiency and effectiveness for next-generation isotope production campaigns, providing an attractive capability to new and continuing sponsors. The success of this work will also position ORNL with a unique capability for performing state-of-the-art sensitivity analysis using cutting-edge HPC tools, enabling the pursuit of additional reactor application sponsors beyond the immediate needs of isotope production.

Results and Accomplishments

A sensitivity/uncertainty (S/U) analysis capability has been integrated into the Shift HPC Monte Carlo code, demonstrating the feasibility of S/U analysis in this context. Optimization of the methodology provides for up to a 99% reduction in memory requirements and up to a 75% reduction in runtime requirements; further optimization efforts have enabled multiple sensitivity coefficient calculations during a single simulation at the cost of a small (on the order of 1%) increase in computational memory footprint. This methodology has been integrated into the Shift code's parallel capabilities and has shown good parallel scalability and efficiency (79% efficiency for simulations with 1,000 processors).

The sensitivity analysis capability was used to investigate the sensitivity of ^{252}Cf production to the geometry of irradiation targets and identified that either an annular or thin a target would improve the efficiency of ^{252}Cf production by up to 10% by minimizing spatial self-shielding effects within the target itself. In this case, "efficiency of production" is defined in terms of preserving the desired quantity of heavy curium feedstock to optimize the production of ^{252}Cf. The sensitivity capability was also applied to investigate the use of neutron filters to preferentially block neutrons at energies that are most likely to cause the target to fission instead of capturing the neutron. It was found that placing ^{176}Lu, rhodium, or indium foil filters around the targets would improve production efficiency by 11%, 157%, and 376%, respectively. When combined, the geometry changes and filter use were found to increase the efficiency of ^{252}Cf production by as much as 1,312%, although additional irradiation targets may be required to produce the desired mass of ^{252}Cf. Depletion simulations were used to confirm the sensitivity-informed design changes. These sensitivity analysis methods are generally applicable to a wide range of applications for irradiation and reactor physics but could be further improved by calculating sensitivity coefficients for the overall yield throughout an irradiation campaign rather than investigating individual reaction rate ratios at state points during the campaign as implemented in this LDRD project.

Information Shared

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07332

Transformational Integrated Fusion Neutronics Modeling and Simulation

S. Mosher, A. Ibrahim, S. Wilson, D. Peplow, W. Wieselquist, J. Rapp

Project Description

Until recently it was impractical to perform high-fidelity neutronics analyses of fusion energy systems (FESs) at a scale that includes detailed models of more than a few primary components. In this project we developed and demonstrated an integrated fusion neutronics modeling and simulation (M&S) toolset that provides this capability. This transformational toolset enables the application of ORNL radiation transport tools to computer-aided design (CAD) models of FESs, integrates the transport tools with the neutron activation capabilities of the ORNL ORIGEN code, and implements a new and powerful hybrid deterministic/Monte Carlo method for the most challenging neutronics analysis in FES design, that of predicting the shutdown dose rate (SDR) field. In addition, we developed and implemented a technique for estimating the uncertainty in the SDR, which is calculated over multiple computational steps. This new capability enables accurate large-scale neutronics analysis of FESs and outperforms all currently existing tools in terms of accuracy, efficiency, and robustness. It is currently being used for facility-scale shielding and SDR analyses of the Joint European Torus (JET) and ITER fusion systems.

Mission Relevance

This project focused on developing a neutronics M&S toolset that is critically needed in FES design, development, and operational planning, specifically including (1) design and evaluation of fusion system components and shielding; (2) evaluation of fuel cycle and power extraction concepts; and (3) full-facility activation and dose-rate analysis to support safe operation, maintenance, and waste disposal activities. In addition to benefiting forward-looking fusion energy projects such as ITER, the Fusion Nuclear Science Facility, and the projected Demonstration Power Plant facility, this new toolset is well suited to supporting end-of-life radioisotope inventory estimation and waste disposal planning activities for the future decommissioning of the currently operating fleet of fission reactors. Nuclear security is another area in which the toolset is useful (e.g., in computing dose rates from materials activated by large neutron exposures, such as those created by the detonation of an improvised nuclear device).

Results and Accomplishments

We developed the Multi-Step Consistent Adjoint Driven Importance Sampling (MS-CADIS) method, a new hybrid deterministic/Monte Carlo method that dramatically accelerates the prediction of shutdown dose rates based on high-fidelity Monte Carlo simulations. This includes a much needed approach for efficiently propagating statistical uncertainties across the neutron transport, activation, and photon transport steps to the final response. We implemented this method within a uniquely powerful M&S toolset that we developed by integrating existing radiation transport and neutron activation capabilities within a high-performance parallel framework. To handle complex and large-scale models of FESs, we also integrated capabilities that enable the application of the transport tools to CAD geometry models. We demonstrated the unparalleled capabilities of the toolset by applying it to detailed models of the ITER facility to calculate nuclear responses in the toroidal field coils and the shutdown dose rate in the upper port region. These analyses are impractical with conventional Monte Carlo simulation techniques. In both cases, the toolset provided well-converged results more than one hundred times faster than existing acceleration approaches. The toolset is currently being applied to shielding and SDR analyses of the JET and ITER fusion systems at a scale and precision that is beyond the reach of other analysis packages.

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07345

Transformational Fabrication Technologies for Nuclear Applications: Demonstration of Hybrid Structures for HFIR Control Plates

K. Terrani, N. Sridharan, M. Gussev, J. Kiggans, M. Norfolk, J. Burns, Z. Thompson, S.S. Babu, C. Bryan, D. Pinkston

Project Description

The objective of this LDRD project is to examine possible integration routes between modern manufacturing and nuclear applications, to develop a prototype demonstration for fabricating control plates for the ORNL's High Flux Isotope Reactor (HFIR), and to identify other opportunities to further this technique in the nuclear enterprise. Fabrication technology has made major strides in recent years. Additive manufacturing (AM) techniques are now capable of creating complex components in nearly final form. The nuclear industry has many applications with complicated and even unique components that are time-consuming, expensive, and more difficult to make using traditional fabrication routes. Modern fabrication techniques have the potential to reduce fabrication lead time and costs while increasing quality and efficiency, but the methods have not been adopted due to the need for strict validation for nuclear applications. In this project it was intended to demonstrate ultrasonic additive manufacturing (UAM) as a potential route for production of control elements for the HFIR. These cylindrical plates consist of neutron absorbers (Eu as europia and Ta metal) dispersed selectively inside an aluminum alloy matrix along the length of the control elements. The control elements are exposed to a very high radiation field and need to operate reliably for ~100 cycles. The UAM methodology could enable design flexibility, enhance integrity, significantly reduce the number of processing steps, and thus result in notable cost savings.

Mission Relevance

This project intended to extend the use of advanced manufacturing to materials that are relevant to the nuclear industry and to demonstrate the fabrication of select components. The use of AM for the fabrication of complex nuclear components has the potential to cut design-to-manufacturing cycle times in half and to reduce fabrication costs by an order of magnitude. For example, weldments in many reactor components are a necessity when traditional fabrication techniques are being used. AM may reduce or eliminate that need. In addition, improvements in the fabrication of unique or complicated test reactor components (e.g., fuel assemblies and control plates) can help to enable NNSA's reduced enrichment mission. New forms of irradiation and isotope production capsules, and specifically, the fertile elements, may be distributed in the irradiation vehicle with greater spatial selectivity, and they may be accompanied by embedded sensors/instrumentation.

After completion of this project, the ORNL Research Reactor Division is considering continuation of this work for further qualification and ultimately for control element production for HFIR. Also, a number of proposals are under review by DOE NE to fund future work related to this LDRD project.

Results and Accomplishments

The main objective of the project, namely demonstration of AM techniques to produce hybrid structures that are candidates as modern HFIR control plates, was accomplished. Specifically, UAM was utilized to encapsulate neutron-poison-bearing compacts inside an Al-6061 plate. The compacts consist of Eu_2O_3-Al and Ta-Al powder mixtures that have been cold-pressed. Both flat and curved plates were fabricated with the latter conforming to the HFIR control element curvature specification. Neutronic analysis of the discrete neutron absorbers (i.e., embedded compacts) confirmed very similar behavior as the current control plates with uniformly distributed absorbers. A great deal of effort was dedicated to understanding the microstructure and mechanical behavior of the plates after UAM fabrication, after various postfabrication thermomechanical heat treatments, and after irradiation. Utilization of advanced characterization techniques revealed small grains at the build interfaces that were surprisingly stable (they did not undergo recrystallization) after heat treatment. This was later explained by the possibility of dissolved oxygen in those grains at the interface along with pinning of the boundaries with small oxide particles. The mechanical properties of the UAM material were shown to be highly anisotropic and low in ductility after UAM fabrication. Simple postfabrication annealing schedules greatly improved ductility in the material and reduced anisotropy, approaching that of bulk alloy. Hot isostatic pressing fully eliminated interfacial voids and produced a more isotropic material. The as-fabricated material after irradiation to ~1 dpa in HFIR either became more brittle or more ductile, depending on the testing direction. It was concluded that the as-fabricated material is not appropriate for in-reactor utilization. The heat-treated materials after irradiation exhibited conventional behavior similar to bulk alloys, and heat treatment was determined to be necessary for UAM components that are fabricated for nuclear applications.

Information Shared

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SUMMARIES OF PROJECTS SUPPORTED THROUGH THE SEED MONEY FUND

BIOSCIENCES DIVISION

07635

Leveraging High-Throughput Sequencing and Genetic Mapping to Determine Genetic Loci and Genetic Networks Underlying Genome-Wide Transcript Variation in *Populus*

J. Chen, W. Muchero, D. Weston

Project Description

Fuels developed from lignocellulosic biomass offer a potential renewable and clean alternative to conventional fossil-fuel-based energy sources. *Populus* is one of DOE's "flagship" plant species that is of special interest as a biofuel feedstock. Hybrids among different *Populus* species are widely used for biomass production. However, there are still significant biological and technological barriers that need to be overcome in order to achieve cost-effective, sustainable production and conversion of *Populus* biomass into biofuels. Our understanding of biomass productivity and conversion is limited by the fact that these complex traits require the regulation and coordinated interactions of many genes. However, identifying such genetic networks remains unaccomplished and is urgently needed to inform genetic improvement of feedstocks for biomass production and conversion. The proposed work leverages the combined power of genomic technologies and genetic mapping to mine large-scale RNAseq datasets generated by DOE's Joint Genome Institute (JGI) Community Science Program (CSP) project. The overall objective is to determine complex interactions among genetic loci and genetic networks underlying genome-wide transcript variation in the bioenergy feedstock *Populus*. This represents a timely and unprecedented research and will open many new research opportunities.

Mission Relevance

This LDRD project is highly relevant to DOE missions. The proposed research can provide direct knowledge to inform genetic improvement of *Populus* for enhancing biomass production and conversion, a major theme in DOE's BER programs. A novel outcome of the proposed research is the determination of genetic networks controlling complex traits. Currently, there are no biodesign tools for plants like biobricks for microbes. The proposed work could be the start of such an effort. This outcome is highly relevant to DOE Genomic Science: Biosystems Design to Enable Next-Generation Biofuels. The developed data and capabilities from the proposed project can also be applied to other bioenergy crops through genomics-based research of USDA-DOE Plant Feedstock Genomics program.

Results and Accomplishments

The major objective of this project is to determine the cis-genetic and trans-acting genetic elements and to construct genetic networks underlying genome-wide transcript variation. We have made several important discoveries. We have analyzed RNAseq data for a total of 438 biological samples from the JGI CSP project. Among these samples, 124 have replicates. In total, the samples represent 312 unique genotypes of the Quantitative Trait Locus mapping pedigree and two parents. In collaboration with scientists at JGI, we aligned the RNAseq data to the *P. trichocarpa* "Nisqually-1" reference genome to count transcripts. Normalization has been performed to standardize the counts among samples from different plates, which allows direct comparison of transcript abundance among all genotypes. Replicate analysis was conducted to calculate the correlations between different samples and between biological replicates. Bioinformatics analysis has been performed to assess genome-wide transcript variation. We found that among a total of 41,335 genes, the transcript of 37,588 genes can be detected in the developing xylems of at least one genotype. In average, a total of 26,923 genes are expressed in the developing xylem, representing approximately 65% of total genes in the *Populus* genome. We also found that several hundreds of genes showing large transcript variation (>50-fold) within the mapping pedigree. We have identified over 10,000 cis-genetic and trans-acting genetic elements underlying transcript variation and constructed genetic networks containing both known and previously unknown transcription factors. These outcomes are very valuable for biosystems design.

Information Shared

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07732

Production of Renewable Chemical Building Blocks via Electro-Fermentation

A.P. Borole, B.H. Davison

Project Description

Biofuel production from biomass has been investigated intensively in the last decade with technologies maturing and moving close to commercialization. However, economic production of biofuels has been limited due to the requirement for high yields from carbon feedstocks. Production of higher-value co-products and chemical feedstocks is seen as a potential means of overcoming this barrier. Butanediol (BDO) is one such chemical that can be generated from biomass, but it has a low yield from glucose (~15%) due to its highly reduced state. A novel method to increase the yield via a modified fermentation process is proposed. The maximum yield for BDO achieved via metabolic engineering is 33%. We predict that application of the new process can increase the yield by more than twofold. Similarly, production of butanol can be increased. This project demonstrates the proof of principle for increasing yield of these products and compares it with conventional fermentation using glucose. This can result in reduction in costs of production of butanol and BDO and could be applied to many other bioproducts from sugars or cellulose.

Mission Relevance

Efficient resource utilization and production of fuels and chemicals from renewable sources is a critical need of the twenty-first century. The proposed work is relevant to DOE missions related to production of biofuels and bioproducts. Biomass is an important resource for liquid fuels production; however, its use for chemical production has not received as much attention. The petroleum-based economy of the twentieth century was based on co-production of chemicals along with fuels to enable economic feasibility. As biofuels are coming of age, limitations in producing them economically are becoming evident. One major problem is the low-value, high-volume aspect of biofuels. Co-production of higher-value chemicals and bioproducts is needed to meet the high cost of the breakdown and processing of biomass that are necessary to produce biofuels.

For this LDRD project, we propose a novel idea to generate BDO, a chemical building block from biomass, using a single-step electro-fermentation (EF), a concept developed in our laboratory. BDO is used for making plastics, elastic fibers, polyurethanes, and butyrolactone and is used as an industrial solvent. Its biggest use is in making spandex and in production of footwear and sports apparel. It has worldwide market sales of $2 billion per year, and sales are expected to increase to $7 billion by 2020. The proposed work has potential to help meet the increasing demand for BDO and butanol and to enable higher yield from biomass and waste as a co-product in biorefineries, thus giving the bioeconomy an early foothold in the twenty-first century. The EF process can be applied to production of other chemicals and fuels as well (e.g., 1,3-propanediol), and thus can have far-reaching implications for climate change and US competitiveness in the global economy.

Results and Accomplishments

Investigations into conversion of biomass to biofuels and bioproducts were initiated using glucose and sugar-derived substrates with *Clostridial* biocatalysts. Small-scale experiments demonstrated production of BDO. Conversion of 1 g/L substrate was observed within 24 h with production of 0.4 g/L of BDO, based on preliminary studies.

Improvement in yield of butanol was also demonstrated under EF conditions. Providing electrons to the fermentation via an electrode allows diversion of the electrons to reduced products, production of carboxylic acids, and increased production of acetone coupled with reduction in ethanol production. The overall electron equivalence analysis indicated a shift from acid production to solvent production, changing the ratio of solvent to acid from 0.27 to 1.65.

A 1 L electrofermenter was designed and constructed. This system is a modified version of the H-type cell used previously and allows better control of process parameters. The H-type electrofermenter was used to understand the electron-uptake behavior of *Clostridial* biocatalysts. Improved production of butanol and BDO was demonstrated. This concept has significant potential for production of chemical building blocks from biomass and sugar-derived substrates.

Information Shared

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CHEMICAL AND ENGINEERING MATERIALS DIVISION

07735

Chemical Reactivity of Solids: Chemical Dynamics of the Atomic Structure of Solids Using Time-of-Flight Neutron Total Scattering

K. Page, P.F. Peterson, J.R. Neilson

Project Description

A host of societal challenges in energy and in health are limited by our understanding of solid-phase chemical reactivity. For instance, in biomineralization, crystal growth, and heterogeneous catalysis, the identities, concentrations, structures, and roles of chemically reactive species remain elusive because we do not have robust approaches to observe them at relevant atomistic length or timescales. In this LDRD project, we are developing a new technique to study the reactive species of functional materials during their operation or growth by combining time-domain cross-correlation of isotope pulse-chase reactions with time-of-flight neutron total scattering data. We are focusing first on a simple, idealized test case: the adsorption of N_2 by zeolites. The project will require (1) careful synthesis and characterization of high-surface-area zeolites, (2) development of flow cells for neutron scattering delivering time-dependent isotope contrast, (3) neutron total scattering data acquisition correlated to time-dependent isotope mixture flows, and (4) a novel data-simulation and data-modeling effort to interpret experimental results. This research will identify and quantify adsorption sites, elucidate their three-dimensional atomistic configurations, and follow their specific kinetics in situ, while providing a methodology that will enable novel scientific studies across a diversity of disciplines.

