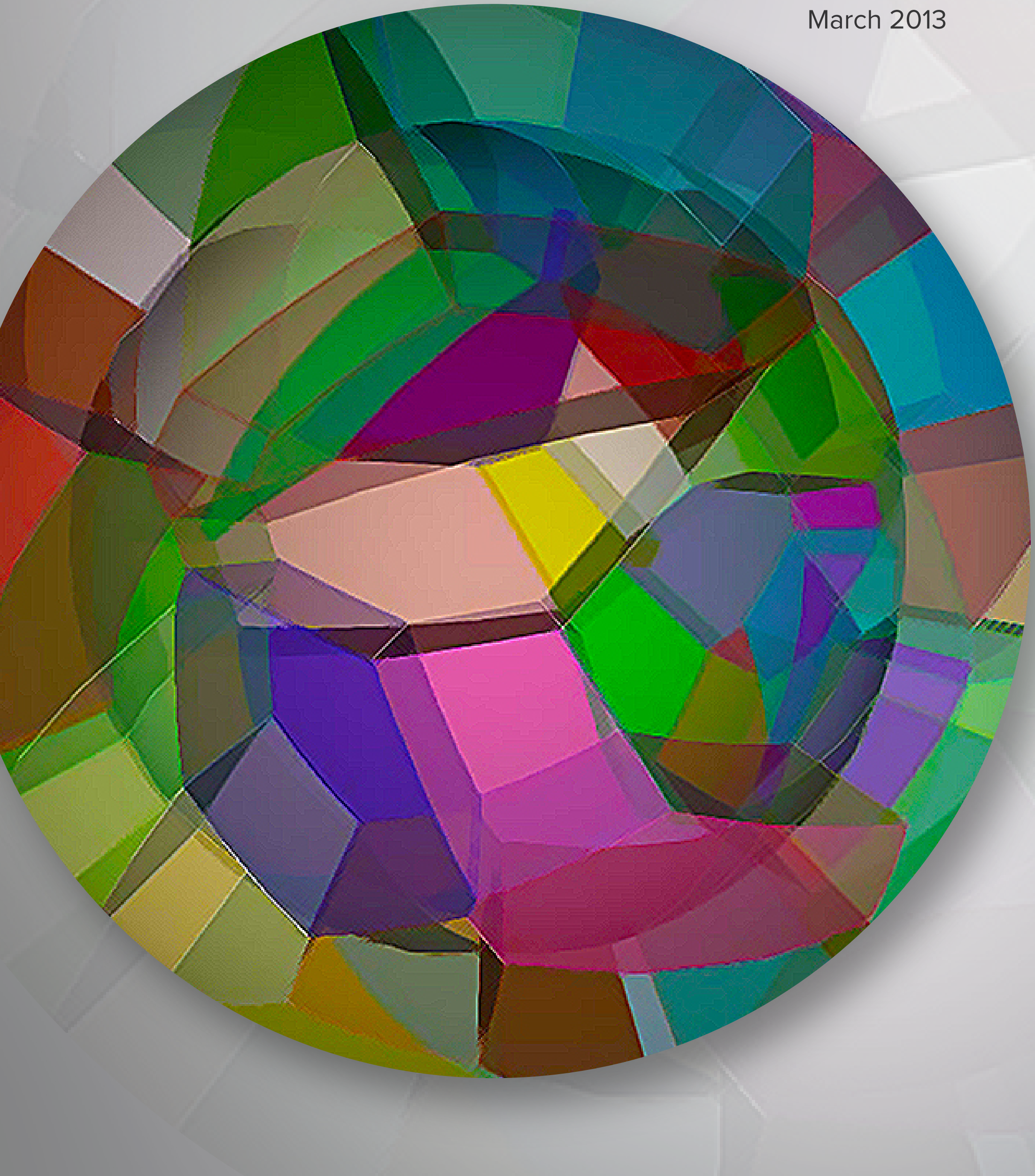
ANL-13/06

FY2012
annual report

LDRD

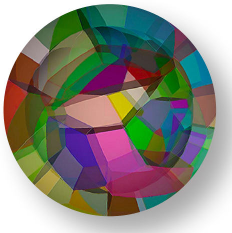
LABORATORY DIRECTED RESEARCH AND DEVELOPMENT PROGRAM ACTIVITIES

Office of the Director
March 2013



Argonne
NATIONAL LABORATORY

ON THE COVER



The image on the cover is a computer simulation of grain structure in a 15-nanometer-diameter spherical core-shell particle. As described in project report "Mesoscale Elastic Problems" (2012-015-N0), the grains were generated by placing seeds at random locations at a density based on an average grain size of a few nanometers. The simulation then allowed grains to grow until meeting a neighboring grain at their mutual midpoint. The computer-generated colors allow visualization of grains of differing crystallographic orientation. Mismatch of the crystallographic axes at grain boundaries gives rise to irregular distributions of strain and stress, quantities that will be modeled as this project goes forward.

ABOUT ARGONNE NATIONAL LABORATORY

Argonne is a U.S. Department of Energy Laboratory managed by UChicago Argonne, LLC, under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see *www.anl.gov.*

DISCLAIMER

I am very pleased to submit Argonne National Laboratory's Annual Report on our Laboratory Directed Research and Development (LDRD) activities for fiscal year 2012. Over the past year, we have made great progress in our mission of discovery and innovation in the national interest.

Our plans to upgrade the Advanced Photon Source are proceeding on schedule, and we hope to receive CD-2 approval sometime in spring 2013. When complete, the APS Upgrade will equip this vital facility for continued scientific leadership in the 21st century, providing the 5,000-plus members of our user community with greatly increased time, energy and spatial resolution. We also have successfully installed "Mira," the new IBM Blue Gene/Q system at the Argonne Leadership Computing Facility. The world's fourth-fastest supercomputer, Mira is now providing leading-edge computational power across all scientific disciplines. I am also pleased to report that Argonne's new Energy Sciences Building is proceeding on schedule; we expect it to be finished and ready for occupancy by June 30, 2013. When complete, the ESB will be one of the most modern and most flexible energy labs in the world, creating a new home for researchers focused on a wide range of energy science challenges.

Research is under way at the new multidisciplinary Institute for Molecular Engineering (IME), a joint program of the University of Chicago and Argonne. Over the past year, four new faculty members, including IME's director, – all pre-eminent researchers who hold joint appointments at Argonne – have joined the IME. We look forward to working in collaboration with the IME to find new ways to address the interfaces between molecular-level science and powerful new technologies.

In FY 2012, we continued support for the final year of the "Beyond Lithium-Ion" Director's Grand Challenge LDRD project. That project enabled significant work on the performance of lithium-based energy storage systems, pointing the way to new high-energy-density lithium-air batteries. I believe this Grand Challenge contributed significantly to our successful bid to win designation of the Argonne-based Joint Center for Energy Storage Research (JCESR) as the DOE's new Batteries and Energy Storage Hub. JCESR, which brings together a world-class "dream team" of national laboratories, universities and private sector partners, strongly benefited from LDRD program investments, both in FY2012 and in previous years. As we move forward in FY2013, the Director's Grand Challenge is now focused on new ways to address the challenges of "big data" – the acquisition, storage, transfer, and analysis of both experimental and simulated data at scales approaching the limits of our current computational capacities.

In managing Argonne's LDRD program, we have adhered to the requirements of DOE Order 413.2b and associated guidelines. Our program management continually strives for increased efficiency. In addition to meeting all reporting requirements during FY 2012, our LDRD Program Office continues to implement intranet-based process enhancements to better serve all LDRD stakeholders, including our DOE Site Office colleagues.

As the following individual project reports demonstrate, Argonne's researchers are pursuing projects at the leading edge of science and engineering, and making significant contributions to the advancement of our laboratory's major strategic initiatives. Evidence of the continuing strength of this program is found in the follow-on sponsorship won by many of these research projects, as well as in the numbers of publications, invited presentations, inventions, and new staff hires that are direct results of LDRD.

LDRD enables exploration of new scientific directions and makes it possible to adapt quickly to a changing landscape with unexpected opportunities, while enhancing the capabilities of our researchers and our scientific facilities. For these reasons, LDRD remains an invaluable resource to address the future science and technology needs of DOE, and of our nation.

Eric D. Isaacs

Eric D. Isaacs
Laboratory Director

FY2012
annual report

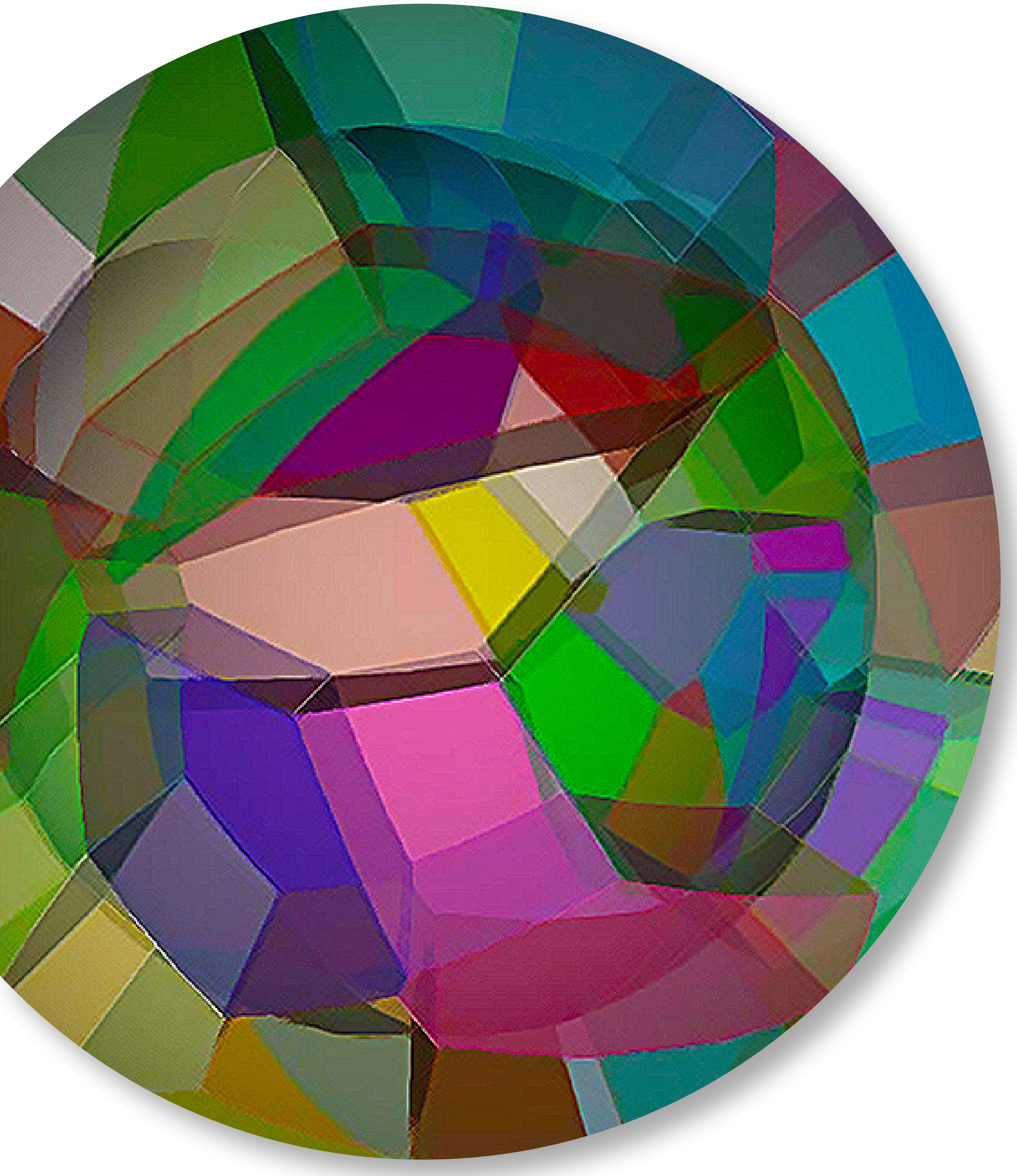


Table of Contents

See following pages for a list of Research Reports by project number and by initiative area

Research Reports – by Component

Director's Competitive Grants

Climate and Biogeosphere Interactions

Director's Grand Challenge

** Some projects topically associated with a strategic initiative area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.*

Exascale Computing Science and Applications

Hard X-ray Sciences

** Some projects topically associated with a strategic initiative area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.*

Materials and Molecular Design and Discovery (M2D2)

National Security

** Some projects topically associated with a strategic initiative area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.*

Other Novel R&D

** Some projects topically associated with a strategic initiative area, as well as other innovative projects, were reviewed and selected by the Laboratory Director outside the normal annual LDRD call for proposals and review cycle.*

Acknowledgments

Argonne's LDRD Program Office comprises the Associate Chief Scientist for LDRD, Dr. Elton N. Kaufmann; LDRD Program Office Manager, Rebecca R. Rank; Administrative Specialist, Marianne I. Lohr-Dietz; and Web Designer (co-op student), Sean M. Sullivan. The program as a whole reports to the Laboratory Director, Dr. Eric D. Isaacs, through the Deputy Laboratory Director for Programs, Dr. Mark T. Peters. Those of us in the program's management are grateful for the critical support received throughout the year, particularly while preparing this Annual Report, from the individuals listed below. Special appreciation, of course, is due to the many experts who perform the research and provide their project reports; to the technical and administrative management of Argonne's programmatic divisions, within which the research and development are pursued; to the many members of the several peer-review panels that evaluate the LDRD proposals; and to the leaders of the Laboratory's strategic initiative areas, whose vision and understanding of the nation's technological needs help guide and refine the content of Argonne's LDRD portfolio.

Computing and Information Systems Division

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Mary Hale
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Office of the Chief Financial Officer

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Andrea Manning
Marita Moniger
Michele Nelson
Katherine Obmascik
Lorenza Salinas
Sana Sandler
Vicki Skonicki
Carolyn Steele
Elizabeth Stefanski

Laboratory Overview

Argonne National Laboratory, as a U.S. Department of Energy (DOE) national laboratory, is dedicated to advancing the energy frontier through science and technology. Argonne works to accelerate innovation in science and technology for its primary sponsor, the DOE Office of Science (SC), as well as DOE's Office of Energy Efficiency and Renewable Energy (EERE) and its National Nuclear Security Administration (NNSA), and for a variety of other federal agencies. Argonne designs, builds, and operates one-of-a-kind national scientific user facilities that enhance the Laboratory's research capabilities and serve a broad community of researchers from academia, industry, and government laboratories.

As a national laboratory, Argonne concentrates on scientific and technological challenges that can be addressed only through a sustained, interdisciplinary focus at a national scale. Argonne's eight major initiatives, as enumerated in its strategic plan, are *Hard X-ray Sciences, Leadership Computing and Computational Science, Materials for Energy, Energy Storage, Applied Energy and Sustainable Transportation, Nuclear Energy, Biological and Environmental Systems, and National Security.* They are organized around the following core capabilities:

Fundamental Sciences

Nuclear Physics
Particle Physics
Accelerator Science and Technology
Condensed Matter Physics and Materials Science
Chemical and Molecular Science
Advanced Computer Science, Visualization, and Data Handling
Computational Science
Applied Mathematics
Biosciences

Applied Sciences and Engineering

Applied Materials Science and Engineering
Chemical Engineering
Applied Nuclear Science and Technology
Systems Engineering and Integration
Climate Change Science

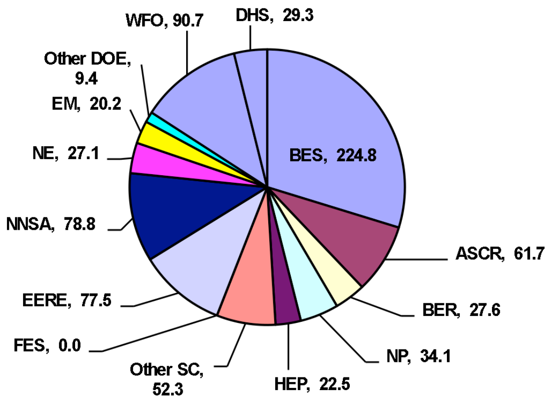
Lab-at-a-Glance

Location: Lemont, Illinois
Type: Multi-program Laboratory
Contractor: UChicago Argonne LLC
Responsible Site Office: Argonne Site Office
Website: www.anl.gov

Physical Assets:
- 1500 acres and 99 buildings
- 4.7M GSF in buildings
- Replacement Plant Value: $2.25B
- 56,811 GSF in 10 Excess Facilities
- 267,000 GSF in Leased Facilities

Human Capital:
- 3,402 Full Time Equivalent Employees (FTEs)
- 163 Joint faculty (if applicable)
- 274 Postdoctoral Researchers
- 148 Undergraduate Students
- 664 Graduate Students
- 3,858 Facility Users
- 36 Visiting Scientists

FY 2012 Funding by Source: *(Cost Data in $M):*



FY 2012 Lab Operating Costs (excluding Recovery Act*)*: $741.9M
FY 2012 DOE/NNSA Costs: $78.8M
FY 2012 WFO (Non-DOE/Non-DHS) Costs: $90.7M
FY 2012 WFO as % Total Lab Operating Costs: 12.0%
FY 2012 DHS Costs: $29.3M

Recovery Act Costed from DOE Sources in FY 2012: $14.2M

User Facilities

- The Advanced Photon Source (APS) provides a high-brightness, high-energy electron beam, which is a unique source of high-energy x-rays for scattering, spectroscopy, and imaging studies, with a timing structure enabling time-resolved research from picoseconds to seconds. The planned APS upgrade project will result in an improved world-class source of high-brightness, high-energy, tunable x-rays for scientific research.
- The Center for Nanoscale Materials (CNM), one of five DOE Nanoscale Science Research Centers, combines advanced scanning probes (including an x-ray nanoprobe; organic, inorganic, and digital synthesis; and nanofabrication), all of which are coupled with theory and modeling.
- The Electron Microscopy Center (EMC) provides state-of-the-art aberration-corrected electron microscopy (e.g., TEAM, the Transmission Electron Aberration-Corrected Microscope) with applications to three-dimensional elemental imaging and *in situ* environmental studies of catalysts and other nanoscale materials.
- The Argonne Tandem-Linac Accelerator System (ATLAS) is a scientific user facility based on a superconducting linear accelerator. It provides heavy ions in the energy domain that is best suited to study the properties of the nucleus, the core of matter, and the fuel of stars.
- The Argonne Leadership Computing Facility (ALCF) offers users access to petascale computing for research on energy systems and catalysis and in the life, environmental, and basic sciences.
- The Transportation Research Analysis and Computing Center (TRACC) operates the largest high-performance computing cluster available to U.S. transportation researchers. It performs targeted research to foster technology transfer from the national laboratory's energy research complex to the transportation research community.
- The DOE Atmospheric Radiation Measurement (ARM) Climate Research Facility provides the world's most comprehensive, continuous observational capabilities for observing atmospheric data specifically for climate change research.

In addition to these facilities, Argonne hosts its Transportation Technology Research and Development Center, Theory and Computing Sciences (TCS) Building, and the University of Chicago's Howard T. Ricketts Laboratory.

Program Assessment

Program Overview

The purposes of Argonne's Laboratory-Directed Research and Development (LDRD) program are to encourage the development of novel technical concepts, enhance the Laboratory's research and development (R&D) capabilities, and pursue its strategic goals. From proposals, projects that require advanced exploration before being sufficiently developed for support through normal programmatic channels are selected for creative and innovative R&D studies. Among the aims of the projects supported by the LDRD program are the establishment of engineering proofs of principle, assessment of design feasibility for prospective facilities, development of instrumentation or computational methods or systems, and discoveries in fundamental science and exploratory development.

The projects supported by the LDRD program are distributed across the major mission areas at Argonne, as indicated in the Laboratory's LDRD Plan for fiscal year (FY) 2012. All LDRD projects have demonstrable ties to one or more of the science, energy, environment, and national security missions of the U.S. Department of Energy (DOE), and many are also relevant to the missions of other federal agencies that sponsor work at Argonne. A natural consequence of the more "applied"-type projects is their concurrent relevance to industry.

In addition to their relevance to strategic and programmatic activities, LDRD projects also naturally fall under one or more areas of science and technology corresponding to the disciplines and fields in which Argonne's technical staff are trained and excel in supporting existing programs. In fact, perusal of the project reports in this document will demonstrate that, more often than not, expertise is drawn from several technical areas to pursue the goals of any given project. Quite often, theory and computational work are integrated with experiments in these projects. This multidisciplinary approach is a hallmark of Argonne as a multiprogram national laboratory, and it reflects the synergistic manner in which both our LDRD and our programmatic work are pursued.

The distribution of LDRD projects across the DOE-defined categories of work, as shown in Figure 1, reflects the types of actual "hands-on" work performed by our LDRD-supported investigators. However, a better indication of the ultimate purpose(s) of the work and therefore of the potential future benefits to specific programs (for example, using high-performance computation to simulate biological or catalytic processes) is found in the description of the research itself in the body of this report.