Mission Relevance

Characterization at national user facilities that validates theory and simulation, evaluates synthesis and fabrication, and demonstrates enhanced performance is necessary to unequivocally identify and characterize nanoscale interface and growth phenomena in biological, chemical, and geological processes alike. The proposed new methodology and instrumentation will enable new understanding of material and chemical processes. Our technique has the potential to uncover, for example, currently inaccessible information about the chemical reactivity of heterogeneous catalysts, atmospheric aerosols, photocatalysts, solid-oxide fuel cell electrolytes, electrochemical insertion electrodes and membranes (batteries), and medical implants—all of which contribute to a healthy and sustainable future. The project will attract new user communities to the neutron and nanophase material facilities at ORNL, and software and instrumentation advancements will broadly benefit the neutron science programs.

Results and Accomplishments

We have designed and commissioned a high-precision gas flow cell for neutron total scattering measurements on the Nanoscale Ordered Materials Diffractometer at the Spallation Neutron Source (SNS), capable of delivering isotope contrasted flow to material surfaces. Simultaneous neutron total scattering and steady-state isotopic transient kinetic analysis were completed for the adsorption of N_2 by Ca-substituted faujasite zeolite ($Na_{44-2x}Ca_xAl_{88}Si_{104}O_{384}$). The gas flow and mass spectrum were correlated with the structure factor determined from event-based neutron total scattering data reduction. We resolved the two different isotopes in the adsorbing zeolite, demonstrating sensitivities to lattice contraction and N_2 adsorption sites in the structure with both static gas loading and gas flow. The flow cell has been adapted for use in the current SNS beam cycle for user program studies on the insertion and extraction of oxygen in an oxygen storage material, carbon capture and storage in carbonates, and the redox chemistry of ceria based catalytic materials.

Information Shared

Authored Article

Daniel Olds, Katharine Page, Arnold Paecklar, Peter F. Peterson, Jue Liu, Gerald Rucker, Mariano Ruiz-Rodriguez, Michael Olsen, Michelle Pawel, Steven Overbury, and James R. Neilson, A high precision gas flow cell for performing in situ neutron studies of local atomic structure in catalytic materials, *Review of Scientific Instruments*, submitted.

Oral Presentations

Daniel Olds, Peter F. Peterson, Arnold Paecklar, James R. Neilson, and Katharine Page, *An In Situ Gas Flow Cell for Stroboscopic Studies of Local Atomic Structure in Catalytic Materials*, 2016 American Conference on Neutron Scattering (ACNS), Long Beach, CA (contributed).

James R. Neilson, Daniel Olds, Peter F. Peterson, Arnold Paecklar, and Katharine Page, *An in situ gas flow cell for stroboscopic studies of local atomic structure in catalytic materials*, 2016 American Crystallographic Association Annual Meeting, Colorado Springs, CO (invited).

Poster Presentations

Daniel Olds, Katharine Page, Arnold Paecklar, Peter F. Peterson, Gerald Rucker, Mariano Ruiz-Rodriguez, Mike Olsen, Michelle Pawel, Steve Overbury, and Jamie Neilson, *Probing the atomic structure of chemical reactivity via a gas flow cell and advanced PDF analysis toolset on NOMAD*, 2016 SNS-HFIR User Group Meeting (SHUG), Oak Ridge, TN.

Daniel Olds, Katharine Page, Arnold Paecklar, Peter F. Peterson, Gerald Rucker, Mariano Ruiz-Rodriguez, Mike Olsen, Michelle Pawel, Steve Overbury, and Jamie R. Neilson, *Probing the atomic structure of chemical reactivity via a stroboscopic steady-state isotope contrasted gas flow cell on NOMAD*, 2016 LDRD Poster Session, Oak Ridge, TN.

CHEMICAL SCIENCES DIVISION

08078

The Potential for Generation of Hydrochloric Acid by Supercritical CO_2 in Contact with Concentrated Brine

M.S. Gruszkiewicz, D.J. Wesolowski

Project Description

One of the permanent geologic carbon sequestration/storage scenarios involves injection of dense, liquid-like supercritical CO_2 ($scCO_2$) into subsurface saline reservoirs sealed at the top by impermeable caprock. The primary goal of this project is to demonstrate experimentally that gaseous hydrogen chloride and aqueous hydrochloric acid can be generated in significant quantities from concentrated brines containing dissolved alkali-metal and alkaline earth-metal (mainly Na, K, Mg, and Ca) chloride salts in contact with $scCO_2$. The reactivity of HCl is a potential threat to long-term performance of the essential features of geologic carbon sequestration (storage) and enhanced geothermal systems (EGSs) using CO_2 as the working fluid, including natural reservoir seals (e.g., shale caprocks) and downhole materials such as well casing cements and piping steel. The concentrations of HCl in both aqueous and $scCO_2$ phases existing at different times and locations across a geologic reservoir can only be predicted by reactive flow modeling of the reservoir based on thermodynamic properties of the fluids and rock matrices. Accurate modeling of the effects of HCl has not been possible until now because of the lack of quantitative information on the processes of generation and partitioning of HCl between brine and $scCO_2$. The results, showing an increase in the volatility of HCl by several orders of magnitude, will serve as proof of principle to obtain external funding for further investigation. Future work would include development of a quantitative thermodynamic and kinetic description of these processes supporting quantitative prediction of their implications in the context of energy technologies based on saline/geothermal reservoirs over a wide range of geologic conditions.

Mission Relevance

The HCl generated as a result of injection of $scCO_2$ will affect engineered subsurface energy systems, such as geologic carbon sequestration and proposed EGSs using CO_2 as the heat-mining fluid; however, its significance has not been recognized by the scientific community or by the funding agencies. The results of this research validate the physicochemical basis of this process and enable rational assessment of its implications. The primary beneficiary is DOE FE, which currently supports the Carbon Storage Program focused on developing and advancing technologies for safe, cost-effective, and permanent geologic storage of CO_2. Among the areas of interest are mitigating risks, increasing storage efficiency, and developing simulation tools. This topic is also relevant to the DOE FE Carbon Capture, Simulation-Based Engineering, and Advanced Research Materials programs. Another beneficiary is DOE's Subsurface Technology and Engineering RD&D (SubTer) initiative. Under that crosscut program, wellbore integrity and physico-chemical fluid rock interactions were identified as critical needs to achieve a reliable and predictive understanding of subsurface processes.

Results and Accomplishments

Taking advantage of unique corrosion-resistant experimental equipment at ORNL (the volatility apparatus), we measured the equilibrium concentration of HCl in $scCO_2$ in contact with 5 mol/kg solution of NaCl at 100°C and 150°C and at pressures between 9 and 17 MPa. The two features of the volatility apparatus that enabled this work are (1) corrosion resistance, making it possible to detect even small amounts of a reactive solute (HCl), and (2) the facilities for slow sampling of the gas phase without disturbing the equilibrium. The first task was to install several upgrades and to test the experimental equipment, which has been recently moved between laboratories. Pressure and temperature measurement systems were updated, and pressure gauges were calibrated. Devices were added for feeding and control of the pressure of the CO_2 in the equilibrium cell. The pressurized samples of the CO_2-rich phase withdrawn from the equilibrium cell were passed through deionized water to absorb the HCl. The resulting aqueous samples were analyzed for Na and Cl by ion chromatography. The concentrations of Na were the same as in pure water (generally below the detection limit), indicating that there was no detectable carryover of the brine to the samples, and all of the Cl present was in HCl. At the pressure of 15 MPa and the temperatures of 100°C and 150°C, the concentrations of HCl in the CO_2-rich phase were $\sim 7 \cdot \times 10^{-4}$ and $\sim 4 \cdot \times 10^{-3}$ mol/L, respectively. These values, representing an increase by more than 5 and 3 powers of 10, relative to the predicted concentrations in absence of CO_2 at these temperatures, may lead to exceeding the levels in geothermal steam considered as safe to equipment. While the volatility of HCl over alkaline-to-neutral aqueous solutions at the saline reservoir temperature is known to be very low, it was found to significantly increase as a result of the lowering of the pH of the brine caused by dissociation of the dissolved CO_2 and, possibly, due to the lowering of the activity of HCl in the $scCO_2$ phase, relative to water vapor. The results were found to be consistent with a roughly linear relationship between the density of $scCO_2$ and concentration of HCl to the CO_2-rich phase. While increasing the pressure of $scCO_2$ causes an increase of the HCl concentration in the brine, increasing temperature promotes association of the HCl present in the aqueous phase and hence its partitioning to the gas phase. Chemical equilibrium and volatility calculations support this conceptual model and the observed relationships between HCl volatility and pressure or temperature. The results of this work will allow for more realistic description of the process of geologic carbon sequestration. They will enable development of a general thermodynamic model of HCl partitioning between aqueous and $scCO_2$ phases as a function of temperature and prediction of HCl concentrations during injection of CO_2 in saline reservoirs. Follow-up DOE funding will be sought for measurements on Ca and Mg chlorides and modeling of the reservoir behavior.

Information Shared

A manuscript is currently in preparation for submission to *Environmental Science and Technology.*

COMPUTATIONAL SCIENCES AND ENGINEERING DIVISION

07510

Large-Scale Cluster State Generation for Fault Tolerant Quantum Computation

B.J. Lawrie, R.C. Pooser

Project Description

The traditional approach to quantum computation requires unitary quantum logic gates that control the interactions between well-defined quantum states (qubits). This approach is inherently difficult to scale because controlling decoherence is hard to achieve. A one-way quantum-computing model proposed in 2000 offers a direct path to scalability by requiring only single qubit projective measurements performed on a cluster state (a highly entangled state of multiple qubits). We propose to exploit the highly multi-spatial-mode nature of atomic four-wave mixing amplifiers to demonstrate a scalable cluster state that exhibits continuous-variable entanglement between the amplitudes and phases of greater than 100 modes in a framework that will enable fault-tolerant one-way quantum computation. These results will be of significant fundamental interest and will also place ORNL in a strong position for an expected program from DOE aimed at developing quantum computation to a Technology Readiness Level of 5–6 beginning in FY 2016.

Mission Relevance

Research in quantum computation directly addresses ORNL's strong interests in cyber security. The development of large-scale continuous-variable cluster states suitable for fault-tolerant quantum computation represents high-impact fundamental science that will place ORNL in an excellent position for a forthcoming DOE Intelligence Information Program on the development of nascent quantum computation technologies to the applied realm.

Results and Accomplishments

Based on discussions with the seed committee and with former committee chair Tim McKnight, our project was funded under a phase1/phase2 format, with the funding of phase 2 contingent on the results of phase 1. The tasks in phase 1 were to (1) demonstrate entanglement between multiple modes and (2) show theoretically that this entanglement could be extended to a cluster state. We achieved both of these goals using a tapered amplifier diode laser as the pump to generate multimode entanglement. It had been predicted by others in the field that such a source would not allow for entanglement measurements due to increased phase noise relative to Ti:Saph lasers, but we satisfied the inseparability criterion $I = \langle \Delta X^2{}_- \rangle + \langle \Delta P^2{}_+ \rangle < 2$, with $\langle \Delta X^2{}_- \rangle = .863$ and $\langle \Delta P^2{}_+ \rangle = .798$. Similar measurements were obtained by changing the signal vacuum modes' angle of incidence on the homodyne detectors while keeping the local oscillator angle constant. This changed the k-vector of the signal being measured, resulting in a different set of optical modes being measured in each case. We therefore measured bipartite entanglement across three pairs of modes and demonstrated that this spatial multiplexing is easily scalable to on the order of 100 pairs of modes.

During Phase 1, we (1) demonstrated the viability of the four-wave mixing process for one-way quantum computation, (2) introduced an experimentally viable "repeat-until-success" approach to generating a non-Gaussian gate required for one-way quantum computation, and (3) described a new algorithm for continuous-variable quantum computers that gives an exponential speedup over the best known classical methods.

Phase 2 of the seed project was intended to support the construction of a dual-rail cluster state that could be expanded to on the order of 100 modes. We have successfully demonstrated a four-mode, dual-rail, spatial-comb cluster state and demonstrated that these modes can be further multiplexed in time and space to scale to at least 100 modes. Because each mode of the spatial comb cluster state can be easily isolated (in comparison with cluster states that are multiplexed in frequency or time), additional nullifiers were identified that offered more flexible system characterization.

A pair of undergraduate students supported by the ORNL Higher Education Research Experiences and the DOE Science Undergraduate Laboratory Internships programs were instrumental to the success of this project, and as a result of the work they performed on this project, one of those students anticipates enrolling in the Bredesen Center graduate program in 2017.

Information Shared

Lawrie, B. J., Yang, Y., Eaton, M., Black, A. N., & Pooser, R. C. *Robust and compact entanglement generation from diode-laser-pumped four-wave mixing.* Applied Physics Letters, 108(15), 151107, (2016).

R. Pooser, J. Jing, *Continuous-variable cluster-state generation over the optical spatial mode comb,* Phys. Rev. A, **90**, 043841 (2014).

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07762

Automated Extractor Generation for Packed Malware

M. Pleszkoch, K. Sayre

Project Description

In order to foil antivirus scanners and hinder analysis, malware is often packed. Packing is a process whereby the contents of the original malware executable are compressed and then written to a new executable containing the compressed malware contents and an unpacking stub to decompress and run the original malware contents. It is estimated that 80% of all malware is packed. Before malware can be analyzed and blocked from execution, it must be decompressed. Currently, packed executables are decompressed either by using a purpose-built extraction tool explicitly designed to decompress executables generated by a particular packer or by dynamically executing the packed executable and then extracting the decompressed executable from memory. Purpose-built extractors reliably decompress executables but must be constructed manually. Dynamic extraction does not require manual effort, but it can be easily blocked by anti-dynamic analysis functionality embedded in the packed executable. This project proposes to implement a system that will automatically generate extractors that are not blocked by an anti-dynamic analysis functionality. Extractor generation will take 1 to 10 minutes, thereby providing a significant speedup over the 6 hours to 6 months it currently takes to write an extractor.

Mission Relevance

In order to successfully block malware prior to execution, we first must be able to recognize the malware targeted against our systems. Similarly, in order to mitigate the effects of a successful cyberattack, we must understand the functionality of the malware used by attackers. Knowing this, attackers use different techniques to make it difficult for defenders to recognize, block, and understand the malware used in attacks. One common technique used to foil antivirus scanners and to hinder the manual analysis of malware is the use of third-party tools to pack the malware.

Packing foils antivirus scanners and manual analysis by providing a quick and simple method for automatically generating difficult-to-analyze variants of a malware executable. Given the ready availability of many different packing tools, called packers, (more than 470 identified as of 2013), and the effectiveness of packing in lowering the detection rate of malware, it is now estimated that more than 80% of all malware infecting computers was packed. This is a significant problem. If we are unable to recognize or understand a piece of packed malware, we will be unable to block or mitigate the malware.

Results and Accomplishments

One of the ideas at the core of this proposal is the representation of unpacking stubs as some form of state machine. A formal model for the state machine format has been developed, which provides a unified generalization of Moore machines and Mealy machines. This formal model has been shown to be absolutely immune to malicious attack, so that executing an automatically generated extractor can never, in itself, cause the machine executing the extractor to be compromised. Additionally, it has been shown that the formal model is sufficiently powerful to be capable of dealing with the unpacking stubs of many common packers (e.g., codeCrypt, UPX, petite, and packman).

Starting from this theoretical basis, a Python program has been developed that extracts the state machine for a given packer by scraping the Hyperion behavior analysis output corresponding to a packed executable. When the extracted state machine is combined with a Python library containing a generic state machine execution framework, the result is an automated unpacker that is specifically targeted to the original packer program.

One challenge has been overcome in the project. It was found that the version of the Hyperion system existing at the start of the project was not able to resolve some of the computed jumps performed by some of the various unpacking stubs. Uncorrected, this would have been a fatal roadblock in constructing the required state machine description of the unpacking stub. However, this issue was successfully addressed by making several independent improvements to the Hyperion system’s computed jump analysis, thus solving the problem.

Information Shared

Pleszkoch, M.G., and R.C. Linger, “Controlling Combinatorial Complexity in Software and Malware Behavior Computation,” *Cyber and Information Security Research Conference*, 2015.

08025

Power Measurement Framework for Cyber Defense

J.A. Nichols, R.A. Bridges, S.J. Prowell, J.M. Hernandez Jimenez

Project Description

The current ability to protect networked assets from infection with malicious software (malware) is proving vastly insufficient, and this poses a serious national threat as compromises result in the halting of critical infrastructure, the disclosure of state secrets, and financial losses in the billions of dollars. Although they are often our first line of defense against malware, antivirus software and, more specifically, signature-based detection methods, are simply unable to keep pace with the rate and sophistication of modern malware, as semantically similar but syntactically different variants are being easily produced and often go undetected. An additional weakness of these detection methods is that they operate on the machine being monitored; hence, successful attackers may disable the monitoring software or modify it to prevent detection after gaining entry to the computer. To overcome these limitations, we demonstrate and test an approach to malware detection by examining the direct current power consumption of the device.

Malware processes will necessarily change the power profile of the device, and results confirm our hypothesis that accurate detection of malware is possible via power profile analysis. Furthermore, this technique extends to the control systems for energy delivery systems, including supervisory-control-and-data-acquisition-system (SCADA) devices and “Internet of Things” (IoT) devices. Preliminary research to extend the results for a Windows PC platform are being investigated.