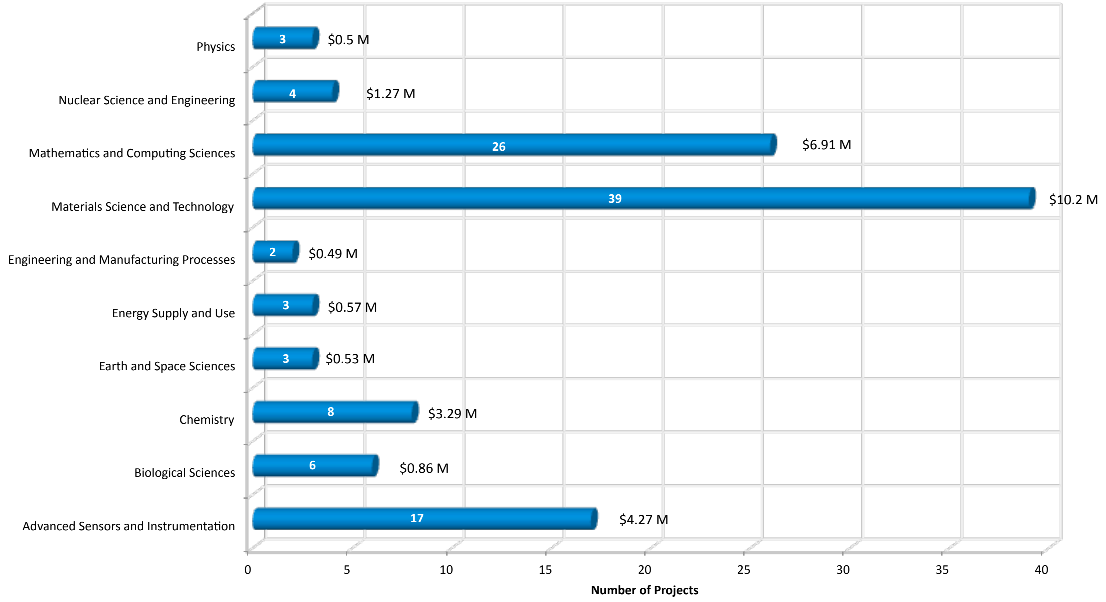


Figure 1. Number and Dollar Values of LDRD Projects across the DOE-Defined "Categories of Work."

The FY 2012 DOE-approved funding cap for LDRD was $30.0 million, or about 4.3% of Argonne's estimated FY 2012 operating plus capital budgets. Actual expenditures amounted to $28.9 million, which includes an overhead levy of approximately 29%. A table of planned or actual funding profiles for each project active in FY 2012 is provided at the end of this section. Individual brief project reports for FY 2012 comprise the bulk of this document. A list, by title, of new projects begun to date in FY 2013 is provided in the appendix.

LDRD Management Process

Argonne's R&D activities are organized under four associate laboratory directors (ALDs), who oversee the research conducted in some 14 programmatic divisions. At the top of the organization is the Laboratory Director, who is assisted by the Deputy Laboratory Director for Programs. This senior management group makes final recommendations concerning the LDRD program.

Argonne's LDRD program consists of four components: the Strategic Initiatives, the Director's Grand Challenge, the Director's Competitive Grants (DCG), and a director's strategic reserve (a portion of the total allowed expenditure temporarily reserved to handle mid-year opportunities, strategic hires for LDRD projects, and LDRD collaborative arrangements). The Strategic Initiatives, Director's Grand Challenge, and director's strategic reserve components fund R&D projects that are aligned with the Laboratory initiatives consistent with Argonne's Strategic Plan, while the DCG component supports exploratory research aligned with DOE mission areas and core competencies of the Laboratory. Annually, the Laboratory Director determines the appropriate balance of funding among the four components. All final decisions concerning Argonne's LDRD program reside with the Laboratory Director. Certain responsibilities regarding funding, oversight, proposal evaluation, and project direction are delegated.

The LDRD Program Office reviews all proposals to ensure their adherence to DOE Order 413.2b and associated guidelines, as well as to Laboratory administrative procedures. The flow chart in Figure 2 illustrates the relationships of the management and review processes for two of the components of the FY 2012 program.

The LDRD program is funded Laboratory-wide through the Laboratory's indirect budget, which is derived from a levy against all program operating and equipment budgets. Although two- or three-year durations are proposed for many projects, funding levels and project selection are determined annually and based on technical progress and the Laboratory's strategic goals and resources.

LDRD funds may be used in collaborative arrangements with third parties to enhance the application or scope of the research, with attendant beneficial interactions. To effect these arrangements, the Laboratory has in place DOE-approved procedures and instruments, such as Cooperative Research and Development Agreements (CRADAs), subcontracts, and site access Guest Agreements. These instruments and procedures enable the application of LDRD funds while ensuring that appropriate terms and conditions are applied thereto, including those related to intellectual property rights.

Line managers in Argonne's programmatic divisions are responsible for monitoring the progress and performance of LDRD research during execution. Strategic Initiative leaders and line managers confirm that mid-year progress reviews have occurred and indicate whether any remedial action or advice is needed. The responsibility for the actual conduct of all LDRD projects, including associated environmental safety and health requirements, resides with the ALDs and their line managers.

During FY 2012, all program management requirements were satisfied. Reports required by DOE, including the Annual Report for FY 2011, the LDRD Program Plan for FY 2013, and project data uploaded to the DOE/CFO (Office of the Chief Financial Officer) database, were submitted completely in a timely fashion.

Concurrence request forms (also referred to as "data sheets" in relevant guidance documents) were submitted electronically, on a project-by-project basis, to the DOE Argonne Site Office (ASO) to obtain the DOE Site Manager's concurrence before work on the FY 2012 LDRD projects proceeded.

Argonne LDRD Proposal Selection Process Schematic

(Applies to Review and Selection Process for FY 2012 Proposals)

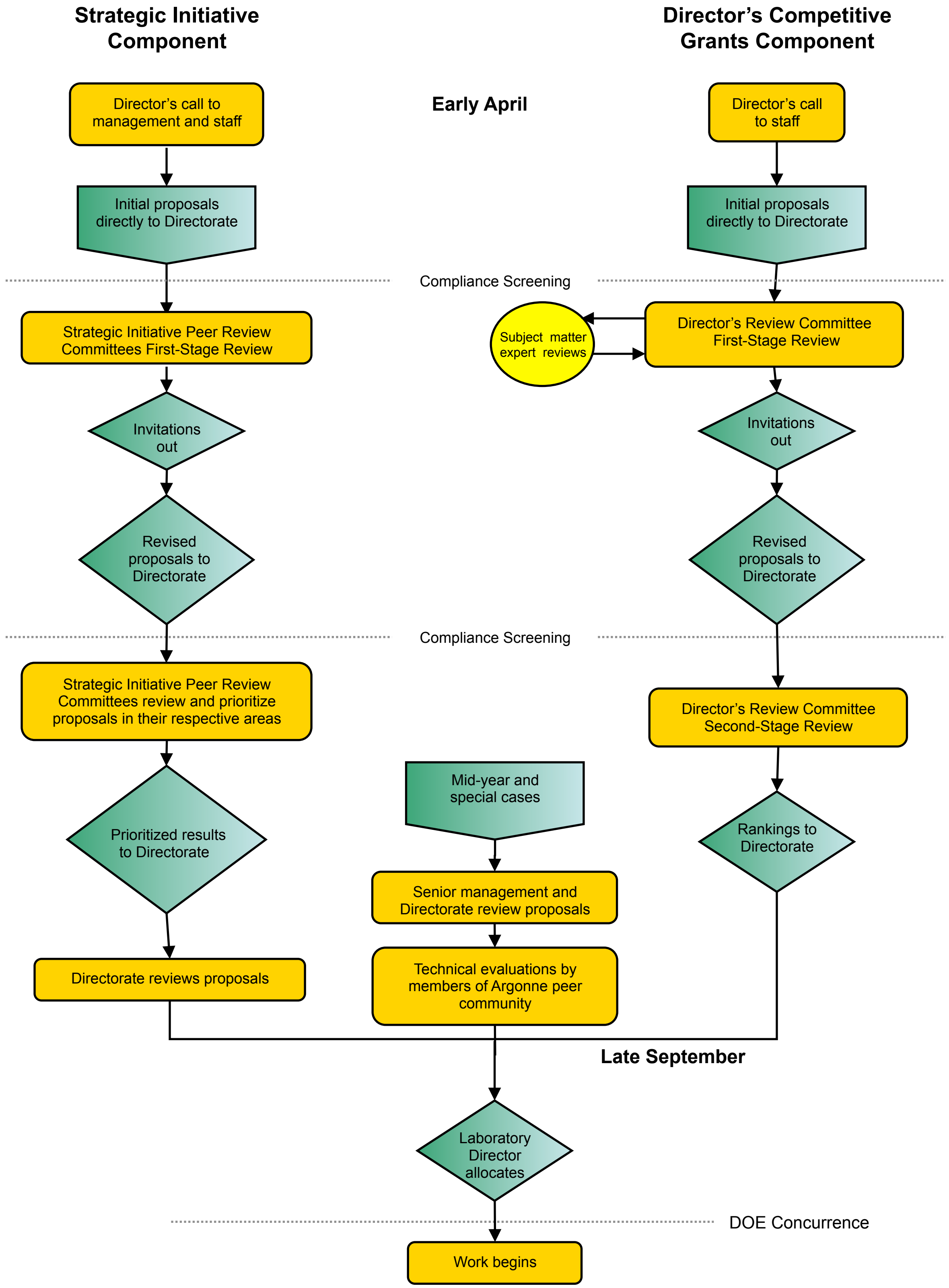


Figure 2. Argonne LDRD Selection Process Schematic.

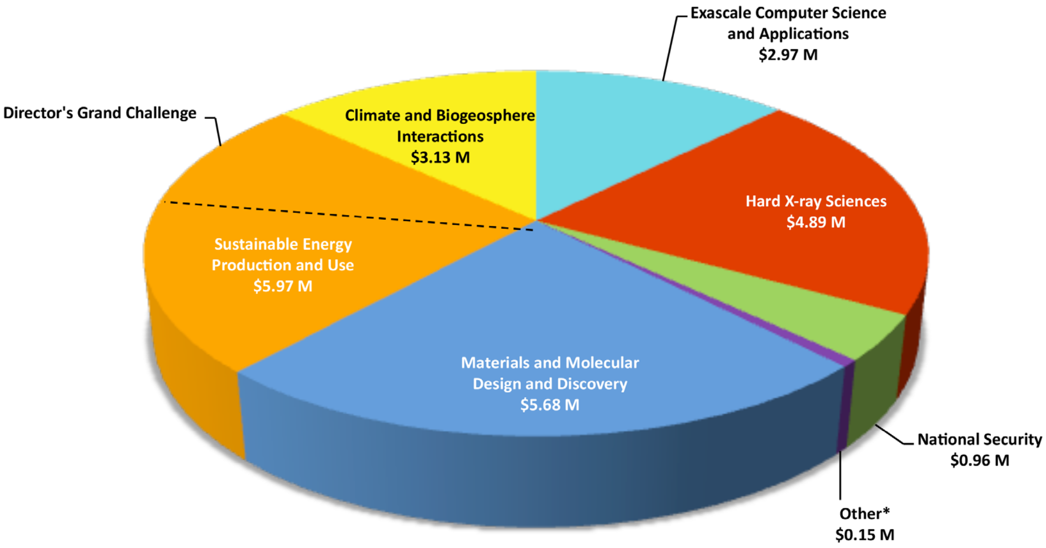
FY 2012 LDRD Components

Strategic Initiatives

This larger component of LDRD emphasizes R&D explicitly aligned with Laboratory and Department missions as reflected in strategic initiatives proposed by senior management and consistent with Argonne's Strategic Plan. Strategic goals are revised periodically and reevaluated as necessary. The choice of initiative areas reflects an evaluation of the state of development of the relevant technical fields; the potential value to the Department and the nation of advancing those fields; and, of course, the compatibility and synergy that these fields have with existing facilities, capabilities, and staff expertise at Argonne.

In FY 2012, there were six strategic initiative areas in which proposals could be submitted. The FY 2012 review procedures continued to ensure that all individual proposals identified as fitting under a strategic initiative were reviewed for their scientific quality, innovation, and value to each respective mission-related initiative.

The review of proposals with regard to the strategic initiatives component relies on a combination of peer and management reviews within initiative areas. The Laboratory Director appoints a Strategic Initiative leader for each of the respective Strategic Initiatives to evaluate and recommend projects for funding. The Strategic Initiative leader selects internal and external subject matter experts to serve on review panels to assist in reviewing the proposals that have been submitted. Results are reported to the Laboratory Director, who makes final selections and approves the content and aggregate budget. In FY 2012, 15 new projects and 61 continuing projects under the six Strategic Initiative areas listed here were funded at an aggregate level of $23.6 M. Some additional mid-year and strategic-hire projects, selected by the Laboratory Director, are included in these figures. One small strategic project ($0.15 M) continued into FY 2012 that fell outside these six areas. The overall FY 2012 funding level for the Strategic Initiative component equaled $23.8 M (Figure 3).



*Special and Mid-year Start Projects

Figure 3. Distribution of Funding among Strategic Initiative Areas.

The six FY 2012 Strategic Initiative areas are as follows:

Climate and Biogeosphere Interactions

The key elements of this initiative fall under the following general areas: leveraging ultra-high-resolution regional and global climate simulations by using the Geophysical Fluid Dynamics Laboratory (GFLD) global climate model and the National Center for Atmospheric Research (NCAR) Nested Regional Climate Model (NRCM) regional-scale model on Argonne high-performance computing systems, conducting metagenomics-enabled analyses of terrestrial microbial communities to demonstrate connections to the global carbon cycle, and enriching metagenomics-enabled approaches for understanding key biotic regulators in carbon cycling.

Exascale Computer Science and Applications

The key elements of this initiative fall under the following general areas: novel system architectures, strategic application development, extreme-scale system software, and extremely scalable algorithms and computing methodologies.

Hard X-ray Sciences

Two key focus areas for projects under this initiative area are as follows: enhanced x-ray instrumentation and hard x-ray science.

Materials and Molecular Design and Discovery (M2D2)

Two research focus themes were selected for this initiative on the basis of how much they represent core areas of expertise and provide an opportunity for future scientific growth: crystal discovery and/or single crystal processing and self-assembled structures. The M2D2 initiative focuses on fundamental advances in the understanding of materials design, growth, and functions in these areas, with credible translation to the use-inspired space.

National Security

LDRD projects under the national security initiative focus on current and emerging scientific and technological challenges in both homeland security and national defense, including, but not limited to, research in the areas of sensors, materials, decision science, nonproliferation technologies, forensics, and cyber security. The key research area in FY 2012 was cyber security.

Sustainable Energy Production and Use

Key focus areas of projects under this initiative include climate change and the impact of advanced energy technologies, science-based engineering for the nuclear energy supply, advanced materials for energy conversion and storage, and transportation science and technology.

Director’s Grand Challenge

The Director’s Grand Challenge component of the LDRD portfolio may be included in the LDRD program of any given fiscal year by the Laboratory Director. Also at the discretion of the Laboratory Director is the schedule for the call for proposals and for the review and selection of projects for this component, which does not need to match the schedules for the Strategic Initiatives or Director’s Competitive Grants components. For a Grand Challenge project, sufficient talent and resources are devoted to a specific technical topic within an area that is of substantial strategic value to the Laboratory and to DOE, in order to allow major strides to be made toward achieving its R&D goals. The emphasis is on crosscutting initiatives that synergistically draw on Argonne’s core competencies.

As a precursor to formal LDRD proposal submission, brief “white papers” are solicited. The white papers are evaluated by a Grand Challenge Review and Oversight Panel that is composed of four to six internal and external subject matter experts. The panel members recommend which white paper authors should be invited to submit more extensive formal proposals. The latter are reviewed and ranked on the basis of their expected impact, creativity, degree of crosscutting utilization of Argonne core capabilities and staff, and potential for success. The successful Grand Challenge LDRD project is expected to target a specific outcome, enabled by a specific innovative approach, with a well-coordinated team. The awarded project is formally reviewed by the Grand Challenge Review and Oversight Panel semiannually to evaluate progress.

In FY 2012, there were no new Grand Challenge topics addressed as part of the LDRD portfolio. However, the energy-storage-related topic addressed in FY 2010 was continued. The project was awarded $2.01 M in FY 2012.

Director’s Competitive Grants (DCG)

The DCG component invests in a full spectrum of investigator-initiated proposals across the Laboratory in DOE-mission-related science and engineering areas. This component provides an avenue for R&D staff to propose highly innovative projects directly to the Laboratory Director. Proposals are subjected to peer review by the Director’s Review Committee to assess their scientific and technical quality. The Committee is composed of nonmanagerial scientists and engineers selected by the Laboratory Director. The Committee currently consists of 21 members who have substantial expertise in their technical fields, are familiar with the peer review process, and represent a broad cross section of the Laboratory. The Director’s Review Committee conducts an initial peer review that results in a smaller number of proposals being retained for further review by the Committee. The products of the review procedure are a rank-ordered list of proposals given to the Laboratory Director and brief critiques of proposals sent to the proposing investigators.

The DCG review process is augmented by the recruitment of members of the Laboratory's research community who served as volunteer subject matter experts to assist the Director's Review Committee in reviewing proposals. Approximately 225 researchers volunteered, and their assistance made it possible for the Director's Review Committee to recommend the highest-quality proposals for funding in FY 2012. These projects make up about 17.6% of the Laboratory's LDRD budget. In FY 2012, 8 new projects and 26 continuing projects were funded at a total level of $5.1 M.

FY 2013 Update

DOE approved Argonne's FY 2013 LDRD Plan and program expenditures not to exceed $30 M. A list of projects begun so far in FY 2013, by title, is provided in an appendix to this report.

For FY 2013, leadership of our LDRD strategic initiative areas and of the Laboratory's major initiative areas as delineated in Argonne's Strategic Plan has been consolidated and focused under respective associate laboratory director-led teams. Advance "concept papers" are solicited from all staff from among which the most relevant and potentially effective ideas are invited to be fleshed out in full proposals to the LDRD Program. This approach is proving to be a more efficient use of reviewer expertise, to require less time and effort on the part of proponents, and to better align our strategic LDRD research portfolio with the Laboratory's Strategic and Business Plans.

Also in FY 2013, the Laboratory Director issued a second Director's Grand Challenge call for topic ideas followed by research proposals. The submission and review protocol was similar to that used for the first such call in 2010. This year, the successful topic emerged as "Integrating Simulation and Observation: Discovery Engines for Big Data." A dedicated review panel will be formed that oversees the project for its duration.

For the 2013 fiscal year, we are continuing to refine our use of electronic tools to communicate with investigators and reviewers and to collect and document performance information on LDRD projects. We are improving existing individual web-based applications and developing new electronic tools as necessary. One recent example is the addition of an "LDRD Highlights" database with web-based submission and management tools. We expect this more organized and archival approach to documenting the notable accomplishments of LDRD research will aid in our support of the Department's continuing efforts to educate and inform stakeholders about LDRD investments.

A more general and broad re-tooling of IT applications supporting management of the LDRD Program is also under way. When complete, a consolidated interactive system will provide our users with a one-stop shop tailored to their specific needs.

Peer Review Experience in FY 2012

The pursuit of LDRD is managed and its performance is reviewed as an integral part of the activities of the respective technical divisions in which the work resides. Periodic peer reviews of each division's programs and research are conducted by committees empanelled by Argonne's management and operations (M&O) contractor, UChicago Argonne, LLC. The quality of the science and technology performed under LDRD funding within a division cannot be distinguished from that reflected in the division's performance of programmatic R&D. By and large, the same research personnel and the same facilities are applied to both, and no discernible qualitative differences have been observed. LDRD is therefore not reviewed separately; however, results and plans relevant to LDRD projects are routinely exposed to Review Committee scrutiny. A tabulation of such reviews for FY 2012 is provided in Table 1, along with an aggregate accounting of the number of LDRD projects exposed to committee review and their total dollar values.

The LDRD Program Office also requires principal investigators to report all other relevant external reviews of their work. LDRD projects from the APS Engineering Support (AES), Accelerator Systems (ASD), Chemical Sciences and Engineering (CSE), Decision and Information Sciences (DIS), Energy Systems (ES), High Energy Physics (HEP), Mathematics and Computer Science (MCS), Materials Science (MSD), Nuclear Engineering (NE), and X-ray Science (XSD) divisions; the Center for Nanoscale Materials (CNM); and the Physical Sciences and Engineering (PSE) and the Computer, Environment, and Life Sciences (CELS) ALD areas were reviewed as part of an overall contractor-chartered review.

Table 1. Summary of Peer Review History by Organization

Organization	Date of Review(s)	Number of LDRD Related Presentations	Number of LDRD Related Projects	Dollar Value of Projects ($ in thousands)
AES	7/18/12	1	1	$561.5
ASD	7/18/12	4	7	$4,511.4
CELS	6/7/12 9/18/12	2	5	$2,493.9
CNM	6/7/12	1	1	$1,512.9
CSE	6/7/12	1	1	$1,264.5
DIS	11/9/11	1	1	$1,033.5
ES	11/9/11 6/7/12	9	11	$6,606.4
HEP	9/18/12	1	1	$1,378.3
MCS	9/18/12	6	9	$5,858.5
MSD	6/7/12	4	9	$10,337.6
NE	11/9/11 6/7/12	4	6	$4,536.3
PSE	6/7/12	1	2	$1,405.8
XSD	6/7/12 7/18/12	5	19	$16,314.6
Totals		**40**	**73**	**$57,815.2**

Performance Metrics

The LDRD Program Office collects statistical data on current and completed LDRD projects. Such data cover various items; examples include publications (see citations in the appendix to this report), inventions (see an itemized list in the appendix to this report), follow-on sponsorship, and the enhancement of staff by post-doctoral appointees and new hires. Although these data are of little value on a project-by-project basis, in aggregate, they do provide a picture of overall program productivity. The management processes employed to collect these data include surveys of current and former investigators, analyses of project annual reports, and validation against records of the Technology Development and Commercialization (TDC) Division; the Legal Department (LEG); and the Publications Release Services section of the Computing and Information Systems (CIS) Division. A summary of the most recently collected data is provided in Tables 2 and 3. Table 2 displays project outcomes realized only during FY 2012 but derived from projects active in any year or years from FY 2009 forward. For the same prior and currently active projects, Table 3 displays those metrics for which cumulative results are monitored, with no restriction as to when the accomplishments occurred.

Table 2. Aggregate FY 2012 Outcomes for Recently Completed and Current Projects

Most Recent Project Year	LDRD Component	Number of Refereed Publications	Number of Students/ Postdocs Supported	Number of New Staff Hires	Number of Non-Publication Copyrights	Number of Invention Disclosures	Number of Patents Issued/ Pending
2009							
	Competitive Grants	2	0	0	0	0	2
	Strategic Initative	16	0	4	0	0	1
2010							
	Competitive Grants	6	0	1	0	1	1
	Strategic Initative	22	0	6	0	1	1
2011							
	Competitive Grants	7	0	1	0	1	0
	Strategic Initative	7	0	2	0	2	1
2012							
	Competitive Grants	24	49	3	0	11	8
	Strategic Initative	149	142	7	1	13	8
Grand Totals: 248 Projects		**233**	**191**	**24**	**1**	**29**	**22**

Table 3. Aggregate Outcomes for All Years of Recently Completed and Current Projects (2009–2012)

Most Recent Project Year	Number of Projects Receiving Follow-on Funds	Number of Proposals Submitted To Sponsors	Number of External Reviews
2009	25	175	15 DOE 18 Other 19 UofC
			52 Total
2010	34	217	27 DOE 19 Other 28 UoC
			74 Total
2011	8	63	8 DOE 3 Other 23 UoC
			34 Total
2012	18	151	21 DOE 16 Other 98 UoC
			135 Total
Totals: 248 Projects	**85**	**606**	71 DOE 56 Other 168 UoC
			295 Total

LDRD Five-Year Funding Summary ($ in thousands) for Projects Active in FY 2012

Proposal No.	2010	2011	2012	2013 (a)	2013 (b)	Total
2010-003-R2	148.0	140.1	134.1			422.2
2010-010-R2	180.8	170.6	148.7			500.1
2010-029-R2	160.9	171.1	151.4			483.4
2010-042-R2	169.2	156.9	149.1			475.2
2010-043-R2	200.1	200.3	176.5			576.9
2010-044-R2	299.3	241.0	493.2			1,033.5
2010-049-R2	155.9	131.8	133.5			421.2
2010-050-R2	173.5	137.9	157.4			468.8
2010-063-R2	132.5	106.4	78.1			317.0
2010-073-R2	159.8	154.9	134.1			448.8
2010-074-R2	177.1	267.6	247.6			692.3
2010-093-R2	160.0	77.1	114.1			351.2
2010-117-R2	170.3	320.5	338.0			828.8
2010-119-R2	133.5	133.9	148.5			415.9
2010-129-R2	129.5	130.0	110.1			369.6
2010-131-R2	702.1	793.0	397.1			1,892.2
2010-137-R2	157.8	176.3	158.1			492.2
2010-138-R2	142.3	112.9	114.7			369.9
2010-139-R2	222.1	215.0	195.9			633.0
2010-158-R2	179.1	189.0	184.7			552.8
2010-161-R2	207.4	169.1	173.0			549.5
2010-167-R2	199.5	225.8	348.8			774.1
2010-183-R2	269.8	273.1	157.8			700.7
2010-185-R2	1,047.5	1,918.0	2,007.8			4,973.3
2010-188-R2	506.5	506.3	500.1			1,512.9
2010-190-R2	118.4	324.6	328.8			771.8
2010-191-R2	715.1	455.3	194.5			1,364.9
2010-192-R2	107.0	111.8	67.6			286.4
2010-193-R2	542.5	219.2	218.9			980.6
2010-194-R2	32.7	220.8	235.6	100.0		589.1
2010-195-R2	83.4	571.9	555.8	480.0		1,691.1
2010-196-R2	128.9	466.7	488.5			1,084.1
2010-197-R2	126.4	536.3	608.6	449.0		1,720.3
2010-198-R2	169.9	340.7	413.2			923.8
2010-199-R2	99.4	422.4	297.9	100.0		919.7
2010-201-R2	193.8	392.7	328.8	300.0		1,215.3
2010-202-R2	26.0	94.6	101.3	76.5		298.4
2010-204-R2	50.5	415.0	456.9	390.0		1,312.4
2011-005-R1		67.2	139.6	145.0		351.8
2011-012-R1		102.6	112.7	140.0		355.3
2011-022-R1		150.0	183.1	200.0		533.1
2011-023-R1		106.8	259.8	157.0		523.6
2011-027-R1		44.6	123.6			168.2
2011-038-R1		179.4	201.8	100.0		481.2

LDRD Five-Year Funding Summary ($ in thousands) for Projects Active in FY 2012

Proposal No.	2010	2011	2012	2013 (a)	2013 (b)	Total
2011-052-R1		220.7	251.7	240.0		712.4
2011-060-R1		599.1	665.4	620.0		1,884.5
2011-063-R1		296.6	315.6	330.0		942.2
2011-067-R1		254.3	164.9	120.0		539.2
2011-071-R1		147.1	132.4	160.0		439.5
2011-083-R1		238.0	360.7	350.0		948.7
2011-093-R1		105.9	94.1	145.0		345.0
2011-097-R1		80.2	120.8	150.0		351.0
2011-101-R1		430.5	507.7	505.0		1,443.2
2011-104-R1		161.4	163.3	210.0		534.7
2011-106-R1		206.3	206.0			412.3
2011-109-R1		176.1	123.2	185.0		484.3
2011-110-R1		73.1	114.4	125.0		312.5
2011-116-R1		110.9	103.7	135.0		349.6
2011-121-R1		183.4	123.1	170.0		476.5
2011-123-R1		194.5	273.1	275.0		742.6
2011-126-R1		221.9	234.2	250.0		706.1
2011-129-R1		81.0	84.6	100.0		265.6
2011-134-R1		548.5	568.2	520.0		1,636.7
2011-140-R1		163.9	218.5	235.0		617.4
2011-147-R1		171.9	230.7	250.0		652.6
2011-149-R1		137.6	259.1	295.0		691.7
2011-153-R1		177.9	226.5			404.4
2011-170-R1		264.7	215.2	243.0		722.9
2011-188-R1		676.4	602.0	550.0		1,828.4
2011-193-R1		185.1	191.8	225.0		601.9
2011-196-R1		474.4	164.6	200.0		839.0
2011-197-R1		236.8	242.0	250.0		728.8
2011-198-R1		145.4	172.6	167.0		485.0
2011-199-R1		150.3	148.4	150.0		448.7
2011-200-R1		286.2	297.4	307.0		890.6
2011-202-R1		148.2	150.4			298.6
2011-204-R1		290.5	722.0	193.0		1,205.5
2011-206-R1		266.8	324.8			591.6
2011-207-R1		200.9	153.9			354.8
2011-209-R1		251.5	403.4			654.9
2011-210-R1		59.1	146.5	136.0	94.0	435.6
2011-211-R1		149.1	194.4	200.0	50.0	593.5
2011-212-R1		130.3	389.9			520.2
2011-213-R1		354.7	1,023.6	1,019.2	473.6	2,871.1
2011-214-R1		138.5	477.8	204.0		820.3
2011-215-R1		234.9	326.6	10.5		572.0
2011-216-R1		67.6	84.0	20.0		171.6
2011-217-R1		51.7	334.4	348.0	267.5	1,001.6

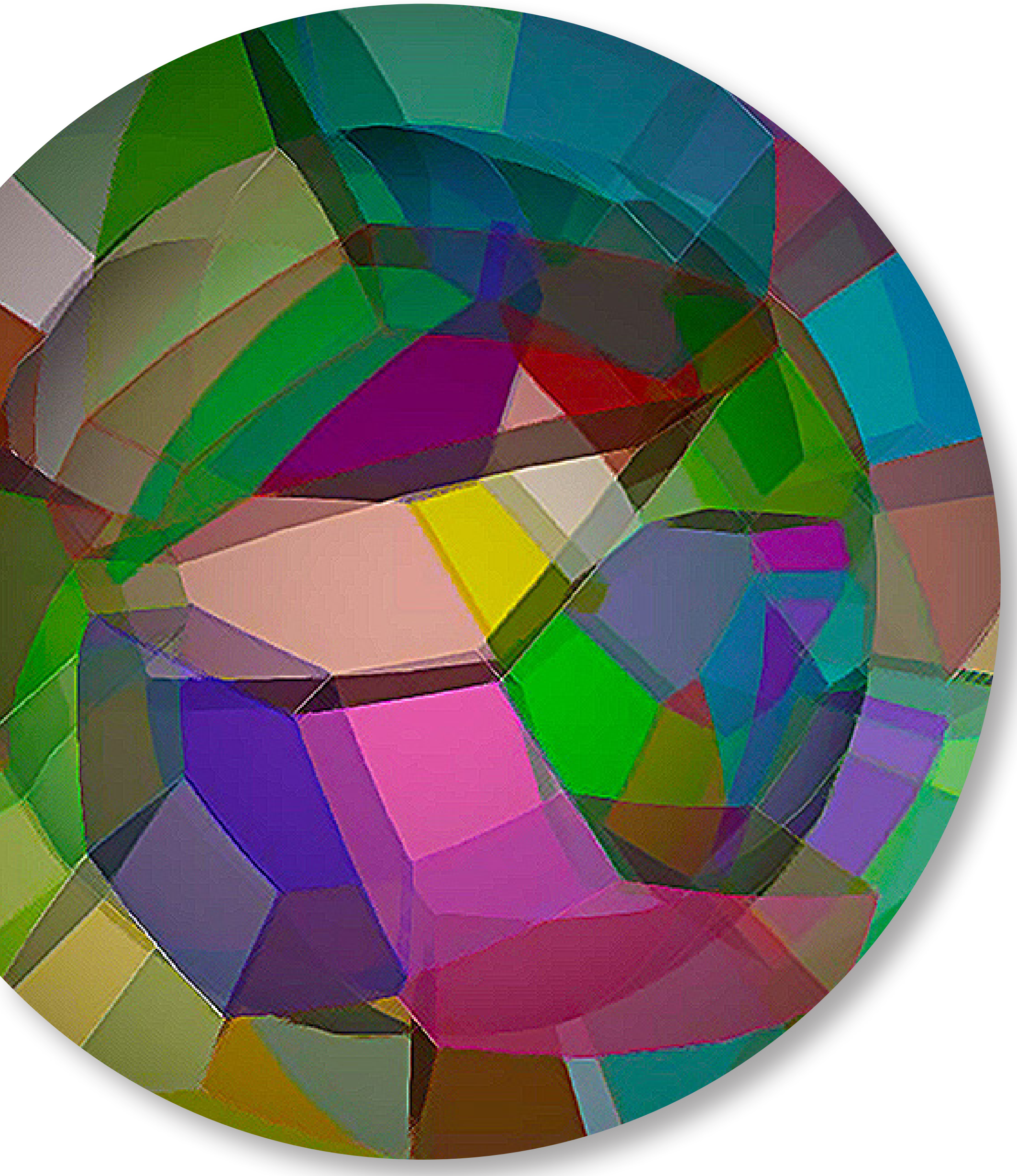
LDRD Five-Year Funding Summary ($ in thousands) for Projects Active in FY 2012

Proposal No.	2010	2011	2012	2013 (a)	2013 (b)	Total
2012-012-N0			173.9	200.0	220.0	593.9
2012-015-N0			266.3	200.0	280.0	746.3
2012-016-N0			125.4	100.0	100.0	325.4
2012-052-N0			101.6	140.0		241.6
2012-055-N0			117.1	120.0		237.1
2012-061-N0			210.0	145.0	155.0	510.0
2012-072-N0			149.7	175.0	200.0	524.7
2012-074-N0			448.6	420.0	452.0	1,320.6
2012-082-N0			192.7	175.0	225.0	592.7
2012-087-N0			117.0	150.0	150.0	417.0
2012-114-N0			202.5	150.0	200.0	552.5
2012-180-N0			217.8	250.0		467.8
2012-181-N0			158.8	150.0	160.0	468.8
2012-197-N0			244.0			244.0
2012-199-N0			317.9			317.9
2012-202-N0			155.2	150.0	150.0	455.2
2012-203-N0			292.5	500.0		792.5
2012-204-N0			69.0	100.0	125.0	294.0
2012-205-N0*			159.6	300.0	300.0	759.6
2012-206-N0*			114.1	300.0	300.0	714.1
2012-207-N0			164.1	405.0		569.1
2012-208-N0			285.2	555.0		840.2
2012-209-N0*			10.0	130.0	200.0	340.0
Totals	**8,578.5**	**22,085.1**	**28,870.0**	**17,045.2**	**4,102.1**	**80,680.9**

(a) FY 2013 figures represent allocations and not actual expenditures.
(b) FY 2014 figures represent projections assuming the project continues into FY 2014.
*FY 2012 late start projects may have costs in FY 2015 that are not shown in the table.

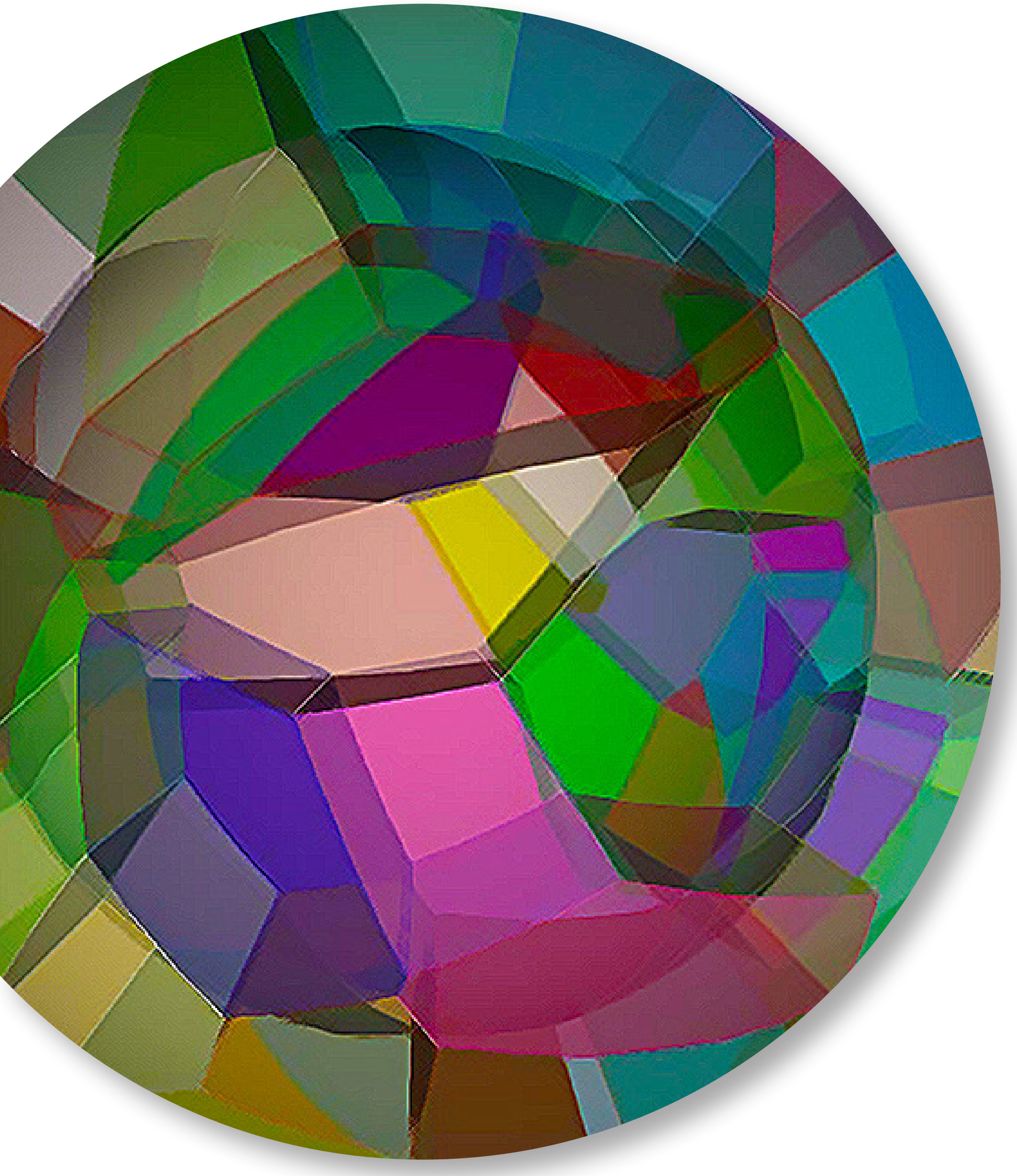
FY2012
annual report

RESEARCH REPORTS



FY2012
annual report

DIRECTOR'S COMPETITIVE GRANTS



Magneto-Vibrational Energy Conversion at the Nanoscale

2010-003-R2

Axel Hoffmann and O. Daniel López

Project Description

In 1915, the seminal works by Einstein and de Haas (magnetization change results in mechanical rotation) and Barnett (mechanical rotation results in magnetization change) proved unambiguously that magnetic moments possess corresponding mechanical angular momentum. Interest in this phenomenon has been renewed since several recent experiments have shown that magnetism-related mechanical torques are sufficient to significantly modify the dynamics of micrometer-sized mechanical objects (usually known as microelectromechanical systems [MEMS]) with kHz-resonance frequencies.

Furthermore, it has been recently demonstrated that patterned magnetic nanostructures have well-controlled magnetization dynamics at frequencies of a few hundred MHz, which is well below their ferromagnetic resonance (typically a few GHz and above). Moreover, the magnetization dynamics of these nanostructures can be excited by passing local alternating electric currents through them. These recent developments open up the possibility of having hybrid magnetomechanical nanostructures with commensurable resonance frequencies. Integration of magnetic nanostructures on top of submicrometer-sized mechanical objects (or nanoelectromechanical systems [NEMS]) will allow very precise control of their mechanical motion and increase the efficiency of the magnetomechanical coupling by orders of magnitude.

Our goal is to integrate magnetic domain wall oscillators with high-frequency torsional NEMS oscillators and to investigate the magnetomechanical coupling between them. When a submicrometer ferromagnetic material with small magnetocrystalline anisotropy (e.g., permalloy) is patterned into a wire, a domain wall can be stabilized in a notch structure. This geometrically defined notch gives rise to a harmonic or an anharmonic pinning potential defined by the shape and slope of the notch sidewalls. This potential, in turn, allows the selection of specific domain wall resonance frequencies, which can be excited and detected via radiofrequency electric transport measurements. Although these frequencies have been demonstrated to be as low as 10 MHz, the low-frequency limit has not been sufficiently explored. The domain wall resonance results in an oscillating net magnetic moment around the notch position. If one of these domain wall oscillators is integrated on top of a nanomechanical system, the change in magnetization will induce an oscillating mechanical torque along the rotational axis of the NEMS oscillator.

The resonance frequencies of either oscillator can be controlled individually by geometry and, thus, varied independently from one another. Furthermore, the resonance frequency of the magnetic domain wall oscillator can be tuned via applied external magnetic fields. This enables us to directly test the role of commensurability of the two resonance frequencies for the magnetomechanical coupling.