Mission Relevance

This research aligns with the DOE OE *Roadmap to Achieve Energy Delivery Systems Cybersecurity*. In particular, the need for intrusion detection is a need explicitly identified in the roadmap. In its later stages, our project expanded into the realm of IoT devices and SCADA devices. This has resulted in interest from DOE BTO, which has provided follow-on funding (about one fulltime equivalent) to continue this work. We will continue the power consumption approach applied to a smart refrigerator. Our project is now included in our group’s Core Capabilities portfolio and has been presented to several sponsors, including the Department of the Navy and the FBI.

Results and Accomplishments

This project was designed in three parts: (1) measurement framework, (2) malware testing on a general-purpose computer, and (3) malware testing on a SCADA device. The first two parts were completed over the course of the entire project. The last one was partially completed as an HBCU/MEI outreach project during June through August 2016 with Qian “Guen” Chen from Savannah State University, in Savannah, Georgia. Professor Chen is an early-career professor, whose PhD degree, in cyber security of SCADA systems, is from Mississippi State University. She brought two senior students and test equipment to ORNL. We modified and implemented our hardware measurement framework to suit her test equipment. The modifications were similar to what we did for general-purpose computers.

For the general-purpose computers we were able to design in a mathematically precise way (i.e., no user-set parameters) a suite of tests that detected with 100% accuracy the presence or absence of malware on our test system. We tested five different malware samples. We trained our system with test uninfected power profile segments to create a baseline. New power profiles were then presented to a suite of five different algorithms, which looked for different changes in the power profile signals. Each would report if the signal it detected was “normal” or not. By totaling the votes of the different algorithms, we determined a clear threshold between the absence and presence of malware.

Cyber attacks are different for SCADA systems because an operating system is not running on the hardware. It took several designs to successfully create a measurement framework that we could use with the small currents in a SCADA device. After doing so, Professor Chen and her students attacked the device with four standard types of SCADA attacks and recorded the data. The resulting signals could be somewhat visually discerned, but the experimental design needs to be refined in order to be rigorous. Ms. J. M. Hernández (West Virginia University) is doing this as part of her dissertation research.

Information Shared

Papers

Hernández, J.M., Q. Chen, C. Calhoun, S. Sykes, and J.A. Nichols. January 2017. “Towards a Cyber Defense Framework for SCADA Systems Based on Power Consumption Monitoring.” Proceedings of Hawaii International Conference on System Sciences. (Accepted and Final Copy Submitted, Pending Conference January 4-7, 2017. Final publication details have not been received.)

A full paper describing the mathematical techniques is in final preparation with target venues of IEEE Security and Privacy Conference or RAID 2017.

- **Posters on the measurement framework and malware detection portions** of the project were presented at these three conferences:
  - Women in Cybersecurity Conference, Dallas, TX, March 2016; IEEE Security and Privacy Conference, San Jose, CA, May 2016;
  - Smoky Mountains Computational Sciences and Engineering Conference, Gatlinburg, TN, September 2016.
  - IEEE Security and Privacy, Oakland, CA, May 2016.

- **Posters on the SCADA portion of the project** were presented as part of the HBCU/MEI program on August 9th (Faculty) and August 11th (Students), 2016 at Oak Ridge National Laboratory.

- **Proposal Defense.** Successful proposal defense and dissertation topic for Jarilyn Hernandez at West Virginia University with Katerina D. Goseva-Popstojanova as her major professor. Ph.D. completion is expected fall semester of 2017.

COMPUTER SCIENCE AND MATHEMATICS DIVISION

07703

Fast Evaluation of Collision Operators for Non-Equilibrium Transport

E. Endeve, C.D. Hauck

Project Description

We propose an exploratory project aimed at the fast evaluation of integral operators that are used to model the microscopic interactions of particles with each other and/or with their physical environment. Such microscopic interactions are often modeled with kinetic equations, which evolve the phase space density $f(p,x,t)$—a seven-dimensional function of particle momentum p, position x, and time t. In this project we consider the application of high-order accurate discretization techniques, such as the discontinuous Galerkin (DG) method. Upon discretization, integral operators for microscopic interactions form a matrix vector product, and if momentum space (containing p) is discretized into N_p momentum space cells, then a naive evaluation requires $O(N_p^2)$ operations. This scaling becomes very prohibitive for many applications, and for this reason, significant research is needed to reduce the computational complexity of the problem.

Mission Relevance

Kinetic equations that model particle interactions are ubiquitous in many DOE science applications that motivate the need for exascale computational resources, including applications sponsored by FES, HEP, BER, ES, and NP. Advances in accurate and robust algorithms to model microscopic particle interactions in kinetic descriptions will enable simulations with much better physical fidelity.

Results and Accomplishments

We have identified two main research objectives: (1) construct separated expansions of collision kernels to reduce computational complexity and (2) parallelize the evaluation of the collision operator to reduce time to solution. For the first objective, we have begun development of high-order discretization for the Boltzmann equation based on the nodal DG method, which has been implemented for reduced dimensionalities in our computational framework for solving kinetic equations. We have tested this implementation, which uses a combination of modal and nodal representations, on several benchmark problems with promising results. To further reduce the computational cost of solving kinetic equations, we have also developed DG methods based on solving for angular moments of the distribution function f. For these moment methods, we have made progress toward a semi-implicit method that maintains physically meaningful solutions during time integration. We have also made progress on a computational library to access tabulated collision kernels. These developments form a basis for using sparse representations of the solution fields (i.e., the phase space density f or moments of f) and kernels appearing in the collision operators. For the second objective we take advantage of the high-order nodal representation, which leads to a large number of compute-intensive, but independent, dense matrix solvers, which can be easily parallelized. We have begun work to develop solvers that take advantage of graphics processing units. Initial results on current hardware indicate that data movement between host and device constitutes a performance bottleneck for moment models. Mitigation strategies are currently being considered, including building dense matrices directly on the device to avoid data transfers altogether.

Information Shared

Endeve, E. "Discontinuous Galerkin Methods for the Two-Moment Model of Radiation Transport", APS April Meeting 2016 (*Session K12: Astrophysics Data Analysis*), Salt Lake City, Utah, April 17, 2016

Endeve, E. "Towards a Realizability-Preserving DG Method for a Two-Moment Radiation Transport Model", talk given at the SIAM-SEAS 2016 conference in Athens, GA, March 13, 2016

Endeve, E. "Towards New Computational Methods for Neutrino Transport in Core-Collapse Supernovae", talk given at the KI-Net workshop *Scalable Methods for Kinetic Equations*, Oak Ridge National Laboratory, Oak Ridge, Tennessee, October 20, 2015

Endeve, E. "Core-Collapse Supernova Simulations", invited talk given at the Banff International Research Station workshop *Higher Order Numerical Methods for Evolutionary PDEs: Applied Mathematics Meets Astrophysical Applications*, Banff, Alberta, Canada, May 14, 2015

Endeve, E. "Discontinuous Galerkin Methods for Neutrino Radiation Transport", talk given at the APS April Meeting 2015 (*Session Y14: Data Analysis and Modeling Techniques*), Baltimore, Maryland, April 14, 2015

Endeve, E. "Solving Kinetic Equations to Model the Core-Collapse Supernova Explosion Mechanism", invited talk given at the mini-symposium *Computational Methods for Kinetic Equations and Related Models*, at the SIAM CSE 2015 conference in Salt Lake City, Utah, March 15, 2015

07747

Colloquium: A Tool For Modeling Hybrid Quantum Computing's HPC Potential

T. Jones

Project Description

First-generation quantum coprocessors are now commercially available, and research into quantum computing technologies is making rapid progress. Certain applications have shown incredible speedups on these initial quantum computers, yet other applications do not currently map well onto quantum computers. At this point, the potential for quantum coprocessors to improve high-performance computing (HPC) is poorly understood. Although quantum algorithms can significantly reduce computational complexity, it is unknown whether an HPC system with quantum coprocessors would be efficient or even practical. We propose to build tools to predict the performance of quantum-assisted HPC systems. Our approach analyzes system-level behavior when a quantum algorithm is mapped onto the quantum coprocessors within a larger HPC system. Our project develops a tool that uses an analytical method that captures quantum hardware (i.e., quantum bits and gates) as well as the pertinent modeling elements for conventional computing (e.g., conventional central processing unit capability, bandwidth, parallelism aspects). We seek to evaluate the system, node, and processor designs with respect to quantum-enabled gain and to quantify the performance of hybrid computation in terms relevant to HPC stakeholders.

Mission Relevance

The development of HPC systems at the exascale and beyond represents a significant challenge to DOE stakeholders. Simply enlarging existing systems would exceed practical constraints on power, communication, and cost; moreover, larger systems would face other seemingly insurmountable barriers in resiliency and programmability due to their extreme levels of concurrence. New methods to reduce resource costs while meeting performance goals are needed.

A disruptive approach to reducing algorithmic complexity is the quantum coprocessor. A quantum coprocessor represents a hardware platform that can implement low-level mathematical kernels based on quantum computation. It has been shown that some quantum algorithms provide speedups relative to their best classical counterparts. Because quantum algorithms reduce computational complexity, an expected side effect is an accompanying reduction in power, bandwidth, and memory resources. In light of these supposed advantages, it is paramount to determine which computations are good candidates for this form of hybrid HPC and how domain scientists might best exploit these new capabilities.

Results and Accomplishments

Our research efforts have produced several artifacts that will bolster ORNL's capabilities in quantum computer modeling and, more generally, in quantum computing as a whole. We developed an abstract machine model of hybrid HPC systems that captures architectural constraints placed on processor hierarchy, connectivity, and behavior for a synthetic model (functional modeling). This was accomplished using quantum extensions to the Structural Simulation Toolkit (SST) modeling tool. We then synthesized execution models for the quantum algorithmic reductions using specific hybrid HPC models and quantum coprocessor designs. Each execution model was designed to capture how a context-specific program is implemented within hardware and to provide the output needed for analysis.

We demonstrated an initial quantum coprocessor modeling capability (i.e., the capability to evaluate architectures with respect to speeds and feeds) that also enables measuring different dimensions (e.g., power, consumption, time to solution). We created SST macros for a true quantum computer circuit (as opposed to an adiabatic model). We also evaluated principal component analysis (PCA) problems for mapping onto an adiabatic machine. Although a recently published quantum PCA algorithm exists, we found its mapping onto an adiabatic machine problematic, even after communicating with the algorithm authors.

Information Shared

Poster: *Rebooting Computing*

Terry Jones, Travis Humble, Ryan Bennink, Keith Britt, & George Ostrouchov. Colloquium: A Tool For Modeling Hybrid Quantum Computing's HPC Potential. *ORNL LDRD Poster Panel*. Oak Ridge, TN. September 14, 2016.

Terry Jones, Travis Humble, Ryan Bennink, Keith Britt, & George Ostrouchov. Colloquium: A Tool For Modeling Hybrid Quantum Computing's HPC Potential. *Smoky Mountains Conference*. Pigeon Forge, TN. September 1, 2016.

07760

Develop an Eddy Covariance Capable Optical Oxygen Sensor

B. Liu, L. Gu

Project Description

Measurements of net ecosystem exchange (NEE) of atmospheric trace gases, water vapor, and sensible heat with the eddy covariance (EC) approach have been widely made by global networks to study biosphere–atmosphere interactions, global change biology, and ecology. Currently, thousands of flux stations around the globe are operating to acquire the data needed to predict climate change. The measurement of eddies is a significant challenge to instruments as it requires fast response (~ 0.1 s) and high sensitivity (~ 1 ppmv). Such measurements are still highly uncertain at night and on hilly terrains. The uncertainty of measurement brings considerable errors and biases to data analysis and prediction of climate change. Newly proposed EC theory suggests that a novel way to significantly improve the measurement accuracy of NEE is with the knowledge of the exchange ratio of O_2 to CO_2 for an ecosystem. A major technological challenge is to measure oxygen with the EC approach (fast response time of ~ 0.1 s and a sensitivity of ~ 1 ppmv over a background O_2 of ~210,000 ppmv). Our strategy is to significantly increase the polarization extinction ratio of a multipass cell (MPC) by use of a novel, potentially patentable design that will preserve the linearity of sensitivity growth of a Faraday rotation spectrometer with the square root of laser power. We will have the capability to increase the sensitivity 600% and to shorten the response time by a factor of 10 as required by the EC approach. We will deliver a potentially field-deployable and EC-approach-capable, prototype optical oxygen sensor by the end of the project.

Mission Relevance

DOE’s overall mission is to advance the national, economic, and energy security of the United States; to promote scientific and technological innovation in support of that mission; and to ensure the environmental cleanup of the national nuclear weapons complex. The dynamics of oxygen in the atmosphere contains vital information about natural and anthropogenic activities related to energy use and underlying processes. Timely collection and analysis of such information are vital to the energy security of the nation. Our new oxygen sensor will allow this collection. Further, the new oxygen sensor will allow more reliable measurements of other gas species, such as CO_2, CH_4, and N_2O. All these atmospheric trace gas species are important to DOE BER programs.

Results and Accomplishments

We designed and built a special MPC with an effective optical length of 15.8 m. The maximum reflection angle inside the MPC is smaller than 2°. The small reflection angle setting preserves the polarization extinction ratio (PER). The higher PER of MPC helps improve the system signal-to-noise ratio. We were unable to obtain a commercial distributed feedback (DFB) diode laser that works at 762.3 nm. Therefore, we built an external cavity to reduce the spectral line width of a Fabry-Perot (FP) diode laser to less than 100 MHz. The wavelength of the external cavity diode laser is tunable around 762.3 nm with a scanning range a few gigahertz. We installed a standard FP diode laser purchased from QPhotonics into the external cavity diode laser system. The spectral line width of the external cavity diode laser narrows from 0.5 nm to less than 0.04 nm. The center wavelength is well aligned to 762.3 nm. We replaced the standard FP diode laser with an antireflection-coated FP diode laser from Sacher Laser. The tunable wavelength range of diode laser system was increased. The output of the external cavity diode laser is ~ 20.0 mW. However, the diode laser was damaged during an alignment operation. We purchased two new diode lasers from other vendors. We redesigned our external cavity diode system. The diode lasers were received, and we will resume our experiment soon.

Information Shared

No information shared in FY 2016

ELECTRICAL AND ELECTRONICS SYSTEMS RESEARCH DIVISION

07669

Multimodal Imaging of Belowground Plant Root Distribution and Dynamics

V. Paquit, N. Srinivas, J. Childs, C. Iversen, H. Santos-Villalobos

Project Description

We aim to demonstrate that it is feasible to perform high-resolution quantitative imaging of roots in soil using a combination of multispectral imaging and advanced optical system design in order to answer important scientific questions regarding carbon uptake and allocation by plants. To achieve our goals, we intend to investigate an imaging technique that relies on the insertion of an imaging system into the ground by means of a transparent tube combined with multispectral illumination to capture multiple panoramic images longitudinally to the tube. The multispectral images will be analyzed using image-processing techniques as well as machine-learning techniques to extract quantitative data that can be correlated with the ecosystem response under specific environmental constraints. If successful, this project will put ORNL in a desirable position to lead new environmental science programs and to create the first global clearinghouse for data on plant root distribution and dynamics.

Mission Relevance

This basic research project can be associated with Strategic Objective 3 of the DOE *Strategic Plan 2014–2018*: “Deliver the scientific discoveries and major scientific tools that transform our understanding of nature and strengthen the connection between advances in fundamental science and technology innovation.”

Results and Accomplishments

This project spanned FY 2015 and FY 2016. The first year was focused on designing the experimental setup and on implementing some software tools. The second year focused on data acquisition, feature extraction, and data analytics.

During the first year, we worked on three sub-tasks. (1) We designed a plant container to enable root imaging, easy manipulation of samples, and consistent data acquisition over time. The container is a cubic foot box with a glass observation port positioned at a 45° angle between the bottom and one side of the box. This configuration enables observation of the roots over time as they grow along the window. (2) We configured the computer vision setup (a camera, a light source, and a computer) to allow multispectral data collection. We also developed a software platform that allows us to calibrate the camera (distortion and quantum efficiency) and to automate the data capture (wavelength selection and reflectance image). Image data collection is performed by illuminating the soil seen through the observation port with the multispectral light and to capture one image for each wavelength of light. (3) We developed machine-learning algorithms and prepared them to run on high-performance computing (HPC) hardware for year-two data analytics. We also performed some preliminary work on data classification using Deep Neural Network architecture using available multispectral data libraries and running the machine-learning code on an HPC/graphics-processing-unit platform.

During the second year, we worked on three sub-tasks. (1) The system developed in year 1 automatically collected multispectral images covering a range of 400 to 700 nm in steps of 10 nm. The database that was created includes data for containers with various soil compositions and plant species; images of the same containers were collected at different times to monitor root growth and other changes. (2) Nonlinear dimensionality reduction techniques combined with machine learning were used to detect roots in the soil. The objective was to narrow down the number of wavelengths needed to successfully classify each pixel as either root or soil. We used a Convolutional Neural Network (CNN) to perform the classification task. (3) We extracted root paths automatically. Systems deployed on the field collect thousands of images per day and require automated quantitative analysis of roots. A curvilinear structure extraction algorithm extracts data for the paths, branching, and dimensions of roots from the multispectral data and classifies the results with minimal input from the user.

As it stands, our system allows for automatic data acquisition and semisupervised root delineation, which is a significant improvement over existing technologies. Preliminary multispectral data classification results are convincing, but additional data collection is needed with more plant species and soil compositions to find stable classification models.