Mission Relevance

This project is relevant to DOE's energy and science missions. The demonstration of frequency-matched magnetomechanical coupling has both direct basic and applied impacts. From a fundamental point of view, measurements of such coupled systems enable researchers to determine the magnetomechanical ratio *g′* in ferromagnetic thin films and nanostructures and to observe magnetomechanical polaritons. An efficient conversion between magnetic and mechanical kinetic energy will provide a novel transduction mechanism to actuate mechanical structures with dimensions below 100 nm. This actuation can excite high-frequency nanomechanical devices by using magnetization dynamics to actuate mechanical motion or enable unique energy harvesting structures to collect power from continuously renewable energy sources, such as vibrations or thermal energy, thereby converting mechanical motion into magnetization dynamics and, ultimately, electricity.

FY 2012 Results and Accomplishments

Before FY 2012, using magnetic force microscopy and magnetoresistance, we verified that we could reliably establish magnetic domain walls in our domain wall oscillator structures. Furthermore, we developed torsional MEMS oscillators and characterized their intrinsic mechanical resonances. In particular we managed to develop a torsional MEMS oscillator with an out-of-phase torsional mode at 7 MHz and a high Q-factor (1030), which had the highest torsional amplitude at the location where the magnetic domain wall was supposed to be positioned. Thus this structure was ideally suited for the integrated hybrid magnetic/MEMS oscillators.

Our main effort in FY 2012 focused on reproducing results about domain wall oscillators that were reported by Lepadatu et al. from the University of Leeds. However, despite systematic efforts to change various possible fabrication parameters, we were not able to reproduce their results. We used different substrates (Si/SiO and GaAs), different geometries to reduce the direct current (DC) resistance, different thin-film deposition techniques (e-beam evaporation and sputtering), and different geometries for pinning notches. Furthermore, we varied the fabrication process from lift-off approaches to negative-resist processing with subsequent patterning by ion milling. In all instances, the pinning fields for the domain walls were several tens of oersteds (Oe) and significantly higher than those reported in the work of Lepadatu et al. Also, we never were able to demonstrate electric current depinning of the domain wall or any signature of domain wall oscillations upon ac drive currents.

At the same time, micromagnetic simulations performed by an Argonne colleague suggested that the intrinsic resonance frequencies of the domain walls pinned in linear notches should be ~500 MHz and, thus, significantly above the useful range for our intended application. This frequency casts serious doubt about the usefulness of domain wall oscillators for frequency-matched MEMS systems.

Laser Manipulation of Nuclear Spin Embedded in Noble-Gas Ice

2010-010-R2

Zheng-Tian Lu and Ulrich Welp

Project Description

Optical pumping is usually performed in the gas phase, during which the atomic structure is well defined. In the condensed phase (liquid or solid), the atomic structure is so severely disturbed that resonant excitation and optical pumping cease to be effective. In this project, we are performing optical pumping on atoms that are embedded in a solid noble-gas matrix. Frozen noble gas at the cryogenic temperature may be an ideal medium that confines atoms (or molecules) indefinitely and, at the same time, only weakly disturbs an atom's internal structure so that optical pumping remains effective. If successful, this novel approach would add to our tools of controlling spins. In particular, we are investigating the use of this technique for testing the time-reversal symmetry and measuring the nuclear moments of exotic isotopes, as well as possibly for quantum computation.

Mission Relevance

The proposed method of spin manipulation is a general technique that is relevant to DOE's mission in science. If it is successfully developed, the technique will benefit many applications across several disciplines, including fundamental symmetries in physical laws, nuclear structure, and quantum simulation and computation.

FY 2012 Results and Accomplishments

We have met both FY 2010 milestones: (1) to investigate the growth of Ne, Ar, and p-H_2 matrix on a substrate and (2) to perform laser spectroscopy of the Yb atoms embedded in a solid matrix.

Unfortunately, we have not yet been able to meet the subsequent milestones of polarizing the nuclear spin of Yb atoms embedded in solid neon. Despite multiple attempts, no polarization signal was observed.

We have:

- Learned to grow thicker, clear crystals of solid neon with Yb atoms embedded. Careful cleaning of the neon gas — both with gettering and liquid nitrogen cooling — is the key to growing a thick, clear crystal.
- Developed a laser system for optical pumping. The laser beam can be chopped periodically by using an acousto-optical modulator at the Larmor frequency (~1 kHz) of the Yb nucleus.
- Installed a superconducting quantum interference device (SQUID) sensor of magnetic field and continue to improve its signal-to-noise ratio.
- Installed a Helmholtz coil set around the cryostat to provide a few Gauss of a uniform magnetic field.

So far, no polarization signal has been observed. A short transverse coherence time (T2) could explain the disappointing results. This could be due to an excessive background of oxygen molecules that were also trapped in the solid neon. Oxygen molecules are known to be paramagnetic, which causes the magnetic field noise and decoherence of the nuclear spin precession.

We will use good vacuum practices to reduce the oxygen content in the cryostat, and, once again, we will attempt to observe the polarization signal.

With support from DOE's Office of Nuclear Physics, we plan to continue this line of research — with the goal of polarizing the embedded Yb and measuring its polarization by using SQUID — and investigating the spin coherence time under various conditions.

Single Quantum Flux Magnetometer

2010-029-R2

Wai-Kwong Kwok, Dario Antonio, O. Daniel López,
and Valerii Vinokur

Project Description

The goal of this project is to use state-of-the-art nanofabrication techniques to create a novel nanomechanical magnetometer (n-MM). The proposed tool will be able to sense the bulk behavior of a single quantum flux in a superconductor under a variety of experimental configurations. Our project will produce a unique tool to be used to tackle some of the most fundamental basic science problems in condensed matter physics in general areas, such as glassy dynamics and, in particular areas, like the dynamics of single vortex pinning.

Mission Relevance

This research is highly relevant to the DOE Office of Basic Energy Science's (BES's) grand challenge to predict and control both the superconductors' electromagnetic behavior from their microscopic vortices and their pinning behavior to achieve significantly higher critical currents. This revolutionary tool will be applied in the field of basic sciences to extract the physical behavior of a single vortex in a superconductor.

FY 2012 Results and Accomplishments

In FY 2011, the design options for the n-MM were narrowed to one: a torsional paddle. We also considered an alternative detection method involving an optical interferometric setup where a laser beam is split in two and focused on two spots on the sample platform. The reflected beams are then joined again, and the fringes resulting from their interference are sensed with a photodetector. The laser beam spots can be focused on opposite sides of the paddle, for example, or perhaps on the paddle and the substrate, giving a signal that is proportional to the height variations between the two points. The setup has other features (e.g., a low-frequency drift-compensating mechanism and automated stage control) that will ultimately allow us to detect the thermal motion of the nano-microelectromechanical system (MEMS) torsional resonators with amplitudes of a few picometers. We used both capacitive and optical detection to characterize the torsional resonators, demonstrating their operability and obtaining information about the required driving signal levels and resonance frequencies.

In FY 2012, we tested the low-temperature characteristics of this original model torsional paddle n-MM by inserting it into a cryostat. We built a non-magnetic copper-based stage to thermally anchor the n-MM onto the cold head of the cryostat and then carefully mounted a very small (30 × 25 × 3 μm^3) single crystal of the recently discovered iron-based superconductor $(Ba,K)Fe_2As_2$ onto the n-MM device (see Figure 1). Because of the complexity of integrating an optical interferometric setup with our current cryostat, we opted for the capacitive detection method. However, the design of the cryostat does contain an optical window to accommodate future optical detection schemes. The circuitry and measurement results are shown in Figure 2. We applied a small magnetic field during the cooling of the sample by placing a rare-earth magnet close to the n-MM. At T ~38 K, we observed a clear signal of the superconducting transition by recording the shift in the frequency response of the MEMS device. The successful operation of the nano-mechanical magnetometer system at low temperatures opens new avenues for exploration beyond single flux quantum physics.

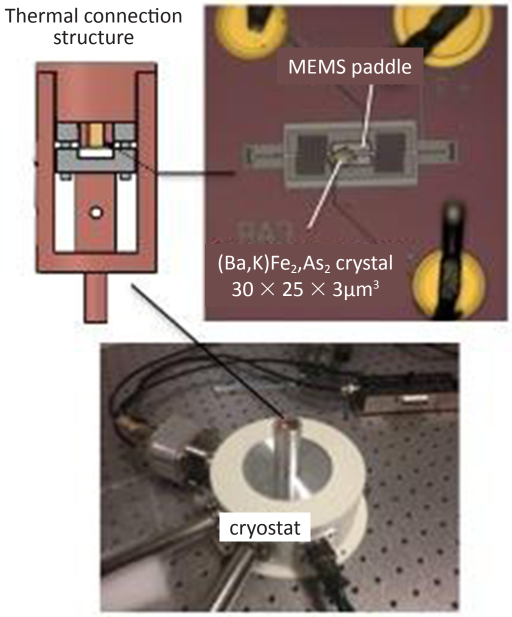


Figure 1. Cryostat and sample set-up for nano-microelectromechanical system (MEMS) operation.

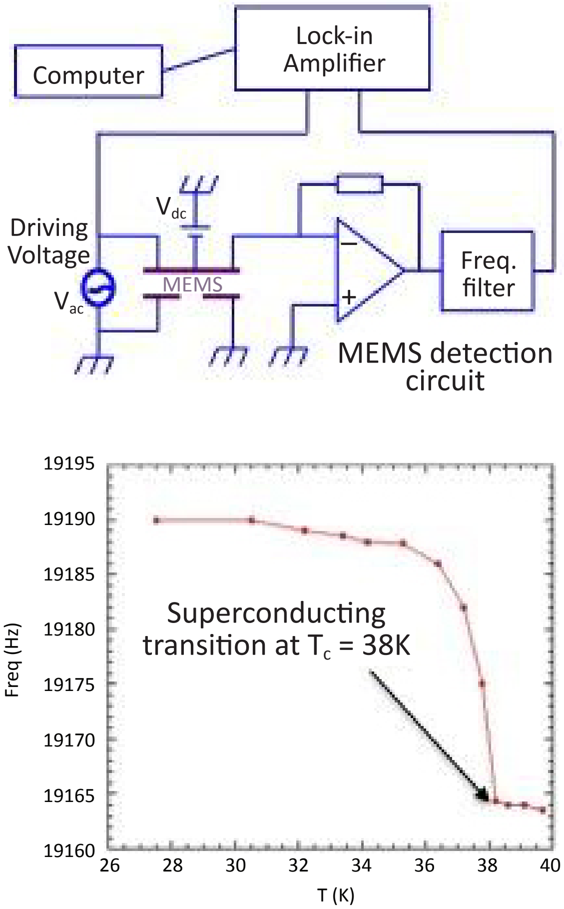


Figure 2. Detection circuit and resonance data.

Emerging Technologies for Scientific Databases

2010-042-R2

David Malon, Jack Cranshaw, Robert B. Ross,
and Peter van Gemmeren

Project Description

While relational databases are widely employed throughout the sciences, such databases are often not used to store the scientific data themselves at any significant scale. There are many reasons, such as:

1. No native support for ry data types, including arrays;
2. No scientific query or transform operators (not even relatively standard spatial and temporal query operators);
3. Transaction models that limit scalability and the potential for parallel and distributed processing, even though many data are in practice read-only (with updates handled by additional data versions rather than by changes to existing data); and
4. Insufficient versioning, provenance tracking, and infrastructure to ensure reproducibility.

For many scientific applications — and for commercial data mining applications as well — the row-oriented storage of a conventional relational database leads to performance issues, even for certain analysis operations that are, in principle, feasible. In this project, we seek to address some of the obstacles to scalable scientific databases, both by taking advantage of emerging technologies and by contributing to their development. In the early phases of the project, we focused on the evaluation of emerging technologies that may contribute to the goal of building scalable scientific databases. In the middle phases, we focused on extensions to those technologies to support scientific data types, and in the later phases, we focused on (1) testing the viability of these developments in an extreme-scale environment and (2) supporting data in their native formats. We used proton collision data from the Large Hadron Collider (LHC) in Geneva, Switzerland, as the principal testbed for the development and evaluation and of these scalable scientific database technologies.

Mission Relevance

This project is relevant to DOE's basic science mission because it relates to the vital technologies that support the efficient scientific analysis of data in which DOE has invested and for which it has custody. DOE is a key contributor to international particle physics work at the LHC, and the technologies that support the analysis of these particle physics data are relevant to the effectiveness of those contributions. This project's relevance is much broader; the tens of millions of gigabytes of data generated by the LHC experiments are just an example of the need throughout DOE's science enterprise for scalable technologies to manage scientific data.

FY 2012 Results and Accomplishments

In FY 2010, we focused on the evaluation of available and emerging technologies, such as those provided by the open-source science oriented database management system (SciDB) project and upon configuration of a testbed of scientific data for evaluation and prototyping. We fabricated a testbed at Argonne, based on event-level metadata records of the earliest proton collisions at the LHC. We imported these data into the earliest releases of SciDB — arguably the first use of SciDB anywhere for real (not simulated) scientific data. We evaluated the early features available in this nascent technology in fragile alpha releases and later in the first genuine SciDB release in June 2011.

In FY 2011, we grew the evaluation testbed at larger scales on the basis of current interest in LHC data, and we augmented and diversified our basis for evaluation and exploration by adding very different data from large-scale cosmological simulations run at DOE supercomputing facilities. We delivered extensions to SciDB by using its fledgling support for user-defined types and operators to support scientific data types, including support for three- and four-dimensional vectors and geometric vector operations, as well as Lorentz vectors and related operators. These efforts were a foundation for outreach, in an effort to address scientific data challenges in areas including high energy physics, nuclear physics, astrophysics, and cosmology.

In FY 2012, one important focus of our work was to explore ways to provide support for *in situ* data (i.e., support for data that does not require that it first be transformed or imported from a "native" format into a database-technology-specific one). For very large data stores, this is often a fundamental roadblock to the adoption of database technologies. We demonstrated support for queries to event-level metadata in the ROOT file format used by almost all LHC experiments for their many millions of gigabytes of derived data, with wide-area query access to the data repository via a caching, read-only file system optimized for delivering data and software to virtual machines. A second focus of our work was to deploy operators on scientific data types in a large-scale data environment. To this end, we successfully delivered selection operators based upon trigger decisions with time-varying bit encodings for LHC data, as well as a plug-in architecture based on Oracle relational database technology, to support an extensible range of data integrity checks, anomaly detection, and statistics.

The ATLAS (A Toroidal Lhc ApparatuS) event-level metadata system is in certain ways an index into its larger file-based bulk data store, and we explored connections with other database research efforts to support *in situ* data augmented by database technologies. One such effort is the so-called

NoDB project under way at the École Polytechnique Fédérale de Lausanne (EPFL).

This project came to an end with the close of FY 2012, but we have attained a leadership role in data storage and access technologies for the ATLAS work at the LHC. Related work will continue, funded by the DOE Office of Science High Energy Physics (DOE-HEP). We will coordinate an international team of developers responsible for the ATLAS event store and supporting input/output and metadata infrastructure. In this capacity, we further expect to oversee the building of an original model effort in the future by using another "big data" technology, Apache Hadoop. Work on support for *in situ* data continues in the context of LHC data, funded by DOE-HEP, working with researchers at the École Polytechnique Fédérale de Lausanne.

Seminars

Malon, D. (2011). "I/O, Persistence, and Database Infrastructure: Emerging Technologies, Software Upgrade R&D, and Planning." ATLAS Upgrade Week, Oxford, UK, Mar. 28–April 1, 2011.

Malon, D.M. (2010). "I/O and Persistence Infrastructure: Emerging Technologies and Software Upgrade R&D." ATLAS Software and Computing Workshop, Geneva, Switzerland, July 15, 2010.

Vaniachine, A. (2010). "Emerging Database Technologies and What ATLAS Might/Should Do in this Arena." 2nd ATLAS Future Computing and Upgrade Workshop, Berkeley, CA, September 17, 2010.

Low Mass Optical Read-Out for High Data Bandwidth Systems

2010-043-R2

David G. Underwood, O. Daniel López, and Robert W. Stanek

Project Description

The project objective is to develop better optical data links, primarily for high energy physics experiments, utilizing light modulators and fiberless beams in air. The goal is to make improvements that will lower mass, lower power use, and increase bandwidth. During the course of the project, we identified other important goals, including developing more radiation hard optical links, finding alternatives to unreliable modulated lasers (VCSELs), and lowering the bit error rate (BER).

Mission Relevance

This project is relevant to DOE's scientific discovery and innovation mission being pursued at several DOE national user facilities and other locations that carry out DOE-sponsored research. Detectors at large particle colliders have limits as a result of (1) mass in the tracking system, (2) limited bandwidth in the readout, (3) failures of the vertical-cavity surface-emitting lasers (VCSELs) that transmit data, and (4) delays in transmitting data for fast triggering. Moreover, tracking detectors need internal triggering electronics, and a path between tracking layers is needed to provide data for calculations. The technology for steering beams in air by microelectromechanical systems (MEMS) mirrors could play a big part in dealing with these issues, as could the development of radiation-hard, low-mass light modulators. Of particular relevance now is the upgrade of the Large Hadron Collider to high luminosity; for this, we need mechanisms for much-higher data transfer rates and to reduce the amount data transferred to higher-level triggers, as well as a factor of 10 improvement in radiation hardness.

FY 2012 Results and Accomplishments

In FY 2010 and FY 2011, we achieved most of the goals of the beam-in-air aspect of the project. We used MEMS mirrors for steering laser beams that carried 1 Gb/s of data. We developed control electronics for steering the MEMS mirrors so that beams could be aimed by means of a feedback loop with optical reflection as part of the loop. With these controls, we were able to steer within a few micrometers to a moving target receiver lens a meter away with no loss of data. We also operated a two-way data link over 83 m at 1 Gb/s with very low power by using diffraction limited beams.

Some initial goals of links in air that were successfully achieved include the following:

- We fabricated two different links that operated over approximately 1 m at 1 Gb/s. One used microelectromechanical system (MEMS) mirrors and optical feedback with sophisticated filters in order to steer and maintain the beam's position. The other used a second laser beam for alignment to enhance the angular range over which steering could be done.
- A MEMS mirror was fabricated by using a design from Argonne's Center for Nanoscale Materials (CNM). The electrical actuation of the mirror as received from the foundry did not work.
- We operated a link over about 80 m at 1 Gb/s. Commercial links use broad beams and lose power with distance as $1/r^2$. Our approach was to use diffraction-limited beams, which are close to being parallel, in order to eliminate most of the $1/r^2$ loss.
- We did some development of the technology to enhance steering over much longer distances. We acquired an understanding of how to combine mechanical telescope steering with either of two technologies that would make steering easier and make the link more likely to be used. Neither project was pursued fully because of a lack of more sophisticated hardware.

In FY 2012, we continued redirecting our efforts to emphasize light modulators more and links in air less, since the modulator aspect is of more interest to potential users who might want to develop the technology. Most of our effort focused on doing radiation testing and support electronics development of light modulators to qualify them for use in the Large Hadron Collider's (LHC's) ATLAS calorimeter system and on documenting the limits to their use in other parts of a collider detector where the radiation environment is much higher and where there is also a need for lower mass readout devices. Three radiation studies were involved:

1. We tested a silicon germanium (SiGe) material that might be used in a modulator. This was done at Argonne's 3-MeV Van de Graaff electron beam.
2. We tested three commercial modulators at Massachusetts General Hospital's (MGH's) proton beam. Results are discussed below.
3. We tested an integrated silicon photonics modulator at Argonne's Van de Graaff electron beam.

The tests on small commercial modulators that are integrated in silicon photonics and on indium phosphide (InP) modulators, which theoretically are extremely rad hard, were done at MGH — these tests are the first in a series of tests to be done at ever-higher radiation levels. We also tested a $LiNbO_3$ modulator that was known to be rad hard.

In our first test with protons at MGH, we tested for both total ionizing dose (TID) and single event upset (SEU). The integrated silicon modulator functioned at the levels required for one of the least-stringent areas of large experiments at the LHC: the Tile Calorimeter (TileCal). No SEU errors were found in any of these tests, although a microcontroller used for setup in a commercial system failed. We are developing a way to bypass this component. The test was successful in all other aspects.

We developed the following items for radiation studies:

- A control board for modulators (Version 1) to control lasers, supply currents to thermoelectric coolers (TECs), supply bias voltages, and monitor voltages and currents supplied to the modulator;
- A connector board for a pseudorandom bit sequence generator (implemented in a high-speed FPGA board and tested for 10-Gb/s operation);
- A control board for modulators (Version 2) containing an 8-channel digital-to-analog converter and a 14-channel analog-to-digital converter to control lasers; supply currents to TECs supply bias voltages; and monitor optical powers, voltages, and currents supplied to the modulator;
- A connector board for InP modulators and 10-Gb/s optical receivers (a high-speed board built for 10-Gb/s operation); and
- Software to control and monitor modulators in real time during operation.

In addition to lowering mass, lowering power use, and greatly increasing bandwidth to 10 Gbps, we found ways to reduce the bit error rate by a factor of 10^6 beyond present specifications for the data links by using commercial silicon photonics modulators with modified electronics.

This work resulted in the following inventions:

- Underwood, D., R. Stanek, and W. Fernando, "A Novel Pixel Detector with Direct Light Modulation," invention report submitted October 2011. [ANL-IN-11-100].
- Stanek, R., W. Fernando, M. Demarteau, D. Underwood, and G. Drake, "A Graphene-based Inline Optical Fiber Modulator," invention report submitted August 2012. [ANL-IN-12-079].

We will continue to develop modulator-based links for the LHC ATLAS TileCal and work with other LHC groups interested in using modulator technology for high-speed-data readout. We will continue to perform radiation hardness tests of the commercial modulator that is to be modified as well as others. We will pursue the development of electronics to replace the non-rad-hard parts of commercial devices. We will pursue development of new kinds of light modulators and new data-collection systems based on the two Argonne invention reports. This ongoing effort will be supported by the ATLAS experiment; a DOE-HEP CDRD (collider detector R&D) grant in collaboration with the University of Minnesota, Southern Methodist University, Ohio State University, and Fermilab; and a joint University of Chicago-Fermilab-Argonne project.

Compact Solid-State Sources of Coherent THz Radiation

2010-049-R2

Ulrich Welp, Nachappa Gopalsami, Kenneth Gray,
and Alexei Koshelev

Project Description

The interest in terahertz (THz) radiation is based on two unique properties: its spectral specificity to the vibrational and rotational modes of a wide variety of important chemical and biomolecular species and its penetrating properties through packaging, clothes, plastics, and other materials. Furthermore, the wavelength range of 30 µm to 1 mm (corresponding to 300 GHz to 10 THz) allows for imaging with good spatial resolution. A typical power level that is considered necessary for imaging and detection application lies in the milliwatt (mW) range.

We previously demonstrated that the unique properties of highly anisotropic high-temperature superconductors, such as BSCCO (bismuth strontium calcium copper oxide), enable the development of a new class of THz sources that can bridge the THz gap. We obtained emission frequencies of up to 0.85 THz and emission powers of up to 0.5 µW from a very compact device that is 300 × 60 × 1 μm^3. More recently, we reached 5 µW at 0.62 THz with harmonics extending up to 2.5 THz. The goal of this integrated experimental and theoretical project is to demonstrate that the output power of properly designed BSCCO resonators can be increased to a level of about 1 mW. Recent modeling of our device structures indicates that such power levels are possible with optimized excitation of the internal high-frequency oscillations and improved extraction of the radiation power.

Mission Relevance

This project is relevant to DOE's missions in national security, environmental quality, and science. The rapidly emerging field of THz science and technology holds immense promise for diverse areas, including medical diagnostics, space science, environmental monitoring, security, manufacturing, and pharmaceuticals. Directly related to DOE's missions are the atmospheric monitoring of ozone and greenhouse gases, detection of drugs and explosives through packaging, and standoff screening of personnel with nonionizing radiation.

FY 2012 Results and Accomplishments

In FY 2011, we demonstrated that an array of up to three optimally doped Bi-2212 stacks of intrinsic Josephson junctions could be induced to emit coherently with respect to each other. The radiated THz power was found to scale almost as the square of the number of stacks oscillating in phase, as expected for coherent-phase emitters. In FY 2012, we performed an accurate power calibration of our setup, by using a blackbody standard source, over a frequency range from 0.5 to 3 THz. The results of this calibration show that the array of three stacks generates 0.61 mW at 0.51 THz, which is very close to the target level of 1 mW.

Our results indicate that a certain amount of thermal inhomogeneity in an electrically powered stack is essential for generating high levels of THz power. The exact reason for this is not yet clear, but strong self-heating in the center of a stack reduces the local superfluid density, which is thought to favor excitation of efficiently radiating cavity modes. It is thus important to obtain accurate information on the temperature distribution and how it relates to THz emissions. In FY 2012, we imaged the surface temperature of Bi-2212 mesas by using a newly developed fluorescent thermal imaging system. A 200-nm layer of europium thenoyltrifluoroacetonate (EuTFC) is deposited on the sample by thermal evaporation, whereupon the sample is mounted in a cryostat with an optical window. The surface temperature can then be measured by using the strongly temperature-dependent fluorescence efficiency at 612 nm of EuTFC (Figure 1a). We find that at bias power conditions typical for THz generation in Bi-2212 mesas, the center of the mesa can readily self-heat to T_c and above (Figure 1b).

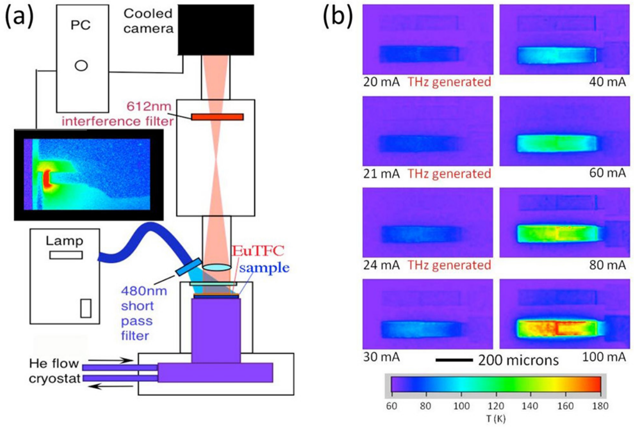


Figure 1. (a) Configuration of microscope and cryostat for thermal imaging experiment (b) Formation of hot spot in Bi-2212 mesa at increasing bias current.

Highly Efficient SERS-Active Substrate with Designer Hot Spots and Multiple-Stage Light Amplification

2010-050-R2

Vitalii K. Vlasko-Vlasov, Stephen K. Gray,
and Elena V. Shevchenko

Project Description

The project addresses development of high-efficiency, high-fidelity substrates for detection and analysis of nanovolumes of biochemical analytes by using surface enhanced Raman spectroscopy (SERS). The work is an experimental and theoretical effort aimed at the fabrication and characterization of precisely controlled plasmonic structures enabling a multistage amplification of the light fields. The first stage of amplification results from controlled hot spots in self-assembled regular arrays of monodisperse spherical metal or metal/dielectric core/shell nanoparticles. A unique aspect of this project, which is designed to increase the SERS enhancement even further, is a second stage of light amplification in which the particles are coupled to surface plasmon polaritons on a metal film substrate. By using periodic modulation of the metal film, intense standing waves are formed through Bragg reflection, leading to an additional resonant increase in the surface field and signal enhancement. The grating effect due to the periodic structure also provides efficient directional emission of the Raman light at the Bragg angle. Our substrates provide a high density of regular hot spots, where the giant light enhancement is the product of the enhancement factors of individual components (nanoparticle arrays, plasmon mirror, and distributed grating resonator) when they are tuned to the same resonant frequency.

Mission Relevance

The results of this research project contribute to DOE's homeland security and energy missions. Successful accomplishment of the project increases DOE's capabilities in the field of biosensor technologies and enhances ongoing programs in biological and chemical research. Furthermore, the development of highly efficient light-enhancing substrates as described here can be relevant for catalytic and fuel-cell projects. Plasmonic structures proposed in the project can also be used for enhancing the efficiency of solid-state lighting devices and solar cells.

FY 2012 Results and Accomplishments

In the previous years of the project, we elaborated procedures for the capillary self-assembly of large (up to 200 × 1000 µm) single-crytalline arrays of 80-nm gold nanospheres yielding strong SERS signals. We established protocols for manufacturing dielectric gratings by means of e-beam lithography, and using computer-controlled substrate motion, we found optimum conditions for the assembly of nanoparticles in the grating templates. Normal incidence optical properties of the samples were studied by using a non-spectrometer that was fabricated at Argonne by using the microscope and a UV-VIS MS257 spectroanalyzer from Oriel. The optimum conditions were closely described by finite-difference time-domain calculations performed by our group.

After successful demonstration of reproducible multiple-light amplification in the hot spots of our substrates, allowing for a ~3×10^{10}-fold enhancement in SERS signal, we investigated the angular optical response of our structures. Multiple samples with different grating designs and nanoparticles with different surfactants were manufactured and measured by using a θ-2θ setup. Dielectric gratings, serving as templates for the nanoparticle assembly in our plasmonic architectures, introduced the folding of Bragg zones, which allowed us to study the substrate dispersion relation $\omega_s(k)$ lying outside the light cone. By varying the illumination angle, we varied the in-plane k-vector and excited eigen-modes of the substrate that resulted in reflection minima at appropriate light energies. By comparing angular spectra of empty gratings on the plasmonic mirror with those after the nanoparticle assembly in the gratings, we observed the spectral features of our SERS substrates and revealed wide optical bands formed because of the strong coupling between the particles and between particles and substrate plasmons amplified by the grating resonator (Figure 1). The appearance of extended optical bands shows that our substrates allow light enhancement over a wide spectral range, which makes them an advanced platform not only for Raman sensing but also for light-harvesting systems, including thin-film solar cells and light-emitting devices.

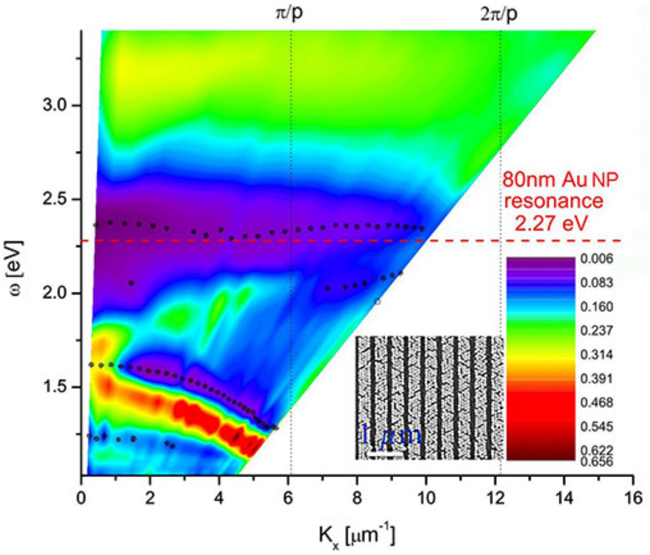


Figure 1. Optical dispersion of 80-nm Au nanoparticles (NPs) self-assembled in SiO_2 gratings on top of silver film. The plot was obtained by using reflection spectra for incidence angles from 0 to 70 degrees. Numbers next to the color scale show the reflection coefficient (the total reflection coefficient is 1). The reflection minima (purple and blue) reveal eigen modes in the system absorbing the light energy.

This research resulted in the following invention/patent:

- Vitalii Vlasko-Vlasov, Aiqing Chen, Ulrich Welp, and Stephen Gray, "Multiscale Light Amplification Structures for Surface Enhanced Raman Spectroscopy," U.S. patent application, Serial No. 13/456,485 filed April 26, 2012.

Seminars

Vlasko-Vlasov, V. K., A. Chen, A. Joshi-Imre, S. Gray, and U. Welp (2012). "Plasmonic Nanostructures for Subwavelength Light Manipulation and Sensing." University of Bordeaux, Bordeaux, France, June 19, 2012.

Tactile MEMS-Based Sensor

2010-063-R2

Young Soo Park and Nachappa Gopalsami

Project Description

This project addresses the development of a high-fidelity tactile microsensor that can replicate and excel in fingertip touch sensation. Its primary use will be to enhance the dexterity of robotic systems (like those used for teleoperations and robotic surgery). It will also have a significant impact on the emerging technology of haptics (a technology that interfaces with the user through the sense of touch), for which it will have numerous applications in daily life. The human sense of touch is a complex, multimodal perception, and this sensor will focus on replicating the most delicate tactile sensing, which requires a highly sensitive microscale sensor array. In this regard, a new type of piezoresistive tactile microsensor element is being developed based on microelectromechanical systems (MEMS) technology to measure the contact force and stiffness of objects with the highest spatial resolution that can be achieved by current tactile sensors. Because it adopts a novel multiple-diaphragm design, the sensor can be integrated to adapt to a wide range of stiffnesses that cover most biological tissues. Also, because it uses SU-8, a photoresistive epoxy, as the substrate and gold as the piezoresistor, the new tactile sensor element is structurally flexible, easy to fabricate, and low in cost. The delicate tactile feedback is essential for expanding the domain of robotic and human-machine interfacing.

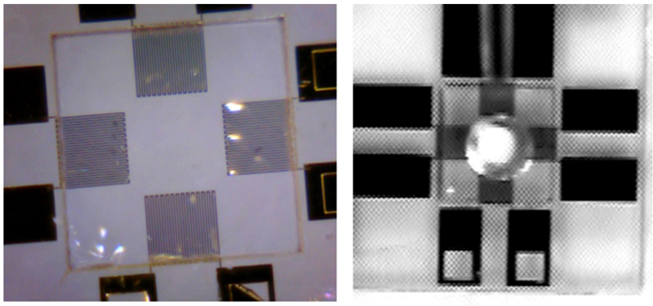
Mission Relevance

This work is relevant to DOE's missions in the nuclear industry, environmental management, and national defense — all three areas could benefit from telerobotic manipulations that demand greater dexterity. This work also represents a significant innovation in haptics technology, with ubiquitous applications in people's everyday lives and the potential to have significant impacts on society. Its application in robotic surgery will be demonstrated immediately; it will address the need for sensory feedback.

FY 2012 Results and Accomplishments

We used gold as piezoresistive element and SU-8 as a stretchable substrate material to develop a novel tactile microsensor element based on MEMS technology. The element exhibits unique characteristics suitable for replicating fingertip touch with excellent results. Being a microscale device, it is suitable for high-resolution spatial array sensing. The sensor provides the highest spatial resolution found among current tactile sensors: 100 µm. The spatial resolution of a human fingertip is 40 µm over a contact area of 1 cm^2; in the future, we expect this resolution to be achievable. Its unique multielement design also allows a wide range of stiffness measurements. In addition, because of the flexible substrate structure, it can be retrofitted as a skin sensor onto irregularly shaped devices. In previous years, we finished developing the early model, which included design, MEMS process, fabrication, and characteristics testing work. This initial development confirmed the efficacy of the desired sensor characteristics.

The FY 2012 effort focused on making adaptations to further verify the sensor's efficacy in practical applications like robotic surgery. First, the sensor structure was modified by adding boss structure (an extrusion to contact biological tissues upon manipulation) (see Figure 1). Simulation and experimental studies with the first sensor elements indicated that the sensor's elastic modulus range is 32–1,000 kPa, which is compatible with most biological tissues (ureter, prostate, kidney, bladder, blood vessel, intestine). A subsequent series of developments was made to prepare for sensory feedback; for this, a tactile array consisting of 5 × 5 piezoelectric transducer elements that were the size of a fingertip (1 × 1 cm) was devised and fabricated. For test purposes, the device was integrated to a custom-made fingertip grip module. Figure 2 shows the tactile fingertip grip retrofit onto a haptic device and a resistive-type tactile sensor array on a surgery robot gripper to be tested with it. A characterization test incorporating frequency sweep revealed that it was possible to achieve near resonance at the tactor elements to be felt by the fingertip.



Sensor without boss Sensor with boss

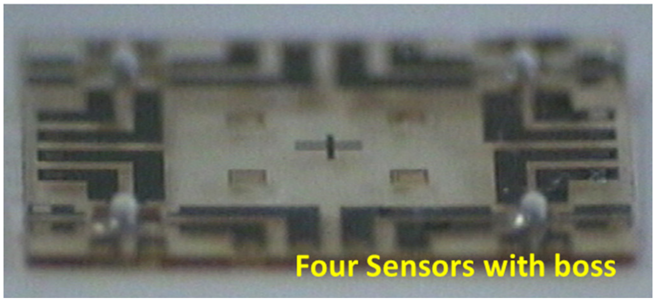


Figure 1. Tactile microsensor with boss structure.

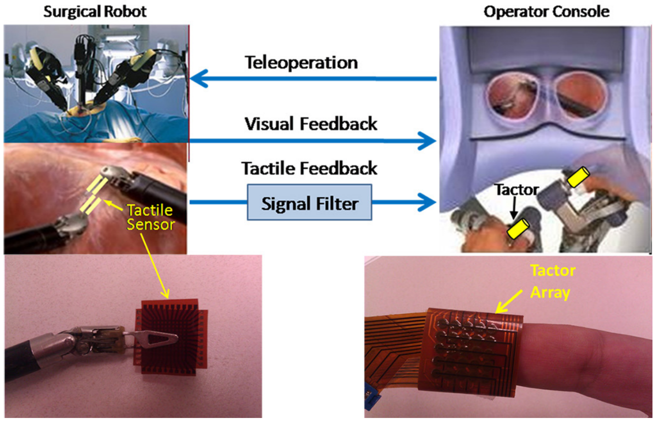


Figure 2. Tactile feedback setup for robotic surgery.

Integrating and testing the tactile feedback on a telerobotic surgery system is expected to continue with support from the University of Chicago medical school.

Polymerized Ionic Liquid Nanostructures for Biocatalytic Fuel Production

2010-073-R2

Millicent A. Firestone

Project Description

This research aims to develop a nanostructured heterogeneous biocatalyst that can be used in the biotransformations needed to produce biofuels. The work involves (1) development of a synthetic platform that will allow stable incorporation of aqueous enzymes and (2) evaluation of the platform to determine its suitability for use in heterogeneous biocatalysis.

Mission Relevance

This project is relevant to DOE's science and energy missions. Currently, fossil fuels supply most of the world's energy. The depletion of global petroleum reserves and the growing concern over the environment (e.g., generation of greenhouse gases) has led to an increasing interest in and need for alternative renewable energy sources. One method of producing alternative fuel sources focuses on biofuels that result from converting plant or animal by-products (e.g., triglycerides) to an alkyl fatty acid methyl ester (biodiesel) with methanol. The results of this project will provide insights into (1) methods for designing and synthesizing materials to advance the emerging field of heterogeneous biocatalysis and (2) low-cost means for producing bio-derived fuels as renewable energy sources.

FY 2012 Results and Accomplishments

Research has focused on the development of synthetic approaches that would allow for the stable encapsulation of a model hemeprotein, cyt. *c*, within a liquid-crystalline ionic-liquid (IL)-based interpenetrating polymer network (IPN). We prepared the IPN sequentially by first photopolymerizing a self-assembled aqueous mixture of the IL monomer. We introduced the enzyme into the polymer; the polyelectrolyte counterion, bromide, served as the anion exchange for acrylate. As a second polymerization step, we employed brief ultraviolet (UV) illumination with 365-nm light, which resulted in a durable, self-supporting network IPN with entrained protein.

These earlier studies provided the foundation for our FY 2012 efforts, which focused on encapsulated lipase. Lipase — an enzyme used for the transesterification of diglycerides — is unlike cyt. *c* in that its structural integrity cannot be readily monitored by using optical spectroscopy because it lacks an optical reporter group. We monitored lipase's secondary structure by using vibrational spectroscopy (attenuated total reflection [ATR]/Fourier transform infrared spectroscopy [FT-IR]). Specifically, we monitored the amide I (1,656 cm^{-1}, C=O stretching), amide II (1,546 cm^{-1}, N-H bending and C-H stretching), and amide III (1400-1200 cm^{-1}, N-H bending, C-Cα and C-N stretching) modes. In addition, we monitored the signature mode characteristic of lipase-associated sugar chains at 1,060 cm^{-1}.

Our latest study demonstrated that the aforementioned collection of modes is readily detectable within the IPN matrix and showed that the lipase retains its structural integrity within the polymer network. We also examined the structural stability of the protein encapsulated within the IPN under various storage conditions (aqueous buffered solutions, ethanol, and air). As in our work examining storage, long-term storage in an unsolvated polymer denatured the enzyme. We examined lipase activity by using an indirect colorimetric assay. In this assay, we monitored the rate of formation of a quinine dye produced by the lipase-catalyzed transesterification of diglyceride at λ_{max} = 545 nm. We compared the IPN-encapsulated lipase's activity to the activity of the free enzyme (in buffered aqueous solution); the comparison indicated that the enzyme remains active within the polymer. The work has produced a critical matrix for the proven stabilization of enzymes that are useful for the development of heterogeneous biocatalyts.

Layered Oxides for Thermoelectric Energy Conversion

2010-129-R2

Kenneth Gray, Qing'An Li, John F. Mitchell, Boyd Veal,
and Hong Zheng

Project Description

A search for improved thermoelectric materials is merited because this all-solid-state technology is inherently reliable. Improved thermopower (voltage output per degree of temperature difference) is predicted for materials with sharp features in the density of electrons versus their energy, as well as for low-dimensional (e.g., layered) materials. We choose materials that exhibit these characteristics and optimize their conversion efficiency through directed synthesis, using feedback from measurements that reflect the desire for a small ratio of thermal to electrical conductivity.

Mission Relevance

Economically viable materials that exhibit high thermoelectric conversion efficiency can utilize waste heat from vehicle exhaust emission and can serve as a mechanically reliable alternative to steam engines for the conversion of heat from solar concentrators. These benefits are relevant to DOE's energy and environmental missions. Other relevant DOE programs include the Vehicle Technologies Programs in EERE and several Energy Frontier Research Centers in SC, including the

Center for Energy Efficient Materials, the Center for Inverse Design, the Center for Excitonics, and the Solid-State Solar-Thermal Energy Conversion Center.