Information Shared

No information shared in FY 2016

07685

Simulation and Algorithm Development for 3D Residual Stress Measurements with Energy Dependent Neutrons

P.R. Bingham, L. Dessieux, D. Stoica, H. Santos-Villalobos, H. Bilheux

Project Description

The attributes of energy-dependent neutrons associated with the ORNL Spallation Neutron Source (SNS) provide ORNL with an opportunity to uniquely study microcracking, macrocracking and residual stress phenomena in three dimensions by using Bragg edge neutron interactions in a computed tomography environment. One of many areas where such measurements would establish ORNL’s leadership is in strain measurement of complex three-dimensional (3D) objects produced by additive manufacturing. Under this LDRD project, we are in the process of developing a simulation tool for energy-dependent neutron interaction for transmission imaging, using this tool to determine capabilities and limitations for tomographic calculation of a 3D residual strain map, and developing a first general reconstruction algorithm for this technique. Successful completion of this project will result in a simulation-based proof of principle for 3D strain mapping, will enable experimental research for measurements with the technique, and will provide motivation for potential new instrument development or instrument upgrades to improve the technique.

Mission Relevance

Development of this general strain-mapping capability will provide a new measurement technique with the potential to benefit DOE research spaces, including advanced manufacturing, geothermal energy, materials processing, and fossil fuels. Three-dimensional nondestructive strain measurements are needed for R&D efforts in a wide range of fields, including development of new materials, evaluation of internal stresses created during material fabrication or joining processes, rock fracture studies for geothermal energy and oil and gas, and development of advanced manufacturing methods. In particular, ORNL has been successful in advancing the understanding and improving the quality of additively manufactured materials through the ORNL Manufacturing Demonstration Facility. Development of advanced manufacturing methods requires understanding the complex strain fields that develop during the manufacturing process. This seed effort will begin to develop a needed solution for nondestructive strain measurement of complex 3D parts to aid in development of new manufacturing methods.

Results and Accomplishments

Simulation of Bragg edge transmission through a polycrystalline material is typically performed under the assumption that the sample is a powder (i.e., a uniformly random distribution of crystallite orientations exists within the sample). Directional strain on the material will break the random orientation because lattice spacing will be changed based on the direction of the strain. To overcome this limitation, our simulation approach is to model the material with single crystals and an orientation distribution. This allows calculations for each crystal orientation within the strain field. As a first step, we have developed a single-crystal simulation model with the incorporation of crystal orientation within the neutron beam and directional strain on the material. This crystal model has also been developed to include grain sizes to study limitations in the measurement technique for various material types. During this effort, the importance of simulating texture in materials became apparent as a result of measurements performed at the SNS. Therefore, additional focus was placed on ensuring that the simulation tool provided the flexibility needed for simulations with grain size, strain, and texture variations. A simulation engine based on the crystal model has been completed that allows the user to define a crystal orientation distribution for study of polycrystalline materials. Allowing the user to define the crystal population characteristics and simulating based on the population enables simulation of strain with the crystal structure geometry characteristics and texture through the crystal orientation parameters. Verification of the simulation tool has been performed through comparisons to experimental data. Comparisons have been performed for three cases: (1) single-crystal materials (copper), (2) materials with non-uniform angular distribution (pyrolitic graphite), and (3) powder (Copper). All three cases match well. Simulations are under way to test the incorporation of directional strains in the material and will be verified against experimental results.

Information Shared

Luc Dessieux, Philip Bingham, and Alexandru Stoica, “Single Crystal to Polycrystal (singpol) Neutron Transmission Simulator,” to be submitted in Feb 2017

Luc Dessieux, Philip Bingham, and Alexandru Stoica, “Neutron transmission simulation of textured materials,” to be submitted in March 2017

Luc Dessieux, Philip Bingham, and Alexandru Stoica, “Simulation of neutron transmission through polycrystalline materials under directional strain,” to be submitted in April 2017

Luc Dessieux, Dissertation to be published in 2017.

07767

Berry Phase Imaging (BPI) Development: A Novel Modality for Back-Reflectance Imaging of Scattering Samples

J.S. Baba, V. Koju, D. John

Project Description

In numerous fields, the importance of imaging to diagnostics and to the scientific discovery process is well established with imaging serving as a powerful tool for hypothesis development, investigation, verification, and validation. For scattering samples, attainable imaging resolution is much less than the theoretical diffraction limit. This is a significant challenge, particularly for the optical imaging of biological and environmental samples that are highly scattering. This project is a proof of concept for extending imaging resolution and depth in scattering media by developing a novel modality termed "Berry phase imaging" (BPI). BPI measures photon path trajectory as a means for utilizing multiply scattered photons to improve and extend subsurface imaging depth through highly scattering samples. Because it entails exploiting the link between scattering and its generation of a Berry phase, it requires access to high-performance computational resources to model and simulate propagation paths for millions of photons through well-characterized highly scattering samples. The results from this work will advance microbial, plant, and environmental sample-imaging investigations directly relevant to the DOE mission and additionally to those of NASA, NIH, DOD, and DHS.

Mission Relevance

The direct magnitude and impact of the proposed BPI modality to the DOE mission cannot be overstated. Examples include but are not limited to facilitating the following: (1) imaging microbial communities to better understand the process and efficiency of their biodegradation of lignocellulose substrates; (2) imaging through turbid environmental and ecological media (e.g., biological organisms in the Walker Branch Watershed); (3 real-time imaging of turbidity in streams, runoff, and waterways for ecological and environmental impact studies; (4) measurement of air and atmospheric quality in the investigation of energy production and utilization impacts (e.g., quantitating emissions); and (5) assessments of carbon fiber and advanced-manufacturing production quality. All of these applications will considerably benefit from the ability to image through highly scattering (i.e., optically dense) samples.

Results and Accomplishments

We incorporated Berry phase physics and translated the optical properties of a standard 1952 Air Force target and embedded it inside a well-defined scattering medium using C code. We ran Monte Carlo simulations propagating trillions of optical photons utilizing high-performance computing resources available through the ORNL Joint Institute for Computational Sciences. The simulations produced results duplicating those collected with a lab-bench experimental system, thereby verifying the underlying physics of BPI.

Information Shared

Baba, J. S., Koju, V., and John, D., "Monte Carlo based investigation of Berry phase for depth resolved characterization of biomedical scattering samples," Proc. of SPIE 9333, 93330O1-6, (2015).

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Rich Brueckner, “Video: HPC Transforms Diagnostic Medical Imaging,” (http://insidehpc.com/2015/11/video-hpc-transforms-diagnostic-medical-imaging/), November 4, 2015.

ENERGY AND TRANSPORTATION SCIENCE DIVISION

07701

High-Efficiency Passive Solar Concentrator Based on PNIPAM Phase Change

B. Smith

Project Description

Our objective is to demonstrate the technical feasibility of a passive (nontracking) sunlight collector and concentrator design that employs a thermally activated nanomaterial to couple light into a waveguide and deliver concentrated sunlight to the surface of a photovoltaic (PV) cell. Our preliminary design calculations indicate that the collection optics have high collection efficiency for acceptance angles ±20° from the surface normal. Approximately 60% of the light incident on the collection optics can be coupled into the waveguide. We predict that the effective concentration factor for the system should range from 100 to 600 sun irradiance, factors sufficiently large to drive multijunction PV cells and possibly conventional PV cells during periods of heavy cloud cover. The proof of principle will require refinement of the optical design, synthesis of the nanomaterial used as the transmission medium in the waveguide, and measurements of the system collection efficiency and effective concentration factors.

Mission Relevance

The cost of concentrator photovoltaic (CPV) systems can be reduced and their reliability can be improved by providing a method to passively track the sun as it traverses the sky while providing a high concentration factor. Our optical model for a concentrating system based on Fresnel zone plate optics and waveguide coupling indicates that concentrating factors larger than 100 are possible with collection areas as small as 20 cm^2. Our interest in proving the design is motivated by the cost reduction goal outlined in the DOE SunShot Vision Study, which is to reduce the levelized cost of energy for PV, CPV, and concentrated solar power to 6¢ per kilowatt-hour.

A more ambitious proposition is the possible application of the concentrator design to conventional (non-CPV) planar PV cells. Experimental demonstration of this application is just beyond the scope of the project, as it will require some modification to the collection optics and waveguide medium (after the critical function is proven) to enhance the concentration of diffuse incident light (also known as indirect solar insolation) that prevails on cloudy days and in regions of high latitude. The ability to generate PV power in cloudy conditions would be an enabling step in fielding PV power generation in locations outside the Sunbelt. There could be significant interest by the DOD, DARPA in particular, in providing PV power at remote military installations.

Results and Accomplishments

The objectives of our research plan are to (1) finalize the design for a proof-of-principle sunlight collection and waveguide concentration system that incorporates a PNIPAM coupling and transmission medium, (2) synthesize the PNIPAM medium, and (3) measure the coupling efficiency and effective concentration power of the passive concentrator. At the end of this project we expect that we will have experimentally proven the critical function of our design for a high-efficiency passive solar concentrator.

We modeled a lens array and waveguide concentrator concept using TracePro optical software. In the model a Fresnel lens focuses sunlight to points in a rectangular optical waveguide. A 3% to 5% concentration of PNIPAM by weight is assumed to be uniformly dispersed in the gel medium in the waveguide. The medium is transparent to visible and near-infrared light when the PNIPAM is below its lower-critical-solution temperature (LCST) of 32°C. Light absorbed by the PNIPAM within the focal point volume raises the temperature of the gel above the LCST in a volume roughly 10 times the focal point volume, transitioning the PNIPAM to an opaque scattering center. Once opaque, the activated volume scatters light into the transmission medium, where it is propagated in guided modes to the surface of a PV cell. A mirror at one edge of the waveguide reflects guided light back to the other edge, where it irradiates the active surface of a PV cell bonded to the edge. Using a Monte Carlo simulation of the solar irradiance on the system, the software model predicts concentration factors of about 75 to 475, depending on the azimuth and elevation of the sun. The collector and concentrator are stationary in our model and do not track the sun. The concentrator system built in the final task was based on this model.

We demonstrated the basic principle of producing a scattering volume in a waveguide using an aqueous solution of PNIPAM, but this approach is not tenable for proving our model. We expected better performance using a PNIPAM gel that we synthesized for proof-of-principle system. We characterized the optical properties of the gel and measured the LCST. We constructed a proof-of-principle concentration system, but the gel did not perform well in the system. We were unable to ascertain its coupling efficiency and effective concentration power.

Information Shared

No information shared in FY 2016

07759

Highly Permeable Graphene Oxide Membranes for Water Vapor Separation

I.V. Vlassiouk, O. Abdelaziz

Project Description

We propose to develop and fabricate a highly permeable graphene-oxide-based water vapor separation membrane. This membrane will be eight orders of magnitude more permeable to water vapor than existing polymer-based membranes while having air permeation rates (i.e., O_2, N_2, Ar, CO_2) up to eight orders of magnitude lower than those for water vapor. Once developed, the membrane can then form the basis of highly innovative, low-energy dehumidifier and air exchange systems. These systems can be used to independently control the relative humidity (latent cooling) in conventional heating, ventilation, and air-conditioning (HVAC) systems, or can be used in high-efficiency, low-energy air exchange filters.

Mission Relevance

DOE's BTO and ARPA-E offices both have recently funded projects in this area. The two recent BTO reports on advanced HVAC research opportunities both recommended that new and innovative separation membrane dehumidifier and air exchange air-conditioning technology be given a high priority for funding due to the potential for large energy savings from the use of these devices. The US Navy and Army have also funded the development of innovative dehumidification systems for use in portable field stations, which are oftentimes established in very humid and wet environments.

Results and Accomplishments

Graphene oxide membranes were prepared that are about 4 in. in diameter and 1 to 30 μm thick. Two different approaches were used for making transport property measurements. In the first one, a flask containing liquid water, alcohol, or alkanes was sealed by a graphene oxide membrane. Decrease in liquid volume/mass was monitored by a regular analytical balance under different experimental conditions, including variations in outside humidity and temperature. In the second approach, a mass spectrometer was connected to the testing chamber, and permeance of different species (water vapor, O_2, N_2, CO_2) were monitored in real time. High water permeance was detected while the permeances of other species were negligible (below detection limit of our experimental setup). Characteristic measured water vapor permeances (0.8 $kg/h{\cdot}m^2$ at 40°C) significantly surpassed those of current state-of-the-art polymeric membranes. Thus we have shown that graphene oxide can be used as a membrane in modern HVAC systems.

Unlike existing polymer-based membranes, graphene oxide membranes produced for this LDRD project are highly permeable to water vapor while remaining impermeable to other liquids, vapors, and gases. The graphene oxide membrane can be press-sealed, as is done in conventional air conditioner particulate filters. Surface modification of graphene oxide can further improve water permeability of the membrane at lower RH levels (30% to 80%).

Information Shared

No information shared in FY 2016

08013

Ion Decoupling in Layered Electrolytes of Boron Nitride and Ionically Assembled Polyethylene Oxide–Li^+ Complexes

G. Polyzos, T. Saito, Y.Y. Stehle

Project Description

Ionic decoupling is one of the most intriguing problems in polymer electrolytes. Above the glass transition temperature, the conductivity relaxation is described by a Vogel-Tammann-Fulcher dependence, which indicates that ionic transport is governed by the motion of the polymeric chains. In the last decade, significant contributions have been achieved in understanding the fundamental principles that govern the ionic decoupling at temperatures close to the glass transition temperature, and correlations between the glass transition dynamics and the polymer structure have been established. However, the decoupling at temperatures above the glass transition temperature remains unsolved, hindering new research horizons in the areas of high-temperature polymer electrolytes and advances in electrochemical energy conversion and storage. The proposed LDRD project will investigate and address fundamental concepts associated with the ion-decoupling mechanism in layered polymer electrolytes consisting of polyethylene oxide–Li^+ complexes that are confined between hexagonal boron nitride (h-BN) planes.

Mission Relevance

The successful completion of the proposed work will contribute to the fundamental understanding of the ion transport mechanism in confined geometries. The results of the project will be utilized to tailor nanoconfined electrolytes that will exhibit ultrafast ion transport compared to the respective bulk electrolytes. The work proposed in this project will be beneficial to DOE EERE programs. The proposed work is also relevant to the missions of the DOE SC and DOD.

Results and Accomplishments

The team has used chemical vapor deposition techniques to synthesize h-BN planes. According to the results of scanning electron microscopy, ellipsometry, and Raman spectroscopy, the planes are single-layer h-BN. A Li^+ conducting electrolyte was synthesized using copolymerization of vinylene carbonate with diethylene glycol methyl ether methacrylate. The electrolyte was fully characterized and was found to exhibit a low glass transition temperature and high ionic decoupling strength. Layered structures of Li^+ electrolyte confined between h-BN planes were assembled. According to ellipsometry measurements, the thickness of the confined electrolyte was homogeneous and precisely controlled (< 5 nm). Impedance spectroscopy was performed on the confined structures. The Li^+ ions were found to transport through the h-BN crystal defects.

Information Shared

No information shared in FY 2016

08035

Additive Manufactured Bimetallic Gradients for High Demand Applications

D. Splitter, A. Shyam, A. Elliot, A. Pawlowski

Project Description

The purpose of this LDRD project is to develop new and unproven approaches to producing novel and favorable bimetallic gradients with unique material properties. Additive manufacturing (AM) is a new and rapidly growing manufacturing process that enables high-fidelity control of material properties, geometry, and complexity. By developing AM-produced bimetallic gradients, ORNL would further strengthen its position as a leader in advanced manufacturing research for high-demand, high-value applications. With the present project, we aim to increase ORNL's leadership in materials, manufacturing, and energy efficiency by using novel materials in otherwise unattainable applications to reduce energy and fuel consumption.

Mission Relevance

The proposal is a proof of concept to demonstrate and determine whether unique attributes of advanced manufacturing can be the next leapfrog innovation in high-efficiency engine design. It will place ORNL at the forefront of this research area. Improving vehicle fuel economy and reducing emissions are the missions of the DOE VTO. VTO has expressed a commitment to fund research involving what they call "leapfrog technologies," which are technological innovations that demonstrate dramatic improvements to vehicle efficiency, emissions and that produce materials that have the potential to overtake the current technology. The work from this proposal is thereby directly aligned with DOE and ORNL mission relevance.

Results and Accomplishments

The process developed in this LDRD project provides a path forward in microstructure design in thermal applications where mass is of critical importance. This process was able to demonstrate both control of physical properties with volume fraction and novel characteristics over the base materials. Specifically, in the composites that were produced, cracks, once formed, were not allowed to continue to grow, due, in part, to the composite structure and the work-hardening of the reinforcing phase. Once a cracked formed in the composite, the reinforcing phase dominated the strain behavior, except in this case the reinforcing phase obscured the matrix's slip planes from the cracks forming in the matrix phase. Based on the evidence from direct testing, the process was found to provide a self-arresting crack propagation process that yielded an order-of-magnitude increase in strain. While the volume fraction of the as-printed preforms were higher than designed for, in part due to the resolution of the printer compared to the size of the strut, the printing process delivered precise objects that had similar volume fractions, given the same design. Thermal conductivity of the samples revealed close connection to the lower bounds of composite theory, consistent with the performance of other layered structures. Based on the results a significant new material behavior was found: high strain and crank arresting behavior can be produced in composites that possess exceptional thermal properties and with reduced mass.

Information Shared

Alexander E. Pawlowski, Zachary C. Cordero, Amit Shyam, Derek A. Splitter, Matthew R. French, and Amelia M. Elliott[5], "Synthesis and Properties of Net-Shape Interpenetrating-Phase Composites with Functionally Graded Microstructures", in preparation for Acta Materia, December 2016 submission targeted.