FY 2012 Results and Accomplishments

In prior years, we made a large polycrystal of the Ce_2PdGa_{12} phase, by using powder synthesis followed by medium temperature sintering. This material was needed to estimate the figure of merit for thermoelectric materials, ZT, which was accomplished by measuring the temperature-dependent thermal conductivity, $\kappa(T)$. We recognized that second phase impurities could lower κ, and so we studied them in our crystalline material by means of x-ray diffraction (XRD), magnetization, specific heat, and powder neutron diffraction. For example, the specific heat showed evidence of the $CePdGa_6$ phase that was not found in the polycrystalline samples by powder neutron diffraction. Low-temperature magnetization identified Ga-rich intermetallics from its superconductivity. Finally, we found evidence for a pseudo-cubic $CePd_3Ga_8$ phase in our crystal samples from XRD.

We found a huge room temperature power factor of 141 $\mu Wcm^{-1}K^{-2}$ in an oriented crystal of the layered Ce-based compound Ce_2PdGa_{12}. This value is more than three times as large as the largest values (45 $\mu Wcm^{-1}K^{-2}$) found for the best conventional material, $(Bi,Sb)_2Te_3$. It is possible that the enhancement of the power factor is caused by the layered lattice structure and/or a density-of-states narrowing near the Fermi surface induced by the hybridization between f-electrons and conduction electrons. While these factors embody our rationale for initially looking at layered oxides, the shift to heavy fermion intermetallics was a revelation gained from our frustration with the oxides. With oxides, one always seems to find either (1) a high thermopower and very high resistivity due to a sizable energy gap or (2) acceptably low resistivity but unacceptably low thermopower. We obtained an estimate of the figure of merit for thermoelectric materials, ZT, from measurements of the thermal conductivity in polycrystalline ingots of Ce_2PdGa_{12} This value of ZT=0.51 further emphasizes the attractive nature of this new class of materials for thermoelectric devices.

Novel Bifunctional Low-Temperature Catalysts at the Subnanometer Scale

2010-137-R2

Larry Curtiss, Jeffrey W. Elam, Jeffrey Greeley,
Michael J. Pellin, Stefan Vajda, and Randall Winans

Project Description

This interdisciplinary project addresses a roadblock to the development of a next generation of catalytic materials for energy applications. The goals are to design, with atomic precision, entirely new classes of materials at the subnanometer scale and to achieve a fundamental understanding of how these materials work. The research is aimed at discovering new catalysts that can perform more than one catalytic reaction on one site and thus save considerable energy. It involves closely coupled theoretical predictions/catalyst screening and experimental catalytic testing and understanding.

Mission Relevance

This project is relevant to DOE's missions in science and energy. Optimizing heterogeneous catalysts at the subnanometer scale, so they are more environmentally friendly and efficient for chemical and fuel production, is a new approach for solving energy-related problems. The Basic Energy Sciences Workshop report, *Opportunities for Catalysis in the 21st Century,* states that the "Grand Challenge for catalysis science in the 21st century is to understand how to design catalyst structures to control catalytic activity and selectivity" — a central topic of this project. Catalysis has reemerged as a centerpiece in DOE-supported research; moreover, it is anticipated that the need to produce classical fuels from resources that are now available but have yet to be used, as well as the need to develop future alternative fuels, will increase the importance of DOE catalysis research even more. In addition, there is considerable industrial interest in new types of catalysts. Subnanometer clusters are a new class of catalysts that could provide breakthrough materials for industrially important processes.

FY 2012 Results and Accomplishments

During FY 2010, we found that cobalt clusters were experimentally active for C-H bond activation as predicted by theory, and that they had a much lower temperature for oxidative dehydrogenation than platinum clusters. The lower-temperature C-H activation is a key requirement for a bifunctional catalyst for ODH-EO catalysis, so during FY 2011 our studies were focused on understanding this unique low-temperature ODH (oxidative dehydrogenation) property of cobalt clusters and how to incorporate it into a catalyst that adds oxygen to an alkene as well. These studies showed that the low-temperature performance of the clusters is due to their suboxide nature (i.e., the Co:O ratio is greater than or equal to one). Experimental/theoretical studies also provided evidence that the Co_4O_y clusters are very stable on Al_2O_3 surfaces, which is needed for these to be practical catalysts. The stability was found from theory to be due to interactions with defect sites. The experimental studies also provided evidence that the oxide substrate is required for both oxidative dehydrogenation and formation of the oxygenate. Theoretical calculations were also done on Ag/Pt alloy clusters to investigate oxygen molecule dissociation on alloy clusters on an alumina support. The results indicate that this is favorable and has prompted experimental studies on these alloys in the final year of the project.

In FY 2012, we completed a full reaction pathway study to explain the activity of cobalt oxide clusters for cyclohexane oxidative dehydrogenation and oxidation. The work was based on a density functional study of reaction products and intermediates. We found that the pathway to cyclohexene has two key steps: the breaking of the C-H bond and the desorption of the cyclohexene. We found that there was a low-energy barrier to the C-H bond breaking on the cobalt oxide clusters and that the cyclohexene desorption energy was small. The adsorbed cyclohexene is shown in Figure 1. The small desorption energy provided a mechanism for overcoming the temperature difference required for oxidative dehydrogenation (ODH) at ~400°C compared to C=C double bond oxidation (EO) at ~100°C, which is needed for the development of bifunctional catalysts. The computational mechanistic study showed that the low barrier was due to the presence of oxygen in the Co cluster. The energies calculated for the subsequent step (adding oxygen to the C=C double bond to form cyclohexanone) were favorable. This finding is consistent with experimental evidence for the formation of some cyclohexanone (as well as cyclohexane) at low temperatures, and it is important because the screening techniques used in designing cluster-based materials can be used in the future to optimize the selectivity of these materials toward ODH-EO bifunctional catalysis, an industrially important catalytic process.

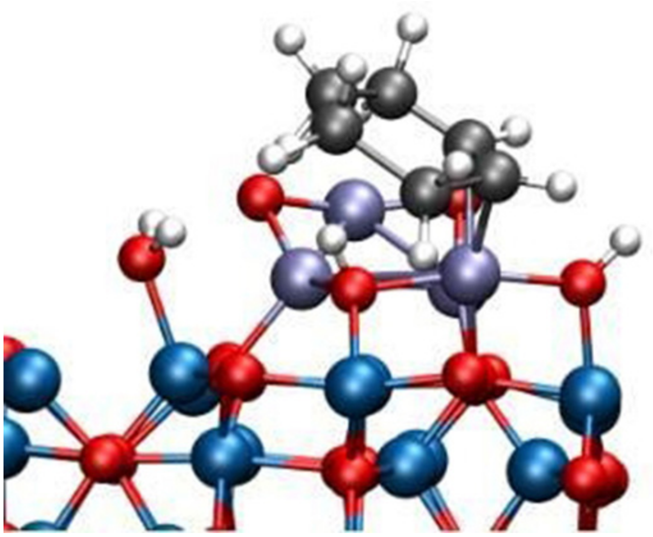


Figure 1. Co_4O_4 catalyst on an alumina surface that has cyclohexene adsorbed on it after two C-H bonds have broken. Color code: red=oxygen, silver=cobalt, blue=aluminum, white=hydrogen.

We also performed the first combined *in situ* grazing incidence small angle x-ray scattering (GISAXS), grazing incidence x-ray absorption (GIXAS), and temperature-programmed reaction experiments on silver/platinum (Ag/Pt) bimetallic clusters. Specifically, Ag_9Pt_2 and Ag_9Pt_3 clusters were compared with monometallic Pt_{10} and Ag_3 clusters. As a test reaction, CO oxidation was chosen, since both monometallic Ag and Pt clusters are known to have highly size-dependent reactivity toward CO oxidation. In the tests, we followed the alteration of the oxidation state of the individual metals in the clusters with the composition change on an atom-by-atom basis under realistic reaction and temperature conditions. The changes in the oxidation states of the different metals that built up the clusters yielded, for the first time, important insights about the presence and the roles of the different catalytic sites adjacent to the subnanometer clusters, while also offering a "control knob" for tuning the type and number of catalytic sites on the same particle for bifunctional catalytic functions, such as OHD-EO.

Trapped Field Magnets: A Paradigm Shift for Applications of High-Field Magnets at a Synchrotron

2010-138-R2

Zahirul Islam, Ritesh K. Das, and Jonathan C. Lang

Project Description

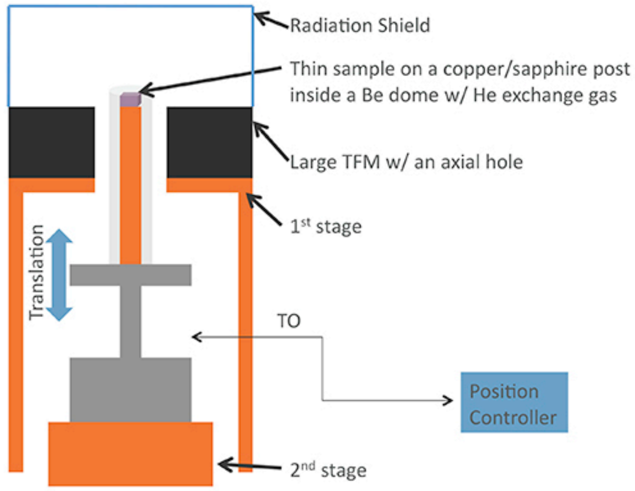
The objective of the project is to develop a practical approach using type-II superconductors (SCs) to mitigate two long-standing problems in scattering studies in applied magnetic fields: (1) limited optical access and (2) the impossibility of applying magnetic fields parallel to the x-ray (neutron) momentum transfer (**Q**). Solving these problems will allow researchers to measure order parameters (OPs) with the primary ordering vector parallel to the applied magnetic fields (**B**) and determine OP anisotropy by measuring scattering intensity on the rotation of the sample around **Q**. With widely used split-pair and solenoid geometries, these measurements are, in general, impossible to carry out. In the proposed approach, a tiny single-crystal sample is placed close to the surface of a melt-textured bulk SC. Once magnetized by trapping vortices below the superconducting transition temperature T_c, such a SC acts as a permanent magnet (or a trapped-field magnet, TFM) with **B** normal to the TFM surface. As a result, the sample is in an ideal geometry for diffraction experiments, such as x-ray resonant exchange scattering (XRES), with unrestricted optical access.

Mission Relevance

The study of materials under extreme conditions (e.g., very high magnetic fields) has been identified as one of the long-term missions of DOE-BES. There are many programs to explore the properties of energy-related functional materials, superconductors, frustrated magnets, spin-gap compounds, and oxides, among others, funded by the DOE and other agencies (e.g., the National Science Foundation). The proposed scheme has the potential to generate magnetic fields beyond 15 Tesla to usher in new opportunities for studying field-induced phenomena.

FY 2012 Results and Accomplishments

In FY 2010, we completed the specifications for a small TFM for initial tests, a suitable cryostat, and a TFM-magnetizing scheme (Figure 1). The TFM was characterized and a cryostat was procured. In FY 2011, we completed our tests on small TFM and implemented a larger TFM to reach fields above 3 Tesla. We performed initial magnetic x-ray scattering measurements of field-induced magnetic phases in a rare-earth axial meta-magnetic compound. These measurements constitute the proof-of-principle study of an application of the TFM instrument. We further developed a dual-stage cryostat instrument for independently controlling TFM and sample temperatures.



Note: Bottom of the cryostat, electrical connections, feedthrough ports, vacuum shroud, compressor not shown.

Figure 1. Scheme for a dual-stage TFM instrument: sample and TFM are cooled on separate thermal stages, with in situ *control of sample-to-TFM distance to vary magnetic field at the sample location.*

Primary accomplishments include (1) demonstration of a dual-stage TFM cryostat instrument, (2) acquisition of a TFM with stronger flux-pinning centers, (3) procurement of a linear stage to increase the range of *in situ* sample translation, (4) design and procurement of a capillary-like Be sample chamber, (5) conception of an *in situ* pulsed-field magnetizing scheme for TFMs, and (6) XRES studies of meta-magnetism to further develop the methodology of using TFMs.

A dual-stage cryostat was used to independently control sample and TFM temperatures. The sample is kept on the 2.8 K second stage while the TFM remains anchored to the ~30 K first stage. Furthermore, the sample is attached to a linear stage to change its distance from the TFM, allowing the field to change at the sample location.

In order to trap larger magnetic fields and increase thermal stability against flux creep, TFMs with strong pinning centers are needed. The best TFMs in this regard contain radiation-induced defects (i.e., induced via the U/n process) and are mildly radioactive. We obtained a TFM that is capable of trapping fields in excess of 5 T, although the current maximum external field available for magnetization is less than ~5 T. Most importantly, in this TFM, trapped fields at or below 5 T will have negligible decays over days, if not weeks. A special mount was fabricated to handle the radioactive TFM, which will be tested soon as part of the X-ray Science Division (XSD) program at Argonne.

In order to change magnetic field at the sample, one varies the sample-to-TFM distance. However, a larger trapped field requires increased distance in order to approach a practically zero field at the sample location. A second stage was procured in order to double the range of this translation. At present, the lowest sample temperature is ~4.5 K; this temperature is expected to rise with increased distance. A Be chamber for helium exchange gas was designed and procured in order to improve thermal links between sample and the cold finger, which will be tested soon as part of the XSD program at Argonne.

The ability to control the magnetic field via *in situ* translation of the sample allowed for detailed XRES studies on $TbNi_2Ge_2$ (Tb122). It is a tetragonal meta-magnet with a strong **c**-axis anisotropy. Tb moments order in a stack of ferromagnetic (FM, denoted by +/- for moments along +/- **c** axis) and antiferromagnetic (AFM, denoted by 0) *ab* planes, according to commensurate wave vectors $\tau_1=(0, 0, 3/4)$ and $\tau_2=(½, ½, 0)$, respectively. τ_1 and τ_2, along with their harmonics, give rise to a number of satellites of charge Bragg peaks. In applied magnetic fields, these satellites change in position and magnitude, yielding detailed information on various stable magnetic states through the magnetization process all the way to saturation. Thorough analyses of their field and temperature dependence show that these ordered phases become incommensurate with the lattice and retain AFM planes at all fields below that needed to reach the FM state. These XRES studies demonstrate the capabilities of the TFM instrument.

This research resulted in the following invention/patent:

- Zahirul Islam, Ritesh K. Das, and Roy Weinstein, “Dual-stage Trapped-flux Magnet Cryostat for Measurements at High Magnetic Fields,” U. S. patent application, Serial No. 13/405436 filed February 27, 2012.

Converting CO_2 to Fuel through Functionalized MOFs

2010-158-R2

Di-Jia Liu, Liaohai Chen, Shengqian Ma, and Dan Zhao

Project Description

Concern about global climate change has drawn unprecedented public attention to CO_2 emissions. At present, the only viable technology for CO_2 capture and storage is to concentrate CO_2 into a nearly pure form before pumping it underground or to the ocean floor. Such processes consume additional fuel and add to consumers' energy costs. The objective of this project is to develop a new class of dual-property materials, functionalized metal-organic frameworks (MOFs), that can effectively trap CO_2 and photocatalytically convert it to methanol or other chemical fuels. The goal is to provide economic and environmental benefits by not only capturing CO_2 but also converting it to value-added products. MOFs can be synthesized through solvothermal reactions between the organic linkers and the secondary building units (SBUs) of transition metals. Our approach is to incorporate photocatalytic activity in MOFs through rational design while retaining their high CO_2 storage capacity. Such designs could result in localization of highly concentrated CO_2 inside the microporous spaces proximate to the photocatalytic reaction center, thus enhancing the conversion rate and equilibrium toward final products that are otherwise difficult to achieve.

Mission Relevance

This project is relevant to DOE's missions in environment and energy. Mitigating the environmental impact of CO_2 emissions from fossil fuel represents a key DOE mission. Converting solar energy for a variety of applications represents a key initiative at DOE. Next-generation adsorbent and photocatalytic materials represent key components in the future energy efficiency and renewable energy technology portfolio.

FY 2012 Results and Accomplishments

The first step toward enhancing the photocatalytic activity of MOFs for converting CO_2 to solar fuel is to reduce its photo-absorption band-gap to better match that of the sunlight spectrum. Since the beginning of this project, we systematically designed and synthesized a variety of MOFs by judicially combining the organic ligands and SBUs of different dimensions. We have found that such an approach could, indeed, improve the absorption efficiency.

In FY 2012, we completed our systematic investigation on reduction of the MOF band-gap through substitution of organic ligands with different conjugations and metal oxide clusters of different sizes. We remeasured the optical absorption for the ligands and determined their band-gaps more accurately. These values were further compared with those of six different MOF materials we prepared. The result confirmed our previous conclusions that (1) the band-gap in MOF is primarily controlled by ligand electronic transition and (2) the electronic coupling between the ligand and SBU is limited because of the high electronic transfer barrier between the carboxylic and ZnO bonds. In addition to experimental study, we also collaborated with Professor Qingfeng Ge of Southern Illinois University to perform quantum mechanical calculations of the MOF band-gaps using density function theory. We found that the result was consistent with the experimental observation. The work on band-gap tunability was completed.

We also explored the feasibility of using inert and water-insoluble MOFs as the template for preparing porous photocatalysts via the aqueous infiltration method. Two "hard" MOFs (ZrBDC and ZrBPDC) were used; the catalysts were prepared by impregnating the MOFs with $TiOSO_4$ solution, followed by thermal activation. X-ray diffraction characterization indicated that the resulting TiO_2 was in the anatase phase. The photocatalytic CO_2 conversion activity over the new porous materials was tested with an in-house-designed reactor. A steady increase in methane production as a function of exposure time was observed.

Another interesting result of this project was the discovery that MOF-based materials can also serve as excellent precursors for producing high-efficiency and low-cost electrocatalysts, as alternatives to platinum group metal (PGM) materials. We developed a number of MOF systems as non-PGM catalyst precursors and found some very promising catalytic activity favoring oxygen reduction reactions. Shown in Figure 1 is a drawing of combining two different zeolitic imidazolate frameworks (ZIF), a subclass of MOFs, as precursors to prepare a non-PGM catalyst.

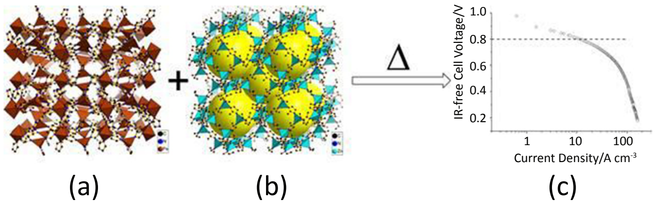


Figure 1. Conversion of the zeolitic imidazolate framework (ZIF) mixture of (a) Fe-ZIF and (b) ZIF-8 produced an effective oxygen reduction catalyst with high current density, shown by the Tafel plot (c).

This work resulted in the following inventions/patents:

- Liu, D.-J., and D. Zhao, "Synthesis of Electrocatalysts Using Metal-Organic Framework Materials," invention report submitted February 2012. [ANL-IN-12-008]; Patent application filed April 2012.
- Liu, D.-J., C. Chen, and J. Shui, "Nanofibrous Electrocatalysts," invention report submitted June 2012. [ANL-IN-12-063]; Patent application filed September 2012.

The new concept of using MOF-based precursors for preparing non-PGM catalysts will be pursued with support from DOE's Office of Energy Efficiency and Renewable Energy.

The Biochemistry of Plant-Fungal Symbiotic Relationships

2010-161-R2

Deborah K. Hanson, Frank Collart, and Philip D. Laible

Project Description

Trees develop complex symbiotic associations with soil fungi such that the interactions provide nutritional benefits to both partners. The goal of this project is to study proteins, such as transporters and two-component sensory systems, that participate in important symbiotic and nutrient exchange interactions between plant and fungal species. The focus is on fungal transporters that are very important with regard to using and regulating carbohydrates, phosphorous, and nitrogen. To date, the biochemical and structural characterization of many of these enzymes is hampered because they are integral membrane proteins that require a hydrophobic environment for stability and functional integrity. This project seeks to develop an integrated suite of systems to produce workable quantities of membrane-bound transporters for functional characterization.

Mission Relevance

Since about 25–30% of every genome encodes membrane proteins, studying them is essential in order to meet the goals in many areas of research being supported by DOE's Office of Biological and Environmental Research (BER). The objectives of BER's genomic science program include using emerging genomic sequence data to study the proteins encoded by microbial and plant genomes in order to explore their amazingly diverse natural capabilities.

FY 2012 Accomplishments and Results

This project focused on proteins derived from the fungus *Laccaria bicolor* and poplar, which serve as a laboratory model for fungal-plant symbiosis. We analyzed transcripts obtained from genes expressed when symbiosis between *Laccaria* and poplar was established in culture, revealing the activity of eight transmembrane carbohydrate transporters. Seven of these genes were cloned from *Laccaria* by a collaborating group at the University of Alabama–Huntsville and were provided to the Argonne team for cloning into expression vectors. We implemented multiple strategies to express these membrane-bound fungal transporters. The focus of FY 2012 work was on purifying them for functional characterization.