08158

Understanding Performance and Optimization of Micro-Propellers

M. Kass, N. Domingo, B. Kaul, D. Edwards, B. Ozpineci

Project Description

The objective of this effort is to improve the efficiency and performance of the micro-sized propellers used to power small unmanned aerial systems (UASs), thereby improving overall system efficiency. Propellers used to power manned aircraft operate under turbulent conditions because their size (diameter) enables the blade surfaces to experience high Reynolds numbers (> 50,000). In contrast, the small propeller sizes used in small UASs force them to operate in the less-efficient laminar regime (Reynolds numbers < 50,000). Small UASs are proliferating at a rapid pace, and significant performance and efficiency benefits can be achieved by overcoming the efficiency losses emanating from their propellers. We propose to improve micro-propeller performance by engineering features on the blade surfaces to disrupt laminar flow into the turbulent regime. Placing micro-propellers into better-understood turbulent conditions will improve their efficiency and will enable the use of established models to further improve performance via blade design and geometry. This approach is highly novel and, if successful, would improve the performance and handling of small UASs (and also potentially unmanned underwater vehicles). The proposed effort seeks to combine modeling with empirical (wind tunnel and test stand) studies to optimize propeller design and efficiency at small scales.

Mission Relevance

This effort supports the DOE EERE program office's missions to reduce dependency on petroleum by improving efficiency of engines and to reduce greenhouse gas emissions. It also supports the mission of the NNSA by improving the performance and ability of UASs to survey and detect nuclear materials movement by extending their payloads and range.

Results and Accomplishments

The research activities included both computational fluid dynamics modeling and empirical observations using a wind tunnel. The initial modeling activity was performed for airfoil (blade) sections containing leading surface edge features such as a raised edge, a single dimple (depression) at the leading edge, and multiple dimples placed on the upper surface. The baseline geometry was an unmodified blade. The model was designed to calculate both the lift and drag for each run. The modeling exercise showed that neither the raised edge nor the placement of small depressions (dimples) improved the lift and drag from the baseline condition. Not surprisingly, the model visual also did not show any delay of air separation, which is necessary for reducing the downstream drag forces. These predictions were confirmed in wind tunnel experiments on airfoil sections using a smoke generator.

A second modeling exercise was conducted using a more radical geometry, which consisted of an open channel from the high-pressure (bottom) side to the low-pressure side to allow airflow to the low-pressure surface to reduce downstream vortex formation (which causes drag). The results showed that an open channel was able to increase lift and reduce drag by 4%. This improvement is significant. The modeling also revealed that the drag reduction increases as the channel exit is moved farther from the leading end of the blade. Wind tunnel experiments confirmed that the presence of open channels effectively disrupts vortex formation on the upper (low-pressure) side of the blade. A study to optimize channel size and length is expected to be forthcoming.

Information Shared

No information shared in FY 2016

08166

Passive Solar Tracker for Optimizing Solar Energy Systems

S. Rajic, M. Lassiter, J. McFarlane

Project Description

Solar energy is starting to be recognized as having the potential to make a significant impact in meeting energy needs within the United States and globally as systems and component costs fall. The total delivered cost per kilowatt has many components, and they must all be optimized to have a chance of displacing or complementing existing approaches. One such area that is not fully optimized is solar tracking. Solar tracking can significantly affect overall system efficiency and thus can influence the final cost per kilowatt. Commercial activity in this area has been under way for some time, but the currently used approaches are far from optimal. To date, the approaches have been overly complex, unreliable, costly, or marginally effective in some cases. We propose an innovative approach that relies on an extremely simple thermomechanical system that could have an immediate impact on system efficiency. The approach is relatively inexpensive to implement compared to existing approaches and has the potential to be substantially more reliable due to its simplicity. We propose to develop a one-way ratchet moving in small increments due to thermal expansion of a bimaterial metering structure.

Mission Relevance

This work was targeted at DOE EERE and is thus directly tied to a DOE core mission. More specifically, this work falls into the purview of the Solar Energy Technology Office. An efficient, economical way of providing a given amount of power while installing 30% to 40% less solar panel area directly addresses a DOE mission.

Results and Accomplishments

We went beyond the conceptual design to examine the materials and geometries required for the project, conceptually simple yet challenging, implementation of a passive solar tracker system. We particularly examined the steel/aluminum bimaterial system as the baseline for the drive mechanism and refined and confirmed the equations governing the thermomechanical drive. We now have sufficient confidence to begin the fabrication effort need to demonstrate this important efficiency-boosting technology, which is needed in the nation's solar energy portfolio.

Information Shared

No information shared in FY 2016

08185

Tunable Transmission Graphene Device

M. Lassiter, P. Datskos, Y. Stehle, H. Luo

Project Description

The objective of this LDRD project was to determine the feasibility of using graphene electrodes to create a tunable transmission device in the visible and near-infrared (IR) regions of the spectrum. Such a device would be useful for buildings and transportation vehicles as a means of managing solar thermal gains (i.e., rejecting solar heating in the summer and accepting it in the winter). The device would be electrochromic, switching in transmission by application of an electric potential, and would otherwise use very low power when not switching, so as to not consume any potential power savings from the solar heating management. Because of its unique optical properties, graphene would be used in the proposed device. It would consist of an electrolyte capacitor constructed on planar transparent substrates using thin graphene sheets as the electrodes of the capacitor.

Mission Relevance

The management of solar heating gains for building energy efficiency is within the missions of DOE BTO, and such a device, if built in a low-cost, low-power-use manner, could improve the efficiency of future buildings and possibly be a technology that could be used to cost-effectively upgrade existing buildings. The proof of principle has not yet been achieved due to the extreme technical challenge of fabricating pristine multilayer graphene with high enough electrical conductivity to achieve Drude absorption in the near-IR and visible regions of the spectrum.

Results and Accomplishments

Graphene is a hexagonal planar arrangement of carbon and can be layered in sheets that are bonded in the plane by covalent bonding and vertically by van der Waals forces. The semiconducting nature of the graphene means that charges can be conducted by either electrons or holes, and so as an electrode in an electrolyte capacitor, charges of either type will build up in the electrodes as the capacitor is charged. The excess charges in the electrodes are free carriers and can absorb photons by the Drude model for free carrier absorption. This is the same mechanism by which metals absorb light. Theoretically, one could change the effective absorption of the graphene electrodes by the applied potential on the capacitor. The resulting device would have high transmission (low absorption) when there is little charge concentration in the electrodes and low transmission (high absorption and reflection) when the graphene electrodes contain a high concentration of charges. The highest challenge of the research is to increase the electrical conductivity of the graphene sheets to a level that significant absorption in the visible and near-IR regions of the spectra will occur. This level has not yet been achieved in this research. Only a small change has been observed in the IR absorption of the graphene electrodes, not enough to create an effective device for solar heating management.

Information Shared

No information shared in FY 2016

08204

Fluorescent Air Leak Detection System for Building Enclosures

D. Hun, B. Smith, C. Thompson

Project Description

Air leakage from building enclosures is responsible for about 4% of the total energy consumed in the United States. A recent DOE study indicates that air-sealing technologies are among the most cost-effective mechanisms to decrease energy loads due to the building envelope. To increase the successful implementation of these products, DOE has been seeking technologies that locate air leaks in building enclosures. In this LDRD project we explored developing an innovative fluorescent air leak detection (FALD) system that meets DOE’s needs by using fluorescent vitamins as an inexpensive, nontoxic, and easy-to-use air leak indicator. Our technology could help decrease infiltration rates in buildings with leaky envelopes by at least 50%. The objective of this proposal was to demonstrate the feasibility of our technology through preliminary laboratory experiments. Results include demonstrating that (1) vitamins can be aerosolized with an ultrasonic humidifier, (2) aerosolized vitamins accumulate around air leaks when transported to those locations by airflow, and (3) the fluorescence of the vitamins upon exposure to ultraviolet light can serve as an air leak indicator.

Mission Relevance

The proposed fluorescent air leak detection system for building enclosures ties to the missions of DOE EERE because it aims to decrease energy use due to infiltration, which accounts for nearly 10% of the energy consumed in buildings and about 4% of the total energy used in the United States. These numbers clearly demonstrate the magnitude of the energy savings that FALD can attain.

Results and Accomplishments

We measured the optical properties and photodecomposition rate of nine B vitamin supplements. Results indicate that vitamin B2 produced the strongest fluorescent emission intensity out of the studied supplements. Subsequently, we conducted a small-scale test using a plywood box (53 × 53 × 53 cm) and a large-scale test using an environmental chamber (52 × 31 × 48 m) at the Building Technologies Research and Integration Center to evaluate the FALD prototype with vitamin B2. Through the large-scale experiments we demonstrated with a nonoptimized FALD system that (1) an off-the-shelf ultrasonic humidifier can aerosolize a 33.3 ppm vitamin B2 aqueous solution, (2) the aerosolized vitamin accumulated around leaks when transported to those locations by air flowing at 3.8 L/s, (3) the vitamin that concentrated around leaks fluoresced upon exposure to a 450 nm light source, and (4) FALD is ideal for occupied buildings in need of a retrofit because accumulation of the vitamin B2 inside the environmental chamber could not be detected by the naked eye; therefore, damaging interior surfaces such as furniture is not a concern. Estimates suggest that leaks in a home could be detected with FALD and sealed with generic products in one day, and that the payback period could range from 2.5 to 5 years.

Information Shared

Hun, D. E., and B. A. Smith. 2016. "Fluorescent Air Leak Detection (FALD) System for Building Enclosures." Poster presented at ORNL's Physical Sciences Directorate All-Hands Meeting.

FUSION AND MATERIALS FOR NUCLEAR SYSTEMS DIVISION

07729

A Plasma Source for Transient Heat Load Investigations

L.R. Baylor, T. Gebhart, J. Rapp, S. Combs, L. Winfrey

Project Description

This Seed Money LDRD project focuses on the characterization and feasibility of implementing a pulsed electrothermal (ET) plasma source for the simulation of transient heat loads in future fusion reactors. The main objective of this project is to assess the potential use of an ET source in MPEX, a planned ORNL device, to investigate transient plasma fluxes representative of those from edge localized modes (ELMs) in fusion devices. ET sources have demonstrated high heat flux pulses (100 GW/m^2, 100 µs). A secondary objective is to assess the ET source capability to accelerate cryogenic pellets for injection to mitigate plasma disruptions. In this project, the ET source is being investigated to simulate transient heat loads of ~1 GW/m^2. The amplitude and duration of the pulse may be varied to reach desired heat and particle fluxes. This will be done by conducting experiments to characterize the plasma for various sleeve materials, pulse amplitudes, and pulse lengths. Plasma parameters will be measured and calculated using diagnostic techniques such as spectroscopy and particle image velocimetry. These measurements will be conducted for various source materials and discharge currents to determine the operating range of the plasma source.

Mission Relevance

For future fusion reactors such as ITER, which is currently under construction in France, developing an operating regime that combines good plasma confinement and acceptable power loads on the plasma-facing materials is the ultimate challenge. Even if the steady-state heat loads can be reduced to technologically manageable levels of 10 MW/m^2, transient heat fluxes due to abrupt confinement terminations, if not mitigated, can result in transient heat loads to the plasma-facing components of 50 to 200 GW/m^2. Investigation of the impact of these instabilities is a high priority in the research of the international and DOE FES program. Hence a plasma source is needed to mimic as closely as possible the transient events of a fusion reactor. The approach being developed here uses an ET plasma source that has previously demonstrated power fluxes of up to 100 GW/m^2.

Results and Accomplishments

The ET plasma source was successfully characterized using optical spectroscopy techniques and infrared imaging. Two pulse lengths, 1 and 2 ms, were tested with and without an applied magnetic field in order to show how current amplitudes and a magnetic field influence output plasma parameters. A shorter pulse length translates to higher current densities and heat fluxes. A pulse-forming network consisting of an inductor and a resistor was designed to obtain the different pulse lengths. Two different size inductors were built in house and have inductance values of 0.427 mH (2 ms pulse) and 0.1 mH (1 ms pulse). The resistances for the 1 and 2 ms pulses are 1 and 2 Ω, respectively. A boron nitride (BN) liner used was for several pulses of the ET source, and the average mass lost through ablation was measured to be less than 0.01 g per shot. The amount of liner material ablated with the applied magnetic field is slightly less. This amount of BN makes up approximately 5% of the atoms in the plasma. The other 95% consists of the fill gas and trace amounts of the anode and cathode materials (tungsten and copper, respectively). Stark broadening of the H_β line was used to calculate electron density. The average densities calculated for the 1 and 2 ms pulse lengths were 2.5×10^{22} electrons/m^3 and 1.8×10^{21} electrons/m^3, respectively. Temperatures were calculated using the relative line method. The 1 and 2 ms pulses produced plasma temperatures of 5 and 1.2 eV, respectively. Heat fluxes were calculated using infrared imaging and a lumped capacitance method. The 1 ms pulse produced larger heat fluxes, with an average at approximately 2.1 GW/m^2. The 2 ms pulse produced heat fluxes of approximately 900 MW/m^2. Applying the magnetic field has no effect on the plasma densities or temperatures, but it slightly decreases the heat flux delivered to the target plate due to the field not extending the entire distance to the target. This project proved that the ET source can indeed produce ELM-like heat fluxes of 1 GW/m^2 in a solenoidal magnetic field.

Information Shared

“Characterization of an Electrothermal Plasma Source for Fusion Transient Simulations,” to be submitted to the Institute of Physics (IOP) journal *Plasma Sources Science and Technology*.

“Material Impacts and Heat Flux Characterization of an Electrothermal Plasma Source with an Applied Magnetic Field” – to be submitted to IOP’s journal *Plasma Sources Science and Technology*.

“Design and Characterization of an Electrothermal Plasma Source for Fusion Plasma Transient Simulation,” T. Gebhart, Ph.D. Thesis, University of Florida, submitted Nov. 2016.

MATERIALS SCIENCE AND TECHNOLOGY DIVISION

07244

High Yield Process for Lignin-Based Activated Carbon Fiber

N.C. Gallego, C.I. Contescu

Project Description

The object of this LDRD proposal is to demonstrate a high-yield, faster method for the production of low-cost activated carbon fibers (ACFs) from lignin, a renewable precursor. We will seek to demonstrate that ACFs can be obtained directly from lignin by chemical activation combined with low-temperature thermal treatment. If successful, this method will eliminate the need to isolate intermediate products (as in currently done in ACF fabrication by the conventional route of carbonization, stabilization, and physical activation), therefore shortening the processing time while increasing the carbon yield and providing a better control of pore size distribution. If successful, this method would represent a significant step toward the development of low-cost, high-yield ACFs based on lignin, a renewable source, with a large market advantage over traditional high-cost, low-yield pitch-based ACFs, which are derived from petroleum products and are currently available in United States only from foreign sources.

Mission Relevance

Demonstration of a high-yield, faster method to produce low-cost, lignin-based ACFs will position ORNL to address energy challenges, including the reduction of energy needed to satisfy building ventilation requirements (and hence lower the energy demand of commercial buildings). Specifically, DOE BTP and AMO would benefit from this research.

Results and Accomplishments

In this project, we used phosphoric acid as the chemical activation agent of the ACFs. Although chemical activation with phosphoric acid is known as a general method for introducing porosity in ligno-cellulosic materials, to our knowledge it has not been previously demonstrated for use with lignin-derived fibers. We employed both melt-spinning and electrospinning for producing lignin fibers from mixtures containing powdered lignin and the appropriate amount of phosphoric acid. Through a systematic study of experimental conditions, we found the optimal spinning conditions and thermal treatment parameters that allowed us to obtain, after carbonization, sizable amounts of lignin-derived ACFs (LACFs). In the course of the experiments, we found out that electrospinning is more advantageous than melt-spinning. The fibers obtained by electrospinning had a smaller diameter and a rounder cross section, were more uniform, and contained fewer defects than those made by melt-spinning.

Carbonized fibers were washed with deionized water to remove any remaining acid. Scanning electron microscopy analysis of selected fibers confirmed the integrity of the fibers (i.e., they did not melt or fuse upon heat treatment). The surface properties [Brunauer–Emmett–Teller (BET) surface area, total pore volume, and pore size distribution] were measured by gas adsorption (nitrogen at 77 K and carbon dioxide at 273 K). The best LACFs obtained have BET surface areas of up to 1,700 m^2/g and total pore volume of up to 0.72 cm^3/g. These properties are comparable to those of AP-400 ACFs derived from pitch that were our target (1,702 m^2/g and 0.76 cm^3/g). The gas adsorption properties of LACFs obtained by chemical activation were measured by high-pressure adsorption of carbon dioxide in a microgravimetric balance. Comparison with an LACF batch obtained by the classical method of physical activation in carbon dioxide demonstrates the net advantage, in terms of performance and yield, of the chemical activation method. A sample of melt-spun, chemically activated LACFs (yield > 60%, BET surface area 1,385 m^2/g) had equal performance as a physically activated LACFs (yield < 30%, BET surface area 1,750 m^2/g). Based on yield only, it can be projected that chemically activated LACFs would have half the cost of physically activated LACFs. Even with lower BET surface area, they have equal performance as the LACFs obtained by the classical method (physical activation). Our adsorption studies showed that chemically activated LACFs are equivalent with pitch-derived ACFs (such as AP-400), and thus we reached the performance target selected for this project.

In conclusion, the chemically activated LACFs have the potential to replace the AP-400 fibers that are available from China. While the Chinese fiber is costly and is obtained from fossil carbon sources, LACFs are obtained from lignin, an abundant natural resource that represents about 40% of a tree's mass. Moreover, the chemical activation process developed in this Seed Money project is more efficient than the classical physical activation route. Chemical activation uses fewer energy-intensive steps, requires shorter processing times, and has overall higher carbon yield based on the initial raw material.

Information Shared

N. C. Gallego, Y. Yue, C. I. Contescu, "High Yield Process for Lignin-based Activated Carbon Fibers", poster presentation at the American Carbon Society workshop on "Carbon Fibers and their Composites," Oak Ridge, TN, April 16–17, 2015.

N. C. Gallego, C. I. Contescu, D. C. Webb, Y. Yue, P. Fulvio, C. D. Tran, "Production and Characterization of Lignin-based Activated carbon Fibers", oral presentation at CARBON 2016, The World Conference on Carbon, State College, PA, July 10-15, 2016 (extended abstract S10-O6-3).

N. C. Gallego, C. I. Contescu, D. C. Webb, Y. Yue, C. D. Tran, P. Fulvio, "High Yield Process for Lignin-based Activated Carbon Fibers (LACF), ORNL poster presentation, September 14, 2016.

07541

Advanced Calibration Development for Inverse Heat Conduction: Exploiting High Thermal Conductivity Nanomaterials and Integrated Thermocouple Technologies

P.C. Joshi, T. Aytug, J. Frankel

Project Description

A transformative calibration methodology has been proposed for resolving inverse heat conduction problems (IHCPs) associated with aerospace, nuclear, mechanical, and chemical engineering applications. This modeling and monitoring approach removes the need to specify thermophysical properties or probe positioning to establish the heat flux and temperature histories at the surface of a solid body. The novel system identification approach to inverse heat conduction effectively translates to accurate, rapid, and cost-effective predictions of the heat transfer on an inaccessible boundary that can be applied directly to benefit the defense, industrial, and commercial sectors. Further refinement and transformation of the theoretical findings into practical possibility demand an innovative, creative, and interdisciplinary vision that integrates theory, computation, instrumentation, sensors, measurements, and novel experimental design to realize a leading-edge calibration technology. In this LDRD project, we intend to develop a unique calibration methodology that decouples accuracy from the explicit knowledge of the specimen's thermophysical properties or explicit probe placement. Exploiting the advances in nanomaterials technology, thin-film processing, and sensor integration schemes, we aim to define three fundamental needs necessary for high calibration accuracy: (1) acquiring interfacial and surface temperature measurements, (2) estimating surface heat fluxes, and (3) minimizing interfacial contact resistance formed between two surfaces. The joint ORNL-UTK team attempts to integrate the unique skill sets among the principal investigators to transform calibration technology with a focus on developing a microscale thermocouple, a high-thermal-conductivity interface, inverse heat conduction experiments, and system calibration methodology.

Mission Relevance

The goal of the proposed research is to introduce a revolutionary and innovative technological concept through theoretical estimation, critical evaluation of novel materials, design approaches, and experimental verification. Successful implementation of the proposed calibration methodology will find applications in the defense sector (e.g., gun barrels, rail guns, nuclear reactors, propulsion systems) and in the commercial sector (e.g., space flight, industrial furnace protection systems, pool fire). For example, hypersonic flight is a significant thrust area for national defense, national security, and future commercial vehicles. Hypersonic flight vehicles require predictable and reliable thermal protection systems that can withstand substantial thermal and mechanical loads during the defined flight scenario.

The capacity to withstand thermal and mechanical loads is imperative for both expendable global-reach strike gliders and the proposed reusable space planes. Hypersonics is central to US interests as other countries have indicated similar ambitions. With successful seed results, proposals to Department of Energy (DOE), Defense Advanced Research Projects Agency (DARPA), Missile Defense Agency (MDA), Test Resource Management Center (TRMC), National Aeronautics and Space Administration (NASA), National Science Foundation (NSF), and Air Force Office of Scientific Research (AFOSR) should receive high degrees of consideration for follow-on funding.

Results and Accomplishments

The advanced calibration development effort is focused on creating a new paradigm for acquiring accurate surface temperature and heat flux predictions by utilizing and integrating heat transfer principles, sensors, and instrumentation. The R&D work focused on modeling, experimental design, test-structure development, and analyzing the impact of thermal interface material on the contact conductance. A one-dimensional computational study (COMSOL) of a copper/stainless steel interface clearly indicated the need to minimize thermal resistance at the interface between the calibration plate (copper) and the sample (stainless steel). The simulations indicated the necessity to focus on improving the interface contact resistance. Therefore, an attempt was made to increase the contact conductance through a function-form design involving a spring-induced mechanism. The springs were calibrated for a controlled experiment, and the measured spring constants (k = 45.5–46.5 lbf/in.) were found to be well within the range of the manufacturer's specifications. Samples of thermal interface materials (selection based on high-temperature durability, pliability, and availability) were evaluated in the clamped configuration to minimize thermal contact resistance. Baseline measurements were conducted on a calibration plate directly in contact with the test sample without any interface material or coating. From the suite of clamped interfaces, a combination of graphene/AlON coatings and interface clamping resulted in the best thermal conductance performance with significant reduction in interface contact resistance as evaluated in terms of the temperature differential between the copper calibration plate and the stainless-steel sample surface. Type K thin-film thermocouples (TFTCs) were developed to further improve the accuracy of surface temperature measurement. The alumel/chromel TFTCs demonstrated excellent agreement with the NIST calibration curve for direct integration into the temperature calibration system. The TFTCs were stable over the investigated 250°C of cycling test. The present modeling and experimental study establishes a path toward the realization of an advanced calibration system exploiting advanced nanomaterials and integrated thin-film thermocouples.

Information Shared

No information shared in FY 2016

07651

Structural Health Monitoring of Compression Connectors in Overhead Transmission Lines Using a Smart Patch

H. Wang, J.-A.J. Wang, F. Ren

Project Description

The objective of this LDRD project is to develop a structural health monitoring technology based on a smart patch for compression connectors in overhead transmission lines. Overhead transmission connectors can be degraded due to thermal aging, which can eventually result in loss of mechanical pullout strength and failure of the connectors. To avoid an unexpected breakdown, utility companies usually conduct routine line inspection using temperature and/or electric resistance measurements. However, these methods have been shown to be quite unreliable. An energized smart patch can probe the surrounding area of the connector and sense the responses of the structure resulting from the coupling effect. The proposed approach can link the structural health of the connectors to the pullout strength and thus can provide a means to determine a value for pullout strength, a capability not available in existing inspection methods. Smart patches will enable the prediction of connector lifetime in real time and will further allow utility companies to optimize the operation and maintenance of overhead transmission lines. The proposed work will position ORNL for extensive follow-on development work on sensor systems based on the patch and will demonstrate ORNL leadership in sensor material development for extreme environments in power delivery systems.

Mission Relevance

The DOE Grid Modernization Initiative is targeting a 10% reduction in the economic costs of power outages by 2025. The work performed in this project on sensing of overhead transmission line connectors is closely linked to Tasks 3.3.5 and 3.3.7, on Asset Monitoring Tools, Sensing and Measurement in the DOE *Grid Modernization Multi-Year Program Plan* (March 14, 2015). The compression connectors continue to be the weakest link in the overhead transmission lines because their failure can cause catastrophic breakdown of a power delivery system. The mechanical reliability of the connectors must be addressed from the mechanical point of view, but current inspection technologies cannot meet the need. The smart patches and underpinning electromechanical impedance (EMI) technology will bridge the technical gap. The EMI technology can provide an assessment of the mechanical condition of connectors, which will be integrated to the next generation of sensing and data management platforms, enabling full system visibility for adaptive wide-area control.

Results and Accomplishments

Commercial candidate piezoceramics were studied. Lead zirconate titanate (PZT, PSI-5A4E) was identified as a suitable "smart" material. A testing matrix was developed with regard to bonding, electrodes, and wiring to address the integration challenge, especially associated with differences in the coefficients of thermal expansion of PZT and the aluminum substrate. With aluminum beam specimens as a host structure, the proposed integration methods were tested under thermal cycling to the target temperature (125°C). The failure mechanism of PZT–metal structure was studied by using an optical microscope and a scanning electron microscope. It was observed that high-temperature epoxy such as Duralco 4538D is more durable in bonding than other materials because it stays flexible.

A PZT integration strategy was developed. The internal steel joint made on the steel core was investigated because it is responsible for ultimate tensile strength of the connector. Tensile testing was used to create structural damage to the joint or to cause steel core pullout while thermal cycling was used to introduce additional structural perturbations. EMI measurements were conducted between the tests. Root mean square deviation (RMSD) of EMI was identified as a damage index. It was demonstrated that use of steel joints enables the structural health monitoring (SHM) to be developed under simulated conditions. The EMI signature is sensitive to variations in structural conditions. The EMI RMSD can be correlated to the structural health of a connector and has potential for use in the SHM and structural integrity evaluation.

Information Shared

Hong Wang, Jy-An J. Wang, Fei Ren, Using a Smart Patch to Monitor the Structural Health of Compression Connectors in Overhead Transmission Lines, ORNL Invention Disclosure 201603791, DOE S-138,440, Oct. 10, 2016.

Hong Wang, Jy-An J. Wang, Joseph P. Swindeman, Fei Ren, John Chan, Structural health monitoring of compression connectors for overhead transmission lines, Paper No. 10169-94, Nondestructive Characterization and Monitoring of Advanced Materials, Aerospace, Civil Infrastructure, and Transportation XI (SSN08), SPIE Smart Structures/NDE 2017, Portland, OR, March 25-29, 2017.

Hong Wang, Jy-An J. Wang, Joseph P. Swindeman, Fei Ren, John Chan, Structural Health Monitoring of Compression Connectors in Overhead Transmission Lines Using a Smart Patch, LDRD Poster Session for FY2016, Sept. 13-14, 2016, ORNL

Hong Wang, Jy-An J. Wang, Fei Ren, John Chan, Smart patch integration development of compression connector structural health monitoring in overhead transmission lines, Proc. SPIE 9806, Smart Materials and Nondestructive Evaluation for Energy Systems 2016, 980606; doi:10.1117/12.2218669 (11pp).

07745

Irradiation Effect on Thermoelectric Materials

H. Wang, K.J. Leonard

Project Description

Thermoelectric (TE) materials are solid-state energy conversion devices that can generate electricity from a temperature gradient, or vice-versa, without any moving parts. Practical values for the figure of merit (*z*T) for TE materials remain a range of about 1.3 to 1.5. One of the unexplored areas for transport properties is the effect of radiation damage from high-flux neutron irradiation. A NASA Jet Propulsion Laboratory study of the effects of irradiation on radioisotope thermoelectric generators (RTGs) found no negative effect of radiation exposure. However, the accumulated dose was determined to be too low to cause any permanent damage. We propose to utilize ORNL's High Flux Isotope Reactor (HFIR) to irradiate TE materials at three to four orders of magnitude higher dose rate and accumulated dose. At those dose levels, thermal conductivity is known to decrease significantly in some materials. There has been no systematic study on electrical conductivity and Seebeck coefficient as a function of accumulated dose for those types of materials. Commercially available bismuth telluride will be used in this LDRD project. Transport properties before and after irradiation will be compared at the ORNL Low Activation Materials Development and Analysis Laboratory (LAMDA). The aim is to understand the irradiation effect on electrical properties and to search for a new way to improve zT of TEs. If successful, this project could lead to new funding opportunities and would make ORNL a leader in a new research area of enhancing TE material performance.

Mission Relevance

The goal of this research is to evaluate the irradiation effect on the transport properties and performance of a TE material. Therefore, the current project is relevant to DOE's mission in that it will help to utilize TE materials in radiation environments for power generation and waste heat recovery. Furthermore, development of TE technology can benefit other government agencies, including NASA, which is currently using TE generators for powering deep space probes, and the US Army and US Navy, which are developing portable sources for field missions. The study of TE materials under radiation may also lead to applications in which spent nuclear fuel as used a heat source for power generation.

Results and Accomplishments

Testing of baseline materials. Bismuth telluride–based materials have been used for commercial TE coolers and possess very consistent transport properties. The baseline bismuth telluride–based TE materials (p-type $BiSb_3Te_6$ and n-type Bi_2Te_3) used in this project were originally purchased from Marlow Industries and were used as samples in a round-robin study to obtain transport-properties measurements conducted for the International Energy Agency. Thermal diffusivity, specific heat, Seebeck coefficient, and electric resistivity were measured for the baseline materials in temperatures ranging from 25°C to 200°C. Measured values are necessary to properly calculate zT. The results are consistent with those of the international round-robin study.

HIFR irradiation. Ten TE samples were wrapped in two aluminum foil packets and were placed in rabbit capsules for irradiation at HFIR in early 2015. The dose rate and activity for each sample from one of the capsules have an assay date of May 1. It required 6 months of cooling following HFIR irradiation to 1.05×10^{18} n/cm^2, E > 0.1 MeV. The main contributor to dose is the Sb-124 isotope.

Irradiated materials testing at LAMDA. After the radiation assessment, the materials were transferred to LAMDA for transport-properties testing. Presently, the thermal diffusivity of n-type and p-type materials have been tested twice from 25°C to 200°C. Neither material showed significant change in thermal diffusivity. This is a very important result, indicating the possibility of using TEs in high-radiation environments without degradation in performance. Measurements of Seebeck coefficient and electrical resistivity were the tasks carried out in FY 2016. Measurements were conducted on ZEM-5 system in Building 4500S at ORNL. The results showed a small decrease in electrical resistivity for the n-type materials. A significant increase in Seebeck coefficient was observed below 150°C. Both electrical resistivity and Seebeck coefficient of the p-type materials were found to be unchanged.

Information Shared

Invited Talk

"Effect of High Fluence Neutron Irradiation on Transport Properties of Thermoelectrics", Hsin Wang and Keith Leonard, International Thermoelectric Conference ICT2016, Wuhan, China, May 29 – June 3, 2016

Manuscript

"A Study of High Fluence Neutron Irradiation on Transport Properties of Thermoelectrics", Hsin Wang and Keith Leonard, to be submitted to the Applied Physics Letter, 2016

08210

Graphite Foam Characterization for Space Applications

J. Klett

Project Description

ORNL has developed a relationship with the Massachusetts Institute of Technology Lincoln Laboratory (MIT-LL) to foster development of research programs that meet their mutual interests. This Seed LDRD project is the start of a collaboration with MIT-LL on the development of applications for its government interests. MIT-LL has requested the data that it needs to determine whether the graphite foam developed at ORNL is suitable for space applications. This project is being carried out to develop the data requested by MIT-LL.

This project had two focuses. The first was to characterize the use of ground graphite foam as an additive to a low-outgassing adhesive to increase its thermal conductivity during use in satellites. The goal was to add the particulates, thin with a solvent (OS-10), and determine whether outgassing would take place after several days in a vacuum. The second focus was to characterize the cooling potential of the graphite foam when used as a cold plate for satellite cooling systems. The research would characterize the flow of water through the pores of the foam and to measure the pressure drop and heat transfer to the water from a hot source.

Mission Relevance

MIT-LL is seeking to produce and test new versions of the ORNL graphite foam with modified densities and porosities, to be used for convective heat transfer. In previous work at ORNL, we have tested a wide variety of densities and porosities, but at flow rates and heat loads that would require extrapolation of data to meet the requirements for programs at MIT-LL. This purpose of this LDRD project is to test a variety of foams and bonding methods at the flow rates and heat duties that are required by MIT-LL. The results of this study will be used to complete a component and/or system analysis of thermal tools to identify key benefits (e.g., mass reduction) to existing and future programs at MIT-LL. In addition to the convective heat transfer coefficients, MIT-LL is interested in developing a room-temperature vulcanization (RTV) adhesive that possesses high thermal conductivity and low volatility. RTVs are used in space applications because they are excellent adhesives, they have ideal mechanical properties, and, most importantly, they exhibit very little outgassing while in space. This makes them ideal for optical benches because little outgassed material condenses on the optical equipment. MIT-LL is interested in having ORNL determine whether adding ground graphite foam to RTVs will improve their thermal conductivity and thus widen their use for space applications.

Results and Accomplishments

For the first focal area, GE RTV566 was characterized. Koppers P1HD foam was ground and sonicated to make graphene. The graphene was added to the GE RTV566 resin in volume fractions of 0%, 0.1%, 1%, 5%, 10%, and 20%. Samples were either left neat or were thinned with a solvent, OS-10, and then cured for 4 days, during which they were weighed daily to measure outgassing. The results for thermal conductivity showed an increase from about 0.4 W/mK to about 1.4 W/mK at 20% concentration. Outgassing testing showed that the neat samples had only a 0.1% weight loss over 4 days in vacuum. The samples thinned with the OS-10 had about 0.6% weight loss over 3 days, but then stabilized.

In the second focal area (cooling electronics using foam in a cold plate system), two graphite foams with different densities were cut into blocks and were bonded to aluminum plates with a thermally conductive adhesive or were brazed onto copper plates. Ten samples each were fabricated and tested in the ORNL cold plate test system. The blocks were then cut into a corrugated structure to reduce pressure drop while maintaining heat transfer and were retested. It was shown that corrugated foams exhibit a lower thermal resistance compared to the solid blocks and that they have a significantly reduced pressure drop. When compared with a typical copper pin-fin heat sink tested in the same chamber, the graphite foams performed better, with thermal resistances nearly half that of the copper pin fin heat sink. However, pressure drop was also measured, and the pressure drop through the foam was significantly higher (between 4 and 10 times higher). Calculations showed that the pumping power to move the water through the corrugated foam samples was roughly half that of the copper sinks. Hence, the foam has potential to reduce size, weight, power consumption, or a combination of these.