Membrane-localized protein is the gold standard for functional studies since detergents will never be completely faithful mimics of the membrane bilayer environment. A more robust approach to the adaptation of assay protocols, however, requires detergent-solubilized, purified protein. The ability to purify target proteins rapidly and reproducibly is critical, since many of them have short half-lives outside of lipid bilayers. In the quest to generate material of sufficient quantity and quality for use in functional studies, standardized protocols were developed and used for tracking the fate of transporters, expressed in *Rhodobacter* membranes, as they entered the processes of solubilization and purification (Figure 1A). Since *Laccaria* transporters are expressed at relatively low levels, we first subjected several *Rhodobacter*-expressed *E. coli* transporters to 10 combinations of detergents and environmental conditions. The success of solubilization and purification was tracked by using SDS-PAGE and immunoblots (anti-polyhistidine; Figure 1B). Both of the *Rhodobacter*-expressed transporters shown in Figure 1B were purified successfully with zwitterionic detergent Deriphat 160C by using room temperature solubilization (20°C). They appeared to be monodisperse, were folded properly, were membrane-localized, were not complexed with other proteins from *Rhodobacter*, and were purifiable in sufficient yield (bottom protein superior to top protein in all categories except yield). If necessary, these targets are of sufficient quantity and quality that they could be exchanged into other detergents (e.g., dodecylmaltoside, which appears to be used widely in publications addressing structure/function studies of sugar transporters). These targets and one *Laccaria* target, screened similarly, are now subjects of characterization experiments that include binding of fluorescently labeled ligands and gel filtration to better understand protein-protein and protein-ligand interactions.

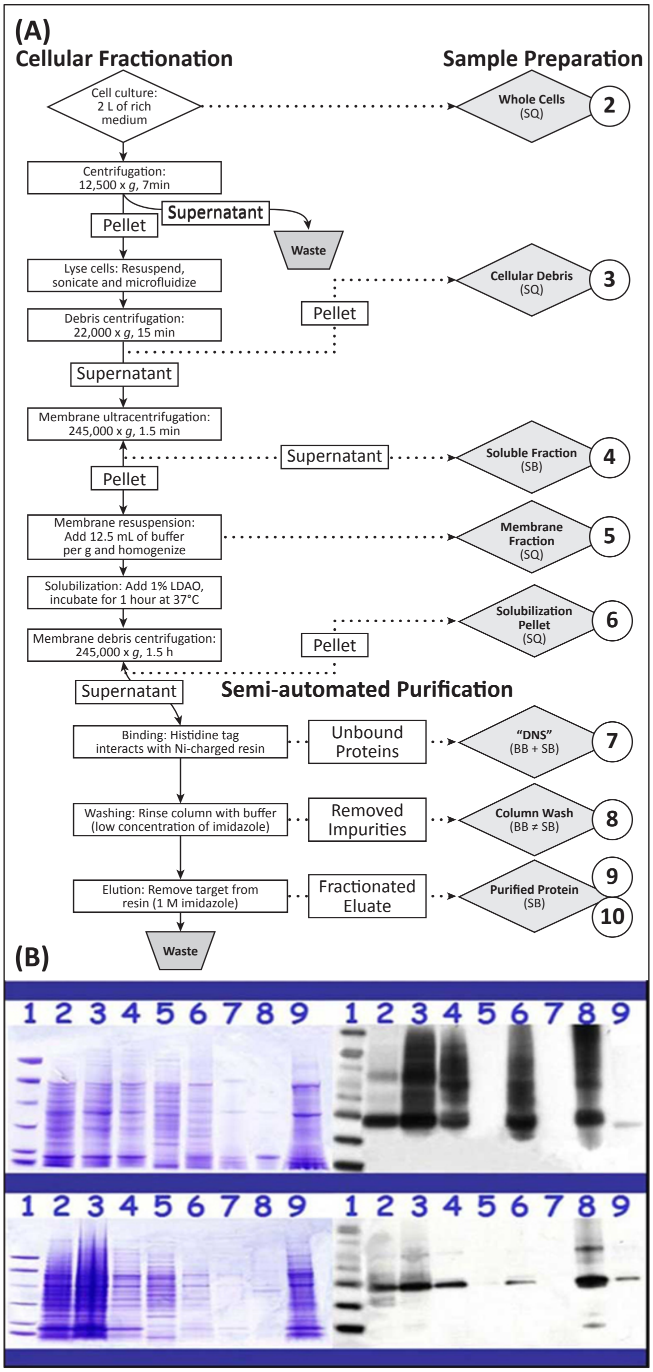


Figure 1. A: Experimental flow to evaluate detergent efficacy in solubilization and purification of transporters produced in Rhodobacter *membranes. B: Successful solubilization and purification of two* Rhodobacter*-expressed* E. coli *transporters (using the mild detergent Deriphat 160C) is shown in stained gels (left panels) and immunoblots (right panels). Purified target protein is found in lanes 8 of gels and blots.*

Aspects of this research — heterologous expression, purification, and characterization of both fungal and aspen transporters — have been incorporated as a subtask in other ongoing research and will be supported under DOE/BER's Environment Sensing and Response Scientific Focus Area project.

Tunnel-Diode Oscillator Detection Technique for Ultrasensitive Magnetometry and Resistivity Measurements of Microscopic Samples

2011-005-R1

Oleksiy Snezhko and O. Daniel López

Project Description

Novel high-temperature superconducting cables based on a complex multilayer structure are currently being tested for applications on the U.S. electrical power grid. The high manufacturing costs of the cables, their poor performance in electric motors (where high magnetic fields are present), and prohibitively high costs related to cooling these cables inhibit their widespread use. Therefore, any increase in the current-carrying ability of these materials or the discovery of novel superconducting systems with higher critical currents would improve the cables' performance and might help justify their widespread use. One of the main factors limiting the current-carrying ability of high-temperature superconductors — apart from the material itself — is the motion of magnetic vortices, nanometer-sized magnetic flux tubes appearing in the superconductor in magnetic fields above the first critical field. The vortices have normal cores and therefore dissipate energy when driven by the applied current. The dynamic behavior of vortices controls the electromagnetic response of a superconductor.

Existing measurement tools, such as direct current (DC) and alternating current (AC) magnetometers and point contact transport measurements, require rather large samples before they can produce reasonable (i.e., above noise) results; however, large samples are not always available, especially with newly synthesized systems. The goal of our project is to develop a novel micromechanical tunnel-diode oscillator platform that is capable of performing ultrasensitive measurements of the AC susceptibility, resistivity, and magnetic field penetration depth of small (micro-scale) samples. This tool is intended to provide unique capabilities that researchers can use to tackle some of the most fundamental and basic science problems in condensed matter physics, such as understanding how the pairing symmetry of Cooper pairs facilitates superconducting properties of the material (pairing symmetry is recovered through ultrasensitive magnetic field penetration depth measurements) and understanding the electro-transport properties of novel superconductors.

Mission Relevance

This project is relevant to DOE's energy mission. One of DOE's primary missions is to develop next-generation superconducting materials that could revolutionize energy delivery via the U.S. electrical grid in the 21st century. This proposal is enabling development of new instrumentation that will provide “materials characterization on a chip” with superior sensitivity (i.e., sub-ångstrom resolution when measuring a magnetic field penetration depth in superconductors). This novel tool will dramatically enhance our ability to address the fundamental questions of electron transport in superconductors, thereby helping to improve the design of next-generation superconducting cables and materials for the U.S. electrical grid.

FY 2012 Results and Accomplishments

In FY 2011, we developed and tuned the circuitry for a room temperature tunnel-diode resonator (TDR) with a 1-mm-diameter sensing coil. To accept much smaller samples, flat gold micro-coils were fabricated on silicon and were isolated from the silicon by a layer of SiN. In FY 2012, we completed the design and developed a low-temperature ^{3}He insert for the TDR low-noise circuitry. The new insert significantly reduced external noise pickup and provided a very stable temperature environment for components of the oscillator, contributing to the part-per-million frequency stability of the TDR required for ultrasensitive measurements. TDR circuitry was further temperature decoupled from the sample stage to improve the sensitivity (signal-to-noise ratio) of the system so that we were able to vary the temperature of the sample while not affecting the temperature stability of the TDR circuitry. The new design helped to significantly reduce the level of external noise affecting the efficiency of the TDR circuitry and thus improve the overall sensitivity of the system.

Micro-coils with 20, 40, 60, and 80 turns were fabricated by using patterning and etching processes. A TDR with micro-coils as the sensing coil of the tunnel-diode oscillator circuit was assembled, and stability tests were completed. Experimental tests of TDRs with micro-coils as a sensing element demonstrated that even at room temperature, the system produced a stable signal with an acceptable signal-to-noise ratio.

To control the developed TDR system and process signals generated by the oscillator, corresponding software drivers were developed, and tests were completed.

Proposed Work for FY 2013

We plan to design and fabricate *in situ* real-time tunable micro-coils with integrated MEMS-based actuators that will provide “stretchability” with enhanced sensitivity of the magnetometer. New coils will be adapted for the current TDR low-temperature setup and tested in experiments down to 250 mK to obtain complete characterization of their performance at low temperatures. The TDR system will be calibrated in external magnetic fields of up to 8 Tesla. Upon completion of tests, ultrasensitive penetration-depth measurements of superconducting micro-samples will be performed.

Synthesis, Characterization, and Properties of Fast-Acting Amorphous Drugs

2011-012-R1

Chris J. Benmore and Johann K.R. Weber

Project Description

Currently, a limited range of amorphous pharmaceutical compounds are commercially available. These amorphous pharmaceutical compounds provide greatly increased solubility, faster dissolution, and higher bioavailability to researchers than their crystalline counterparts. However, synthesizing the amorphous forms of a drug is not always possible by using conventional pharmaceutical processes. As such, it is becoming increasingly important to develop the amorphous forms because of the emergence of new drugs that are virtually insoluble in their crystalline forms.

This project, therefore, has two principal objectives: (1) to establish the scientific basis for a next-generation drug delivery technology and (2) to advance the capabilities for generating amorphous pharmaceutical and other compounds. These experiments demonstrate a new proprietary method for processing these materials, which involves an acoustic levitation technique that uses the pressure from intense sound waves to suspend pharmaceutical materials (see Figure 1). The technique provides a way to solidify the atoms or molecules in a liquid without risking interaction with the potentially contaminating effects of a container, either by solvent evaporation or laser quenching. Pharmaceutical materials are characterized before and after “containerless” processing by using hard x-rays and nuclear magnetic resonance (NMR) spectroscopy. Colleagues who have contributed to this effort include pharmacists, Professors Stephen Byrn and Lynne Taylor (both of Purdue University), and an NMR expert, Professor Jeffery Yarger (Arizona State University).

Figure 1. Drops of solution remain suspended indefinitely in an acoustic levitator, by the interference of two opposing sound pressure waves.

Mission Relevance

The results of this work have the potential to improve the quality of life through innovation in science and technology and to increase U.S. economic competitiveness through the synthesis of new, faster-acting pharmaceuticals. This project is relevant to DOE's basic science mission, as it utilizes and demonstrates the utility of DOE science-based facilities in support of national needs. Other agencies that may benefit from this research include the National Institutes of Health, research divisions of pharmaceutical companies, and universities. Over the long term, the introduction of new drug compounds will improve patient treatment outcomes, reduce drug delivery costs, and decrease the percentage of drug dosages that patients are unable to absorb. These innovations also may lead to less-expensive and higher-yielding drug-processing routes.

FY 2012 Results and Accomplishments

In FY 2011, the potential of the method was demonstrated for several drugs and new materials synthesis methodologies were developed — the most important of these was the laser heating and quenching of droplets in the levitator.

In FY 2012, we applied these methodologies to a wide variety of drugs of current interest in drug delivery and characterized the generation process with detailed *in situ* measurements of their structure by using the unique high energy x-ray measurement capabilities at the Advanced Photon Source. We also performed x-ray experiments on a selection of pharmaceuticals to characterize their time-resolved structure during the containerless melt-quenching process. The effort involved the installation and setup of a laser-controlled area for a low-power laser system for melting drugs. Furthermore, we tested human immunodeficiency virus (HIV) drugs and investigated the effect of the containerless processing technique on liquid crystals. Throughout the year, we monitored the processed drug products to develop a detailed understanding of how amorphous drugs crystallize over time.

This work resulted in the following patent:

- Benmore, C.J. and J.K.R. Weber, "Containerless Processing of Amorphous and Nanophase Organic Materials," patent application filed in January 2012. [ANL-IN-10-011, C&F Ref No. I 0003-02403].

Proposed Work for FY 2013

We plan to install cooling to the transducers on the acoustic levitator to minimize drift and to integrate an infrared thermal imaging pyrometer to measure the surface temperature of the suspended droplets. Currently, we are developing a computer program to help analyze the scattering results to achieve a better understanding of the structure-property relations. This piece of information is vital, since it can establish the difference between a drug that works effectively and a drug that does not work or may cause adverse effects.

From Plastic Bags to High-Performance Lubrication Additives: A Green Chemistry Solution to Energy Efficiency and Environmental Challenges in Transportation

2011-022-R1

Ali Erdemir, Vilas Pol, and Michael Thackeray

Project Description

In this project, we employ a revolutionary approach to convert waste plastic into micro/nano-scale carbon spheres and carbon tubes. These carbon spheres and tubes subsequently are used as micro/nano-colloidal additives in lubricating oils to obtain superior friction and wear performance under the severe operating conditions of internal combustion engines. The main objectives of the project are to develop novel carbon particles with excellent physical, chemical, and tribological properties and to demonstrate their usefulness under the very harsh operating conditions of engine and drive-train components in advanced automotive systems. Moreover, the project also focuses on (1) an understanding of the science behind the lubrication mechanism and (2) the optimization of lubricant properties to attain significantly improved friction and wear performance.

Mission Relevance

This project is relevant to DOE's mission in energy and environment in that it fosters new ideas to facilitate energy savings and protect the environment. On the energy front, we consume about 13 million barrels of petroleum per day for transportation alone. Engine and drive-train friction accounts for 10–15% of the total fuel energy used in current vehicles. This translates to approximately 1.3–2 million barrels of petroleum per day lost to friction. Furthermore, a significant amount of energy is spent to remanufacture and/or replace worn parts as a result of poor or inefficient lubrication in these systems. The energy efficiency, durability, and environmental compatibility of all transportation vehicles are very closely related to the effectiveness of the lubricants that are used on their rolling, rotating, and sliding contact surfaces. This project focuses on the development of a low-cost solution to the efficiency, durability, and environmental compatibility problems in advanced transportation systems. In short, we address a very important scientific and societal problem for our nation.

FY 2012 Results and Accomplishments

In previous years, we concentrated on the optimization of autogenic synthesis process for the production of larger quantities of carbon spheres and tubes and on blending them with a variety of base and formulated engine oils. In our bench tribological studies, these carbon-based lubricants demonstrated excellent anti-friction and wear performance under severe sliding conditions and at high temperatures. Using TEM (transmission electron microscopy), we also confirmed that improved performance was mainly due to the formation of a thick (i.e., more than 200 nm thick) carbon-rich protective boundary film on sliding surfaces. Further analytical studies with Raman and x-ray photoelectron spectroscopies helped us elucidate the fundamental lubrication mechanisms.

In FY 2012, we evaluated the tribological performance of several types of carbon particles (with and without additional surface functionalization) and confirmed their superior lubrication properties. In particular, carbon spheres with tin, silver, and antimony coatings demonstrated outstanding wear performance under severe sliding conditions that involved high loads, high temperatures, and starved lubrication conditions.

We used a higher-temperature synthesis and processing route to graphitize carbon spheres in their outer surfaces (see Figure 1). With this structural transformation, these latest spheres afforded much lower friction and wear to boundary-lubricated steel surfaces, even under severe test conditions. Surface and structure analytical studies confirmed the formation of relatively thick carbon-rich boundary films on rubbing surfaces. We determined that the formation of such slick and protective films is the primary reason for their superior tribological performance.

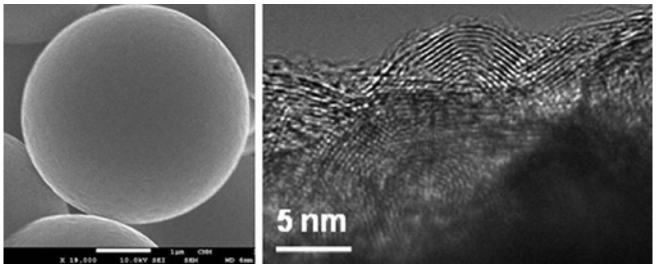


Figure 1. One of the carbon spheres subjected to high-temperature treatment (left) and its high-resolution transmission electron microscopy (HRTEM) image near the outer surface. This HRTEM image confirms a concentric shell structure (like graphite, right), which is believed to be the reason for its superior tribological performance under lubricated sliding conditions.

These findings resulted in the following invention:

- Erdemir, A., V. Pol, K. Mistry, and M. Thackeray. "Novel Materials as Additives for Advanced Lubrication," invention report submitted March 2012. [ANL-IN-12-006].

Proposed Work for FY 2013

In FY 2013, we will concentrate on a larger-scale demonstration of the production process and process optimization, as well as testing of the optimized carbon spheres and tubes in bench tribological systems that closely mimic actual or intended applications in advanced engines. We will also continue our fundamental studies to understand the relationship between the tribological performance and surface functionalization of carbon spheres.

Achieving Efficient Thermal Energy Transport with One-Dimensional Polymer Nanofibers

2011-071-R1

Zhang Jiang, Joseph W. Strzalka, Tao Sun, Hsien-Hau Wang, Jin Wang, and Zhenxin Zhong

Project Description

It is hypothesized that polymers that are usually good thermal insulators in bulk form can turn into good thermal conductors when they are drawn into one-dimensional fibers with high draw ratios and nanoscale diameters. The confinement-induced changes in the internal structures, chain entanglements, and defect morphologies are believed to affect the phonon propagation that is directly related to a polymer's thermal conductivity. Understanding the correlation between the structure and thermal properties of these nanofibers is crucial to the design and fabrication of polymer nanofibers that meet the need for efficient and practical thermal energy transfer, which requires high thermal conductivity — as well as electrical insulation, high chemical stability, light weight, and high mechanical performance — as well as the eventual ability to be mass-produced at low cost. Our goal is to resolve the structure-function relation by using x-ray-based techniques (such as wide-angle x-ray scattering [WAXS] and x-ray microdiffraction), in combination with the *in situ* drawing process and thermal conductivity measurement.

Mission Relevance

This project supports DOE's basic science and energy missions. Its success will have a great impact on both the technical applications of a new type of energy-efficient material and the fundamental understanding of low-dimensional, nanoscale thermal transfer physics. This project aims to unveil the correlation between material structure and the functional properties of polymer nanofibers. The knowledge we acquire throughout the project will apply directly to the design, optimization, and production of nanostructured polymer nanofibers with enhanced thermal transfer capabilities and other properties that are desirable in energy-efficient devices.

FY 2012 Results and Accomplishments

In FY 2011, an electrospinning device with parallel collectors was fabricated for fast and controlled nanofiber fabrication of a series of polymer candidates. We also designed and fabricated an *in situ* hot-stretching apparatus for a time-resolved x-ray scattering study of the nanofiber internal structures. For the first time, the microstructure development in the polymer nanofibers was investigated via WAXS. The feasibility of characterizing the thermal transport properties was explored on individual polymer nanofibers by noncontact Raman spectroscopy.

In the past year, using electrospinning techniques, we continued fabricating highly stretched fibers of semi-crystalline linear polymers, such as polyethylene, nylon, and polyvinylidene fluoride. The as-spun nanofibers, of well-controlled diameters ranging from several micrometers to one hundred nanometers, formed highly aligned bundles on parallel grounded collectors. The characteristics of their internal crystalline structures, such as degree of crystallinity, crystalline lattice parameters, domain size, and orientational parameter along the axis of the fibers, were quantified by using wide-angle x-ray scattering (WAXS) at the Advanced Photon Source. We found that more crystal domains orient along the direction of the fiber axis as the fiber diameter decreases. Post-spun processing was systematically applied in order to investigate the evolution of the internal structures as functions of annealing temperature and stretching. These processes were monitored by WAXS in a customized *in situ*, hot-stretching x-ray vacuum chamber. We managed to significantly increase the crystalline domain size along the fiber axis by thermally annealing the fibers near the polymer melting temperature. Both the degree of crystallinity and the crystal orientation parameter were found to be increased upon a slow-rate uniaxial hot stretching.

Thermal properties of individually suspended nanofibers were measured on a micro-scale Wheatstone differential bridge circuit, which provides an ultra-high-sensitivity measurement of the thermal conductance (~0.1 nW/K). These measurements were done in collaboration with the University of California-San Diego. A thermal conductivity increase of approximately one order of magnitude, as compared to thick fibers and bulk samples, was achieved in as-spun fibers with diameters of ~100 nm. Uniaxial hot stretching was found to further increase the conductivity. This enhancement has been correlated with the change in the internal crystalline structures and domain orientations in the nanofibers (see Figure 1 for details).