Information Shared

No information shared in FY 2016

NUCLEAR SECURITY AND ISOTOPE TECHNOLOGY DIVISION

07549

Maritime Explosives Detection Using Active Neutron Interrogation

D.E. Archer, I. Garishvili, M.J. Willis, D.E. Hornback

Project Description

This LDRD Seed project is follow-up to an FY 2013 Seed project titled "Investigation of Underwater Bulk Detection of Explosives Using Neutron Interrogation," which studied that possibility through modeling and simulation showing that a signature is produced that could be detected. The goal of the current project was to experimentally explore the capability to detect explosive materials in an underwater environment via active neutron interrogation, a technique that allows the object in question to be analyzed without affecting the integrity of the container. This neutron interrogation procedure, also used in medicine and in studying the terrestrial environment, uses a neutron generator to bombard a target object with a high flux of neutrons. The bombardment is followed by the spectral measurement of subsequently produced associated gamma ray signatures, which vary depending on chemical composition of the interrogated object. We used two different neutron generators that produce 14.1 MeV neutrons from the deuterium-tritium (D-T) nuclear reaction. A swimming pool was used as a water tank for the interrogated object. A gamma detector was placed with the neutron generator on the outer wall of the pool. A second gamma-ray detector was placed in the vicinity of the explosive simulants AN (ANFO) and G9 Melamine (RDX) to measure the emitted gamma spectra.

Mission Relevance

Explosives exist in the maritime domain for many reasons, including: mines protecting an area, terrorist devices targeting ships or critical infrastructure, and the dumping of unexploded ordnance in the past. Current detection of explosives relies primarily on the ability to identify the explosives container without detecting the explosives materials. An ability to detect explosives in this harsh environment in a reliable automated fashion would be a major advancement in environmental restoration efforts, homeland security, and homeland defense. Active neutron interrogation can detect explosives, and the capability can be extended to look for chemicals, illicit drugs, and other substances. Based on previous inquiries, possible future funding could come from the following government agencies: ONR and ONI, the Joint Improvised-Threat Defeat Agency, US Navy Explosive Ordnance Disposal, and DHS (US Coast Guard and Infrastructure Protection).

Results and Accomplishments

We conducted multiple experiments on AN, G9 melamine, and graphite targets that were placed in the pool. The main goal was to detect and benchmark the presence of the primary elements of concern in an explosives search (carbon, hydrogen, oxygen, and nitrogen). This was done by measuring the energy spectra of gamma particles produced as the result of neutron interactions with the interrogated material.

Two different types of neutron generators have been explored for this project. Initially, a pulsed D-T neutron generator (Thermo MP 320 with 10^8 neutrons/s) was used. A pulsed generator allows for thermal and fast neutrons to be segregated using timing from the pulse input driving the operation. Using a pulsed generator in conjunction with gamma spectroscopy is difficult because of the elevated background generated from neutron interactions with the surrounding materials. Our measurements using a pulsed generator with different geometry configurations showed no clear gamma signatures from the interrogated targets due to the large background. Therefore, in the second phase of the project we switched to an associated particle imaging generator (Thermo API 120 with 10^7neutrons/s) that measures associated 3.5 MeV alpha particles within a varying size small solid angle window. This allows the tagging of neutrons emitted into a specific solid angle opposite to direction of emitted alpha particles. For gamma detection, we explored the use of high-purity germanium (HPGe) and various sizes of NaI(Tl) gamma-ray detectors. HPGe detectors have much higher resolution, but they are much less efficient due to their smaller size. The best results were obtained using 2 × 4 ×16 in. NaI detectors. Final results with the large NaI detectors show that gamma ray signatures are visible from a variety of targets when bombarded with neutrons. In particular, we were able to cleanly detect C, O, and N elements from associated energy peaks in the measured gamma ray spectra. Elemental ratios can be further explored to determine the type of explosive present. The measurements provide a successful proof of concept that can be improved and developed into future applications that may be of interest to government agencies.

Information Shared

Our findings and measurements were presented at the ORNL LDRD seed poster session on Sep 15, 2016. Additionally writing ORNL technical note describing in detail setup and results of this project is under way.

07568

Mission-Critical Heavy Element Separations Using Electrolysis and Superionic Conduction

M. Du, K.G. Myhre

Project Description

The overarching goal of this work is to investigate the use of electrolysis and superionic conduction to accomplish elemental separations of the lanthanides and actinides (4*f* and 5*f* elements). The ability to effectively and efficiently carry out such separations is critical in many different areas, such as in the nuclear energy and medical industries. The first specific aim is to investigate the superionic conduction of *f*-elements. This involves the synthesis and characterization of novel inorganic materials given that actinide ions have never been shown to be mobile in solid electrolyte materials. The second specific aim is to study the redox behavior of the *f*-elements within solid electrolyte materials with molten salts being used as solvents. It is expected that well-controlled oxidation state equilibria will enable more effective and efficient separations when solid electrolytes are used as separation materials. Molten salts are needed as solvents due to the high temperature requirements for multivalent cationic conduction. The third specific aim is to investigate a number of different separations involving the *f*-elements.

Mission Relevance

Although the novel separation method being developed is widely applicable to many elemental separations, the focus of this research is on the separation of europium and samarium, extending to americium and curium. This specific separation is primarily important to separating milligram quantities of europium-155 from the gram quantities of irradiated isotopically pure samarium-154 target material, which is of use in various technologies, such as beta-voltaic nuclear batteries. This novel separation method is also important to ORNL's continued global leadership role in producing heavy elements such as californium-252 and berkelium-249 if the method proves to be applicable to separation of americium and curium. Additionally, it could be applied in numerous other settings to accomplish elemental separations important to other DOE missions as well as to the missions of other federal agencies and even commercial entities (e.g., the rare earth production industry). For instance, an advanced version of this separation method could be used to recycle used nuclear fuel for DOE or the commercial nuclear energy industry. It could also be used to more effectively accomplish separations of a variety of radioisotopes, which is of high importance to DOE NP as well as certain programs within DOD. The developed actinide ion conducting solid electrolyte materials could also have applications in nuclear safeguards and security settings.

Results and Accomplishments

Investigations have focused on one solid electrolyte material, Beta″-Alumina (BDPA), which has previously been studied for mainly optical applications and is known to conduct lanthanide ions. Two separation approaches have been studied: ion exchange and electrolysis. In the ion exchange studies, sodium preloaded into the BDPA material was exchanged with europium and samarium in molten chloride salts. The europium and samarium loaded into the BDPA material was then reacted with several different pure or mixed molten chloride salts containing groups IA and IIA elements. Ion exchange reactions of europium and samarium both into and out of BDPA have been studied in different atmospheres (air, vacuum, or Ar). An important result was that with a simple ion exchange separation, we showed that we could accomplish a europium and samarium separation. An important aspect of this was the selective reduction of europium to its divalent state while keeping samarium in its trivalent state during the ion exchange reactions. We were able to selectively extract europium or samarium out of the BDPA material based upon the oxidation state of europium. The loading capacity of BDPA for the lanthanides was typically measured to be at about 6% by mass. One set of conditions resulted in the selective extraction of 52% of the samarium but only 4% of the europium out of BDPA (separation factor of 26) when the [Eu^{2+}] was low. Another set of conditions resulted in 38% of the europium and none of the samarium being extracted when the [Eu^{2+}] was high in the europium/samarium loaded BDPA material. The two different directions of Eu enrichment (being kept inside BDPA or out of BDPA) can be utilized in future engineering designs of multiple-step processes for europium-155 production. Thus far, we have gained a new understanding of how to simultaneously control the oxidation states of europium and samarium in the BDPA structure. Also we initiated testing of novel pieces of equipment inside a glove box for use with radioactive actinides. This equipment included a high-temperature furnace with several quartz windows for in situ spectroscopy of a multichambered electrochemical cell that allows for real-time monitoring of the separations. This setup will allow the use of solid electrolytes for studying the separation of americium and curium.

The electrolysis approach involved the selective conduction of targeted species (such as europium) from a molten salt solution into and through a BDPA membrane. This separation approach was also tested with one selected set of conditions, achieving extraction of 6% of the original mass of europium into the BDPA membrane (with no samarium being detected in the BDPA) from 1:1 $EuCl_3$ and $SmCl_3$ molten salts at 5 V for only 20 minutes. These results are obviously encouraging but certainly require further tests for optimization.

Analysis of nonradioactive lanthanides in sample matrix of solid BDPA was new for data normalization and calibration. A significant effort was made in the case of developing laser-induced breakdown spectroscopy (LIBS) for quantitative analysis of europium and samarium in BDPA. Both LIBS and x-ray photoelectron spectroscopy were successfully applied, while neutron activation analysis was also studied.

Overall, the results from this work have shown that solid electrolytes can be used to accomplish separations involving the *f*-elements. However, a great deal of work still needs to be done to understand this novel separation approach and make it useful for routine production of radioisotopes of interest. Follow-on funding is currently being pursued through several avenues, including a recent submission to the DOE Nuclear Energy University Program FY 2017, solicitation in collaboration with researchers at the University of Tennessee. It should also be noted that this project resulted in a provisional patent application for the ion exchange and electrolysis separation methods. It also served as the subject for Myhre's doctoral dissertation, which he successfully defended in October 2016.

Information Shared

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07695

The Detection of Ionizing Radiation via Stimulated Emission

H. Huckabay

Project Description

In scintillator research, substantial effort is devoted to material design and modification to improve detector yield, efficiency, and response time. Although considerable strides have been made on this front, most scintillation techniques rely on the tendency of scintillators to emit light spontaneously. The goal of this project was to obtain proof-of-principle measurements that utilize stimulated emission rather than spontaneous emission to detect the excited state of scintillators. This LDRD project pursued two research topics: (1) the capability to drastically reduce the decay time of traditionally slow scintillators and (2) the ability to measure excited states that would otherwise decay via nonradiative pathways. The first topic has applications to improve existing scintillators that have good light output but otherwise are rendered ineffective due to afterglow effects. This is especially useful in situations where multiple radiative events must be measured in succession, often encountered at the National Ignition Facility. The second topic will yield the capability to employ previously unused materials as radiation detectors, exploiting otherwise nonradiative states for stimulated emission. This technique could provide numerous opportunities in scintillation detector research as well as the capability for commercialization of a new class of ionizing radiation detector.

Mission Relevance

Scintillator materials are widely used in radiation detection applications for both basic science and national security. Among the numerous desired attributes for scintillator assemblies is a fast rise/decay time to provide a rapid response and low afterglow. In the context of decay times, the vast majority of work performed involves materials research, which includes chemical modification or doping of the scintillator material to modify material response. This project interrogated the possibility of utilizing stimulated emission rather than spontaneous scintillation as a means to detect ionizing radiation. This approach holds the potential to significantly improve detector decay times and to open the possibility for completely new detector materials research.

Results and Accomplishments

Initial work on this project was geared toward obtaining a stimulated emission signal from the singlet state of anthracene in solution undergoing excitation from a sealed source. These measurements have yet to yield a measurable signal; however, a stimulated emission signal at 670 nm (which matches the $T_1 \rightarrow S_0$ transition) may have been observed from the triplet state of anthracene undergoing continuous excitation from a 365 nm source. If confirmed, this result is important because radiative decay from the triplet state is rare for anthracene due to competitive nonradiative relaxation. Methods used to probe these states usually require cryogenic conditions or necessitate the use of specialized host systems, whereas the approach utilized in this work can be performed in a nondestructive manner at room temperature. The approach has potential applications pertaining to the measurement of fundamental photophysical properties, the use of new materials in radiation detection applications, and developing new contrast mechanisms for optical microscopy. While the measurement of stimulated emission from the singlet state has not yet been observed, results thus far provide evidence that this approach is feasible, and future work is intended to investigate this phenomenon further.

Information Shared

No information shared in FY 2016

REACTOR AND NUCLEAR SYSTEMS DIVISION

07631

Development and Investigation of Advanced Monte Carlo Fission Source Convergence Acceleration Methodologies

K. Banerjee, G.G. Davidson, S.P. Hamilton, T.M. Evans

Project Description

The Monte Carlo (MC) method is the "gold standard" for performing reactor calculations and criticality safety analyses because of its ability to accurately represent complex geometries and physics. However, one major drawback of MC is slow fission source convergence for large and/or loosely coupled systems. Additionally, the traditional MC sampling of the fission source introduces correlation among the source points between cycles, which has been shown to result in underprediction of the variance of an MC estimator. This Seed LDRD project focused on (1) the investigation and development of a new class of fission source convergence acceleration methodologies based on sampling fission source points from an estimated fission source distribution and (2) the development of improved MC variance estimators. The kernel density estimator (KDE) was used in this research to estimate the fission source distribution from which fission source points were sampled. This novel KDE-based fission source acceleration methodology was compared with the existing methodologies, such as fission matrix and hybrid methodologies, to determine the reliability and relative efficiencies of various accelerators by comparing their performance on a set of realistic engineering problems. Additionally, two new MC variance estimators were developed.

Mission Relevance

Quantifying the effective neutron multiplication factor (k_{eff}) of a fissionable system is essential for designing and operating nuclear reactors and for addressing criticality safety issues associated with virtually all operations involving fissile material (e.g., fuel fabrication, fuel reprocessing, spent fuel handling and storage). Numerical methods, both deterministic and MC (stochastic) are used frequently for designing and ensuring the safety of systems with fissile material. However, deterministic methods lack the spectral, angular, and geometric flexibility and fidelity of the MC method. Therefore, because of its ability to accurately represent complex geometry and physics, the MC method is increasingly being used for performing reactor analyses. Unfortunately, for some systems involving fissile material, MC criticality (eigenvalue) calculations require exorbitant computing time to complete. Moreover, MC eigenvalue simulations employing power iteration (the traditional MC source iteration method) suffer from tally variance underprediction because of the cycle-to-cycle correlations. The tally variance underprediction issue is important because it may impede convergence of the tally itself (sample mean). This research investigated new fission source acceleration approaches and developed new MC variance estimators, which will support the broader objective of enabling reliable and efficient MC modeling and simulation of large and complex nuclear systems at ORNL.

Results and Accomplishments

The major objectives of this research were (1) development of innovative fission source accelerators and determination of the relative efficiencies of various new and existing accelerators by comparing their performance on a set of engineering problems and (2) development of innovative methodologies to improve the MC variance (standard deviation) estimator. Three fission source acceleration methodologies were investigated: (1) KDE, which samples fission source points from an estimated fission source distribution; (2) Sourcerer, which is similar to power iteration but uses a fast, approximate deterministic (SPN-based) solution as an improved initial guess to power iteration; and (3) a fission matrix that uses a fast deterministic solution to calculate an additive correction to the power iteration method. The various fission source acceleration methods were tested on a series of pincell problems, based upon the Organization for Economic Cooperation and Development (OECD) source convergence benchmark. Three problems, a uniform pin, OECD Problem 2.1 (axially symmetric), and OECD Problem 2.3 (axially asymmetric), were studied. The fission source acceleration results demonstrated that an SPN-based source acceleration method (Sourcerer) is superior to other methods under consideration. This finding will guide all future MC code development at ORNL.

Two novel MC variance estimators were developed, one based on covariance-adjusted methods and the other based on bootstrap methods to reduce the variance underestimation. Three test problems were used to study these newly developed methodologies. For these three test problems, it was observed that both new methods improved the estimation of the standard deviation of the sample mean by more than an order of magnitude. These new methodologies are based on postprocessing the tally results and are therefore easy to implement and code agnostic.

In conclusion, this Seed LDRD project developed two new MC variance estimators with reduced bias and investigated various new and existing fission source convergence methodologies and determined the relative efficiencies by comparing their performance on a set of realistic engineering problems.

Information Shared

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SUMMARIES OF PROJECTS SUPPORTED THROUGH LABORATORY-WIDE FELLOWSHIPS

WEINBERG FELLOWSHIP

07499

Investigation of Hydrogen Behavior in Tungsten for Fusion Reactor Divertors

L.M. Garrison

Project Description

A safety and operational concern for fusion reactors is predicting the amount of hydrogen isotopes that will be retained in the plasma-facing materials. The retention in the divertor is of special interest because the divertor will experience the highest heat and particle fluxes within a reactor. While there is a large body of literature on the effect of hydrogen and helium implantation in tungsten, there are still discrepancies and gaps in the understanding of hydrogen trapping. Beyond the single effect studies, there are few data regarding combined effects of multiple ions on hydrogen isotope retention in tungsten. Studying the influence of multiple ion implantations is important because it more accurately reflects the conditions in a fusion reactor divertor which will be bombarded by a variety of ion species including D, T, He, Be, W, C, and N. This study proposes to create a set of basic permeation and retention data for deuterium in tungsten and then compare to those for more complicated systems such as multiple ion implantations.

Mission Relevance

One of the DOE FES program's four main goals is to "support the development of the scientific understanding required to design and deploy the materials needed to support a burning plasma environment." One of the unique areas of materials design required for fusion reactors is the divertor and first wall materials. These materials experience extreme conditions of neutron, particle, and heat flux. The material behavior under these conditions is not well understood and current models are not advanced enough to replicate what is observed experimentally. Predicting and mitigating tritium retention in plasma-facing materials is a key challenge that must be overcome to develop fusion energy. This research will support the DOE FES program by furthering the understanding of hydrogen behavior in tungsten as a potential divertor material.

Results and Accomplishments

To investigate the basic science of gas interaction with a tungsten surface, it is beneficial to have a surface free of polishing artifacts that accurately represents the microstructure of the bulk material. However, a real fusion component will not be created with a defect-free surface, so it is also useful to examine the interaction of gas atoms with a surface modified by polishing. Single crystal tungsten samples with two types of surface polishes were implanted with 2 keV He^+ at 1,000°C to a fluence of 2×10^{20} He/cm^2 at the Multicharged Ion Research Facility at ORNL. After implantation scanning electron microscopy revealed that the mechanically polished sample had subgrains near the surface, even though the bulk material was a single crystal, and these surface subgrains were accentuated by the ion implantation in the low to medium fluence regime. After a fluence threshold, the surface atoms undergo enough rearrangement that the original surface finish is "forgotten," and samples that had different preimplantation surface treatments now have indistinguishable morphology. To investigate the influence of surface finish on deuterium retention, polycrystalline tungsten samples with mechanical polish, electropolish, or recrystallized preimplantation surface conditions were implanted with 350 eV D^+ at 230°C to peak fluences of 1×10^{20} D/cm^2 at the ion facility. The initial results show there are more trapping sites in the mechanically polished material and fewer in the recrystallized material. This work was presented at the 22nd Topical Meeting on the Technology of Fusion Energy in August 2016 and was submitted to *Fusion Science and Technology*. In addition to retention of hydrogen isotopes, the sputtering of tungsten surfaces is a critical concern for fusion reactors. A method for evaluating the sputtered depth on an ion exposed sample using white light interferometry was developed and published as part of the *Review of Scientific Instruments* article.

Information Shared

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Garrison, L. M., Meyer, F. W., and Bannister, M. E. "The Influence of Microstructure on Deuterium Retention in Polycrystalline Tungsten." *Fusion Science and Technology*. Submitted.

07620

Synthesis of Novel Semiconductors through High-Pressure Indentation

B. Haberl

Project Description

This project aims to synthesize novel metastable semiconductor materials using high-pressure indentation for the first time. Metastable phases of semiconductor materials are well known from standard high-pressure experiments in diamond anvil cells and result from a transformation into metallic phases on compression. On decompression, these metallic phases then transform into metastable phases. Theory and experiment have shown they possess unique electronic properties that make them interesting for technological exploitation. This is prevented, however, by small sample yield in such experiments. This is not the case if indentation is used for pressure application. This method allows for direct incorporation into existing wafer technology, but achievable pressures are not usually sufficient for pressure-induced metallization, preventing these novel semiconductors from forming. I therefore propose to develop a method that exploits the advantages of diamond anvil cell experiments with those of indentation probing in a synergistic manner to synthesize novel semiconductor structures.

Mission Relevance

The performed research aims to synthesize novel semiconductors with unique band-gap structures using new methods of high pressure application. This method enables pressure-induced band-gap engineering to achieve novel advantageous, functional band-gap structures from the ubiquitous semiconductor silicon in a technologically interesting and inexpensive manner. Several of these new structures are expected to be vastly superior for photovoltaics, and their synthesis may pave the way toward the next generation of photovoltaic materials. Thus, this project falls fully within the DOE BES mission to “control matter . . . at the electronic . . . level in order to provide the foundations for new energy technologies . . .” It also clearly addresses DOE’s energy challenge, which is one of department’s key missions.

Results and Accomplishments

Significant progress has been made to utilize indentation for the synthesis of functional metastable semiconductor phases. Two main avenues of research were pursued: (i) improving confinement during indentation and (ii) exploiting amorphous precursors.

A square-shaped flat punch indentation tip was created using diamond polishing techniques. During indentation of silicon two different plastic regimes are observed: plastic deformation without phase transformation at lower loads and via phase transformation at higher loads. Together with other work on indentation behavior and the onset of plasticity, this finding shows that a semiconductor can be forced to phase transform after it has deformed plastically via dislocations. This is a result of sufficient confinement under a suitable tip. Hence, indentation can overcome the current pressure limit (i.e., pressure can be increased after plastic deformation commences).

Because of their inherent metastability and structural diversity, amorphous precursors are highly advantageous for high pressure synthesis. This structural diversity also results in an equally diverse high pressure behavior. Therefore, it is crucial to further understanding with in situ high pressure studies and detailed studies on the structure of the amorphous precursor. To use the unique capability of neutron scattering, a new approach to high pressure application in the so-called Paris-Edinburgh cell available on the Spallation Neutrons at Pressure (SNAP) beamline of the Spallation Neutron Source was developed. This now allows for the first time for the synthesis of large volumes of pure amorphous materials for detailed structural studies and also for in situ studies on this material.

Information Shared

Publications

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Conferences

Haberl, B. 2016. "Does Amorphous Germanium Exhibit Polyamorphism?" European High Pressure Research Group, Bayreuth, Germany, Sept. 4–9.

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Haberl, B. 2016 "Recent Advances in *in Situ* High Pressure Neutron Diffraction on Disordered Materials." Invited presentation at American Conference on Neutron Scattering, Long Beach, CA, July 10–14.

Haberl, B. 2015. "Improving the Understanding of the Microscopic Material's Hardness through Detailed Assessment of Four Different Pure Silicon Structures." Presentation at 5th International Indentation Workshop, Dallas, TX, Nov. 1–5.

Habel, B. 2015. "Synthesis of Metastable Si and Ge Structures via High Pressure Indentation." Poster presentation at Joint Association Internationale pour Avancement de la Recherche et de la Technologie aux Hautes Pressions/European High Pressure Research Group Conference, Madrid, Spain, Aug. 30–Sept. 4.

Habel, B. 2015. "Phase Behavior of Pure Amorphous Silicon and Germanium Under Pressure." Senior Poster Award winner at Joint *Association Internationale pour Avancement de la Recherche et de la Technologie aux Hautes Pressions*/European High Pressure Research Group Conference, Madrid, Spain, Aug. 30–Sept. 4.

07670

Experimental and Computational Evaluation of Optical Materials for Instrumentation in Extremely High Temperature Irradiation Environments

C.M. Petrie

Project Description

This project will provide an experimental design and a multiscale computational model for evaluating the performance of optical fiber-based sensors in extremely high temperature radiation environments. Fiber optic sensors could potentially enable in situ measurements of peak temperatures, dimensional changes, and thermal properties of advanced nuclear fuels and materials during irradiation. Other potential applications for fiber optic sensors include in-pile instrumentation for research and commercial reactors, fusion applications, and other extreme non-nuclear environments (e.g., coal gasifiers or downhole applications).

The key deliverable will be a computational model of broadband temperature-dependent radiation-induced attenuation (RIA) in optical materials and an experimental design for validating the model. Results will provide initial evidence that optical instrumentation could be used for making in situ measurements of irradiated nuclear fuels and materials, and they will serve as the basis for a future instrumented irradiation experiment to definitively verify that conclusion. Under this work scope, the PI will (1) design and fabricate an irradiation "rabbit" capsule for irradiating optical samples in the flux trap of the High Flux Isotope Reactor (HFIR) at very high temperatures, (2) fabricate a broadband optical transmission test system for interrogating the samples post-irradiation to determine broadband RIA as a function of irradiation dose and temperature, and (3) develop a multiscale computational model for predicting RIA as a function of irradiation conditions, temperature, and time.

Mission Relevance

The capability to make in situ measurements during nuclear fuel and materials tests would be extremely attractive to a number of programs within the DOE NE, including the Reactor Concepts Research, Development and Demonstration program, the Fuel Cycle Research and Development program, the Nuclear Energy Enabling Technologies program, and the Idaho Facilities Management program. The Light Water Sustainability and Advanced Reactor Technologies subprograms of the Fuel Cycle Research and Development program support the development of advanced severe accident instrumentation. The Advanced Fuels Campaign and the Idaho Facilities Management program could benefit from improved fuel characterization during steady-state and transient fuel irradiation testing. Advanced fiber optic instrumentation could also support validation of the computational tools being developed in the Nuclear Energy Advanced Modeling and Simulation subprogram. Other DOE programs including the FES program in the DOE SC and the DOE National Energy Technology Laboratory could benefit from the development of advanced fiber optic instrumentation for harsh environment applications.

Two preproposals related to fiber optic sensing were submitted to the FY 2017 DOE-NE call for proposals and were encouraged to move forward to full applications. Decisions about these full proposals are expected in July 2017. Additional proposals will be submitted that will leverage an optical backscatter reflectometer sensing system that was purchased using funding from the Reactor and Nuclear Systems Division at ORNL. This system can be used to interrogate a variety of distributed fiber optic–based sensors for measuring temperature, strain, or both.

Results and Accomplishments

A multiscale computational model was developed to predict RIA as a function of wavelength, irradiation dose rates, temperature, and time. Predicted RIA after one cycle (24 days) of irradiation in the flux trap of the HFIR is on the order of 5–10 dB/m in the wavelength range of 750–900 nm at temperatures of 300°C and below. At higher temperatures (600°C and 900°C), the attenuation is reduced below 5 dB/m in the same wavelength range. This amount of attenuation is acceptable for most fiber optic–based sensor systems with a dynamic range on the order of 20–50 dB for a reasonable length (1–2 m) of fiber in the high flux region. These results indicate that implementing fiber optic–based instrumentation in HFIR irradiation experiments may be feasible, depending on the temperature and wavelength.

To validate the computational model, “rabbit” capsules were designed to irradiate “slab” specimens made of fiber optic materials in the flux trap of the HFIR at temperatures ranging from 100°C to 1,200°C. Measuring the broadband optical transmission before and after irradiation will determine the combined effects of high radiation dose and temperature on RIA. Five rabbit capsules have been assembled and will be irradiated during FY 2017. Proposals have been submitted to receive funding for building more rabbit capsules and performing the post-irradiation transmission measurements. A broadband optical transmission measurement system to measure RIA in the irradiated specimens was successfully designed, fabricated, and tested.

A distributed fiber optic sensing system was acquired and tested in a high temperature (up to 1,000°C) helium environment representative of high temperature gas-cooled reactor applications. The sensors tested survived temperatures of 700°C–800°C, with some sensors approaching 1,000°C.

Information Shared

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WIGNER FELLOWSHIP

07223

Unconventional Magnetism and Superconductivity in Noncentrosymmetric $CeTX_3$ (X = Ge,Si) Studied by Neutron Scattering

T.J. Williams

Project Description

This proposal focuses on the series of noncentrosymmetric heavy fermion compounds $CeTX_3$, where X = Si or Ge, and T is a transition metal. The f-electrons in Ce form the basis for the magnetism and heavy fermion characteristics. Previous work has measured the physical and thermodynamic properties of several compounds in this series. It was found that variations in the lattice constant, which affects the strength of the electronic interactions, produce dramatic differences in the magnetic transition. Surprisingly, this change had an opposite effect in the $CeTSi_3$ series as it did in the $CeTGe_3$ series. Further neutron-scattering work on $CeRhGe_3$ shows incommensurate ordering. This work is a strong motivation for exploring other compounds in this series using neutron-scattering techniques. Particular open questions that will be addressed will be to understand the nature of the magnetic ordering in compounds that display static ordering, to elicit the underlying electronic interactions that determine that ordering, and to elucidate how those interactions cooperate or compete in heavy fermion materials. This will provide a deeper understanding of magnetic ordering in this class of materials.

Mission Relevance

This project concerns measuring the properties of materials, including ferromagnets, semiconductors, and superconductors using neutron scattering. This makes it relevant to ORNL and DOE BES programs related to neutron scattering and research on novel materials.

Results and Accomplishments

The first objective of this work was to produce suitable quality samples of the materials in one or both series. To this end, a collaboration was initiated with David Mandrus at the University of Tennessee, who has significant expertise in growing Ce-based heavy fermion materials. Mandrus has been supportive of this project, offering the use of his laboratory to grow the samples. It was decided that the series X = Si would be a better series to start with, considering the additional literature and the growth conditions, which are more likely to succeed. So far, three materials have been successfully synthesized: $CeRhSi_3$, $CePtSi_3$, and $CeIrSi_3$. The growths have produced large (4–5 g) single crystals, which are a sufficient size for performing both elastic and inelastic neutron-diffraction measurements.

Additionally, the scope of my fellowship work has expanded to include other novel magnetic systems. Several experiments have been performed, including measurements of MnBi on HB-1, ARCS, and

HYSPEC; measurements of $U(Ru,Fe)_2Si_2$ on HB-1A, HB-1, HB-3, and SEQUOIA; measurements of $U(Ru,Os)_2Si_2$ on HB-1A and HB-3; and measurements of CrSiTe3 on CTAX, HB-3, and SEQUOIA.

The work on the itinerant ferromagnet MnBi has been focused on two aspects of the material, so the work has been split into two papers for publication. The first of these, concerning measurements of the spin waves to quantify the electronic exchange interactions was published this year. The second portion of this work has been to use polarized neutron diffraction to measure the magnitude and direction of a much smaller moment on the Bi atom relative to the Mn magnetic moment. This work is being analyzed and should be submitted for publication in the near future. This work was presented at two recent national conferences.

The work on the hidden order compound URu2Si2, as well as the Fe- and Os-doped compounds have resulted in two coauthored papers that were published this year: the first on inelastic x-ray measurements of the phonon dynamics in the parent compound and the second concerning muon spin rotation and susceptibility measurements of the Fe- and Os-doped compounds. In addition, my neutron scattering studies of the parent compound under pressure and on the Fe-doped series have both been recently submitted for publication. Also planned is the completion of the analysis of the Os-doped compounds and publication of those results.

Other projects included work on the quasi-2D semiconducting ferromagnet CrSiTe3, which has resulted in one coauthored publication and one first author publication. In addition, this project was recently presented at a conference. The next of the projects to be completed is on the itinerant ferromagnet MnBi. The measurements have been focused on two aspects of the material, so the work will be split into two papers for publication. Lastly, the measurements on $U(Ru,Fe)_2Si_2$ have produced significant quantity of data that is in the process of being analyzed, which should reveal novel properties of this doping series that will also be prepared for publication. Additionally, the work on $U(Ru,Fe)_2Si_2$ has been presented at a conference this past year.

Information Shared

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07623

Crystal Growth of Lanthanide-Halide Metal Organic Scintillators for Applications in Radiation Detection

W.M. Chance

Project Description

Previously, a family of novel inorganic/organic hybrid scintillators based on alcohol-$CeCl_3$ adducts were produced at ORNL. These represented a first amongst cerium-based scintillators and exhibited unique crystal structures that showed distinct trends with relation to alcohol chain length and branching. These compounds showed significant promise for radiation detection applications due to their ease of scaling to large crystal size, high scintillation efficiency, fast decay times, and discrimination between different radiation sources. However, since the first string of reports, no new alcohol adducts have been reported, no other solvent classes have been investigated, and optimization has not been performed for detector-level testing. The goal of this project is to design lanthanide metal organic materials with significantly improved scintillation characteristics for both gamma and neutron detection applications. To do this, a structural catalog is being created through experimentation with different alcohols and a number of other polar organic solvent classes. Using this survey and its results, structure-property relationships are being drawn to allow for design of optimized scintillator materials through ligand modification and/or lanthanide halide substitution. After identification of optimal scintillator materials from this class of compounds, crystal growth conditions will be optimized to allow for production of large ($>5cm^2$) crystals for testing in detectors.

Mission Relevance

New and improved scintillators are needed for efficient radiation detectors with applications in homeland security, nuclear nonproliferation, defense, environmental assessment, nuclear physics, neutron science, and medical imaging. Scintillator materials with high efficiency, fast decay times, and discrimination between different radiation sources can be produced from lanthanide-halide metal organic adducts. This work will answer the three basic questions: How does crystal structure affect scintillation efficiency in this class of materials? How does the choice of molecular adduct affect crystal structure? Can we combine these two pieces of knowledge to maximize scintillation efficiency while also minimizing water sensitivity? By producing a number of new hybrid crystals from diverse organic moieties and comparing their physical properties and crystal structures, this information will be obtained and used to design optimized scintillators based on this class of materials. This research topic is anticipated to prompt specific interest from Domestic Nuclear Detection Office (DNDO), Defense Threat Reduction Agency (DTRA), and the Office of Defense Nuclear Nonproliferation's Nonproliferation Research and Development Program (NA-22).

Results and Accomplishments

An initial solubility survey was conducted on a number of solvents in regards to $CeCl_3$ and $CeBr_3$. From these experiments, organic solvent classes have been down-selected and a number of organic families are being studied as solvents/adducts. Inorganic/organic hybrid crystals that have been grown thus far include adducts of cerium chloride with the following solvents: 1,2-ethanediol, 1-pentanol, 2-pentanol, γ-caprolactone, 2-methyl-1-propanol, methoxyethanol, and ethoxyethanol. Of these, only the ethoxyethanol adduct was of a size (~1cm x 1cm x 0.5cm) that allowed for testing of basic scintillation characteristics. Crystal growth conditions are being evaluated to slow the rate of nucleation in other samples to allow for significantly larger crystals necessary for device testing. Crystallographic data have been collected for new materials resulting from this work. Topological trends that have been proposed from the previously reported alcohol adducts will be compared to the new crystal structures and their physical properties to help elucidate structure-property relationships and drive further experimentation/optimization.

Information Shared

No publication

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