In addition, we attempted x-ray micro-diffraction from a single nanofiber and, for the first time, demonstrated the feasibility of resolving the structure of a suspended single fiber by using a micro- or nano-sized x-ray beam.

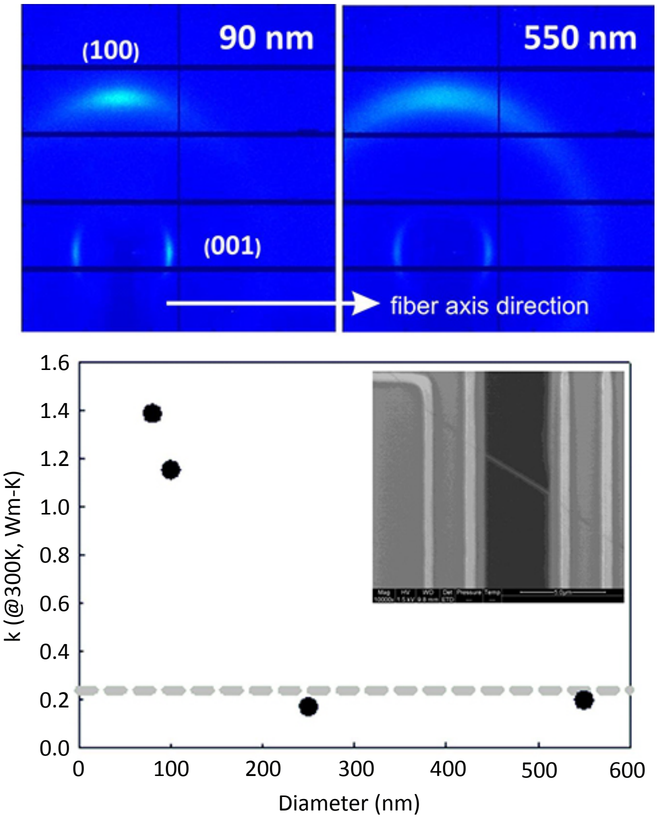


Figure 1. (Top) X-ray diffraction patterns from electrospun Nylon-11 nanofibers, 90 nm and 550 nm in diameter. Fiber axis is horizontal. (Bottom) Thermal conductivities of single nanofibers measured on a highly sensitive micro-scale Wheatstone bridge increase significantly as the fiber diameter decreases to 100 nm. Inset shows SEM image of a nanofiber draped across contacts of the Wheatstone bridge.

Proposed Work for FY 2013

We plan to optimize electrospinning conditions for better quality and size control of nanofibers with diameters of only a few tens of nanometers. We expect to observe drastic changes in the internal structures of these ultra-drawn fibers as the dimension of confinement approaches the size of the single-polymer molecular chain. Quantitative characterization of their structures will be carried out with both *ex situ* and *in situ* x-ray scattering experiments with thermal annealing and hot-stretching processes applied. The structures of these ultra-drawn fibers can then be correlated with their thermal properties, which will be determined on Wheatstone bridges through the collaboration with the University of California-San Diego. As a result, we will be able to construct a comprehensive diagram of the correlation between the polymer fiber nanostructure and its functions, in particular its thermal transport capability. Meanwhile, we will continue developing the method of single-polymer nanofiber x-ray micro-diffraction, including the design and optimization of a helium/vacuum sample chamber in order to enhance the signal-to-noise ratio and minimize radiation damage to the fibers.

New Technologies for Label-Free Antibody-Based Multiplexed Biosensors

2011-093-R1

Rosemarie Wilton and Anirudha V. Sumant

Project Description

Development of robust, protein-based binding reagents for biosensors — as well as integration of these reagents into sensitive detectors — is an essential step toward the development of field-deployable multiplexed biosensors. Such biosensors, which are capable of sustained exposure to harsh environmental conditions, will find application in the detection of multiple threats related to bioterrorism and biowarfare, in medical diagnostics, and in environmental monitoring. For this project, we are producing "cuprebodies" — stabilized, redox-active binding proteins that uniquely combine antibody-like binding activity with signaling functionality. We are incorporating these binding reagents into ultranano crystalline diamond (UNCD) -based sensors, which will detect changes in redox activity of the engineered proteins upon target binding.

Mission Relevance

The proposed research is applicable to DOE's mission in environmental monitoring. In particular, the project integrates materials development, engineering of novel biological sensing components, and new methods for signal detection in support of the 2011 Strategic Plan for Materials in Energy and Security-Related Systems. Other federal agencies that could benefit from our research in sensitive antibody-based detectors include the Department of Homeland Security and the Defense Threat Reduction Agency (DTRA); the research in this project responds to a Request for Information (RFI) issued by DTRA on the development of ruggedized antibodies.

FY 2012 Results and Accomplishments

The immunoglobulin domain — the fundamental protein fold of the antibody molecule — has structural similarity to a family of redox-active proteins, the cupredoxins (Figure 1A). We propose to combine the functions of these two molecules into a single entity termed the "cuprebody." Research in previous years focused on establishing a suitable protein framework for constructing the redox-active binding domain. We explored engineering a redox site into an immunoglobulin domain, as well as the converse experiment of introducing selectable binding activity into a cupredoxin domain. Ultimately, we selected the cupredoxin protein azurin as our framework. Of the cupredoxins that were tested, azurin displayed the highest stability and produced the highest expression levels in *E. coli*.

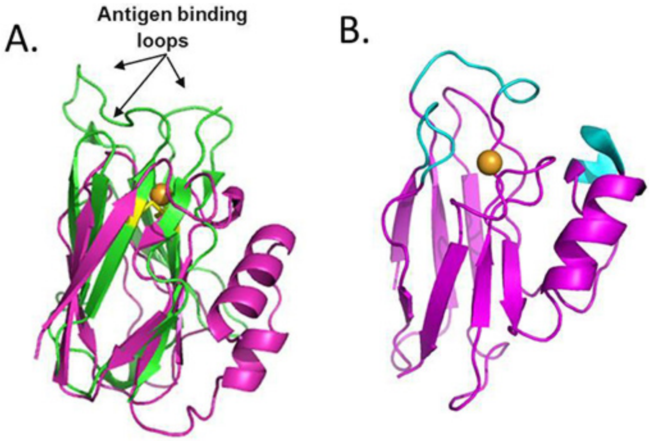


Figure 1. A. Superposition of an azurin protein (magenta) with an antibody variable domain (green). The copper ion of azurin is shown in orange. The disulfide bond of the immunoglobulin domain is shown in yellow. The proteins are structurally similar in their beta-sandwich domains. Azurin has a helical segment that is not present in immunoglobulin domains. B. Azurin showing the loop regions (cyan) that are being targeted for randomization in the combinatorial library. (Antibody coordinates from Dr. R. Pokkuluri (BIO); Azurin PDB 4AZU, 1AZU).

Cuprebody Design and Synthesis

- To produce a target-specific binding variant of azurin, it is important to show that amino acid variations in loops near the redox-active copper site of azurin would not destroy its expression, stability, or redox activity. We completed mutagenesis studies on azurin loop regions and determined the suitability of the azurin scaffold for use in a combinatorial phage display library. The azurin protein framework and the copper binding site were found to be remarkably robust in response to changes in loop regions surrounding the copper binding site (Figure 1B). Spectroscopic characterization of loop-modified azurin variants demonstrated that the redox-active copper site retained bound copper for most of the mutations characterized.
- We cloned azurin into a phage display vector for azurin display on the surface of M13 bacteriophage. The vector is designed to express azurin as a fusion with the M13 pIII protein. A FLAG octapeptide — a polypeptide protein tag that can be added to a protein using recombinant DNA technology is included to verify proper display of the fusion protein on the M13 phage surface.
- We are optimizing azurin phage display through the modification of the copper site and by producing an ultra-stable azurin framework by using homologous sequence/structure analysis, a technique that was developed in our laboratory.
- Random mutagenesis of the azurin loop regions will be used to construct a combinatorial phage display library for selection of binding reagents based on the azurin framework.

Proposed Work for FY 2013

Cuprebody Design and Synthesis

- We will complete stability optimization of the azurin framework and build the final version of the azurin phage display vector.
- We will complete construction of a combinatorial phage display library based on the optimized azurin scaffold.
- We will select binding partners for two targets: (1) lysozyme, a widely used control target for the development of novel binding reagents and (2) botulism toxin-binding domain.

Fabrication of UNCD Nanowire Field-Effect Transitor (FET) -Type Structure

- We will synthesize and functionalize UNCD nanowires for attachment of target bio-molecules/proteins. The change in the electrical response of the FET as a function of attachment/detachment of these bio-molecules and target proteins will be recorded, and all electrical data will be further analyzed to demonstrate consistent and characteristic electrical response to these events.
- Electrochemistry will be conducted with our collaborator, Prof. Greg Swain (Michigan State University, Dept. of Chemistry). His laboratory is well equipped with unique resources for detecting the attachment of bio-molecules on diamond surfaces in real-time in an electrochemical cell.

Dynamics of Spin-Polarized Carriers in New Spin Electronic Materials and Devices

2011-097-R1

David J. Keavney and Philip Ryan

Project Description

This project seeks to enhance our understanding of spin dynamics in semiconductors through direct imaging of spin-polarized carrier populations in real device environments. We use x-ray photoemission electron microscopy and x-ray excited luminescence microscopy to obtain magnetic images. The major objective of the work is to obtain element-specific images of spin injected into a semiconductor device, ultimately with a time resolution of 100 ps, in order to study how device geometries and structure influence the spin currents. These spin currents are small, producing an expected signal of 1 part in 10^6 in our x-ray experiments. Therefore, development of low-noise techniques has played a role in the initial stages of the project.

Mission Relevance

The data obtained through this project will help in the synthesis and discovery of new electronic materials for low-power electronics and information storage, which is of relevance to DOE missions of energy technology and basic science. These materials, by enabling spin instead of charge to process information, are expected to enable a new generation of non-volatile electronic devices, including non-volatile memory technologies and field programmable gate arrays. Such devices would enhance functionality and operate at lower power, thereby enhancing energy security on the consumption side of the equation. In addition, a basic understanding of spin dynamics in semiconductor materials is relevant to four of the five Grand Science Challenges in the DOE-BESAC Report “Directing Matter and Energy: Five Challenges for Science and the Imagination:” control of materials at the electronic level, emergent properties, information at the nanoscale, and physics far from equilibrium.

FY 2012 Results and Accomplishments

Toward the experimental goals for FY 2012, we performed measurements using x-ray magnetic circular dichroism (XMCD) spectroscopy on optically pumped spin populations in gallium arsenide (GaAs). During FY 2011, we performed several spectroscopy experiments on electrically injected structures, and we established a noise floor of 1 part in 10^5 on the observable dichroism signal. The lack of an observable signal in electrical injection experiments led us to try optical spin pumping as an alternate means of creating the spin-polarized carrier population.

Figure 1 is a schematic of the optically pumped XMCD experiments. Highly doped (up to $10^{18}/cm^3$) n-type GaAs was simultaneously illuminated by the soft x-ray beam at the Ga L_3 edge (1116 eV) and by a 150-mW diode laser tuned to just above the GaAs bandgap (850 nm). The laser was circularly polarized by using a quarter-wave plate, and the power was modulated at 13 Hz to allow lock-in detection. The laser and x-ray beam focal spot sizes were matched as closely as possible (~200 and 100 μm^2, respectively), and there was a 45°angle between the x-ray and laser beam directions.

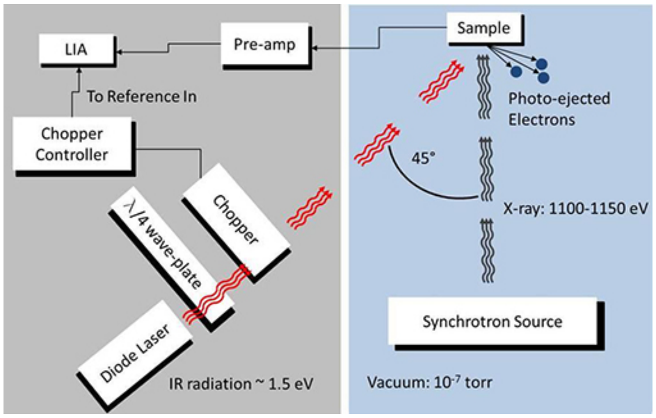


Figure 1: Diagram of the excitation scheme for measurements of optically pumped spins. The n:GaAs sample is excited by a circularly polarized laser that is amplitude modulated by a mechanical chopper. X-ray–induced photoemission of electrons creates a current that is detected by the pre-amp. The lock-in amplifier (LIA) measures the difference between the laser-on and laser-off states by measuring the photoemission current amplitude at the chopping frequency. Both pre-amp and lock-in amplifier signals are recorded. (Note: Concurrent measurements on another GaAs sample that is not subject to optical excitation using a portion of the x-ray beam are not displayed.)

Using this approach, we are able to detect two effects on the x-ray absorption caused by the influence of the laser-induced carriers. The first is an enhancement in the total absorption signal measured by total electron yield. This effect occurs because of an enhancement in the conductivity from additional carriers excited into the conduction band, and is proportional to the total x-ray absorption signal. The second effect is a clear and reproducible dichroism that appears at the L_3 and L_2 resonances, as shown in Figure 2. This represents the first measurement of a spin-polarized carrier population by XMCD, and is one of the primary goals of this project. The sizes of the dichroic effect were measured to be ~0.1% on the L_3 and ~1.0% on the L_2 resonances, which are surprisingly large compared to the noise floor established by the electrical injection experiments, as well as expected values estimated from published density functional theory calculations. Work is in progress to explain this large signal in the framework of an enhancement of the spin polarization resulting from band bending at the surface.

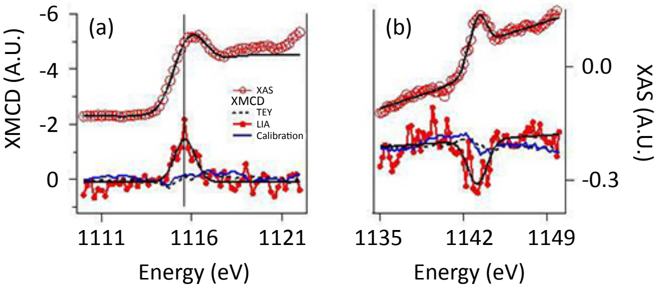


Figure 2: GaAs XMCD shown along the L_3 (a) and L_2 (b) edges as measured by the lock-in amplifier (LIA). For comparison, we also show the XMCD of the direct current channel and the non-optically excited channel. The XMCD measured on the lock-in channel is significantly larger than both of these. X-ray absorption spectroscopy (XAS) is not scaled with respect to XMCD.

Proposed Work for FY 2013

In FY 2013, we plan to build on the preliminary spectroscopy work carried out in FY 2012. With the first-ever detection of a measurable XMCD signal attributable to a spin-polarized carrier population, we are now able to pursue more of the original goals of the project. We plan to start by obtaining time-resolved pump-probe spectroscopic measurements to examine the dynamics of the spin population. These measurements will use the same experimental approach as that shown in Figure 1, but the laser will be modulated and synched with the x-ray bunch frequency. We are also evaluating the signal level to determine whether imaging experiments using photoemission electron microscopy are still feasible. If so, we plan to perform either laser-induced or electrically excited imaging experiments with time resolution in the latter part of FY 2013.

Development of a Design Concept for a Ring Imaging Cherenkov Detector

2011-110-R1

Kawtar Hafidi

Project Description

The goal of this project is to develop a design concept for a ring imaging Cherenkov (RICH) detector for the CLAS12 spectrometer to be located at Thomas Jefferson National Accelerator Facility (JLab) in Virginia. By providing clean separation between pions, kaons, and protons over a momentum range from 2.5 to 8 GeV/c, the RICH detector will have a strong impact not only on the CLAS12 physics program but also on JLab's 12-GeV mission as a whole. This physics program is also an important component of the Medium Energy Group (MEP) in Argonne's Physics Division. Several design concepts will be studied to explore all available options (including radiators, optical systems, and light detection methods) for maximizing particle identification and minimizing the cost.

Mission Relevance

This project is relevant to DOE's basic science mission. Adding a RICH detector to the CLAS12 physics program will enable researchers to learn whether the anti-up and anti-down quarks contribute symmetrically to the polarization of the proton, to precisely measure the contribution of the strange quark to the polarization of the proton, and to study whether the quark energy loss in the nucleus and hadron formation time depend on quark flavor. Moreover, these three important accomplishments are only a few of the ones we can expect. All of the research topics align very well with the DOE Office of Science's mission to advance understanding of the structure of the nucleon and nuclei from their most fundamental degrees of freedom: quarks and gluons.

FY 2012 Results and Accomplishments

In FY 2011, we developed and tested GEANT4 simulation and reconstruction software, benchmarked it against previous codes, and studied design options. The result was the adoption of an inward reflection design with an aerogel radiator and visible photon detectors. In FY 2012, we completed and improved those simulations and used them to study detector performance via resolution calculations and a reconstruction algorithm for particle identification quality, and we cross-checked them with theoretical expectations. We implemented detailed optical properties for media and their surfaces in the simulation, then studied their effects (including chromatic dispersion, surface roughness, and reflection efficiency). We also studied more design options: additional mirrors to contain the photons within one detector sector, multi-radiator setups (both aerogel of various thicknesses and aerogel plus sodium fluoride radiators) to increase photon detection at low momentum, and various photon detector options to decrease the cost. GEANT4 visualizations of the prevailing design are shown in Figures 1 and 2 with examples of Cherenkov photon trajectories and detection.

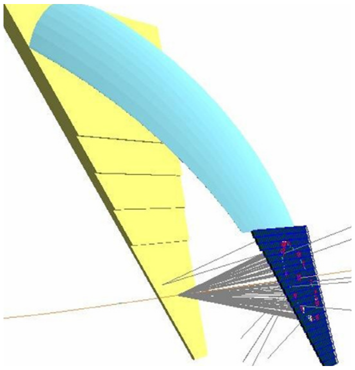


Figure 1. GEANT4 visualization of the RICH design in action. (The yellow material is the aerogel radiator, light blue is an ellipsoidal mirror, and dark blue is the plane of photomultipliers. Tracks at small angles [left] have their photons [grey lines] detected directly, with no reflections.)

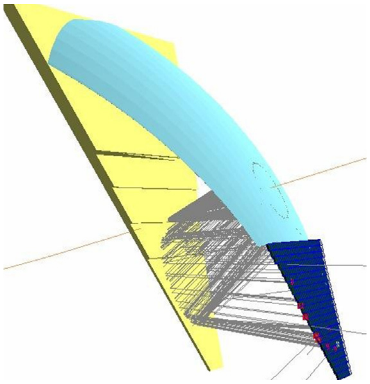


Figure 2. GEANT4 visualization of the RICH design for a track at a large angle, the photons of which undergo two reflections before reaching the photomultipliers.

Proposed Work for FY 2013

Our work will include an analysis of results from recent and future test runs with a simplified prototype at CERN in Switzerland, a comparison with simulations to perfect our GEANT4 modeling of the full-scale design, and the finalization of our tolerances on material properties. With the MEP Group's new Helmholtz coil, we can test the effect of magnetic fields on the performance of photon detectors (including the Large-Area Picosecond Photo-Detector [LAPPD] project's new photon detector, also being developed at Argonne).

Synthesis of New Sodium Layered Oxide Cathode Materials for Ambient-Temperature Sodium Batteries

2011-116-R1

Christopher S. Johnson, Mahalingam Balasubramanian, Eungje Lee, and Michael Slater

Project Description

Ambient-temperature sodium-ion batteries have the potential to meet the growing needs of energy storage, but new battery electrodes are needed to advance the technology. This project consists of a synthesis-based approach to produce new Na materials to overcome performance barriers in electrodes, such as cost, safety, and long-term cycling performance. We are studying the electrochemical property-function-structure relationships in candidate electrode materials. The focus of the project is synthesis of (1) layered Na-containing materials that can provide a two-dimensional intercalation space for the fast transport of Na cations into and out of the structure and (2) Na-based intermetallic alloys that have high capacities.

Mission Relevance

Sodium-ion batteries that operate at ambient temperatures provide an appealing low-cost energy storage option for certain applications. For example, large-scale energy storage for renewables requires batteries that can conveniently and transiently store large amounts of energy for peak regulation and output during off-hour periods. This is a goal of the DOE Office of Electricity and Energy Reliability (OE), which released a report in December 2010, "Advanced Materials and Devices for Stationary Electrical Energy Storage Applications." OE has acknowledged that a materials-based approach to advancing grid-scale energy storage technologies is needed. Research and development work on advanced materials has the potential to overcome many of the technical, economic, and design barriers that are currently preventing energy storage devices from meeting the needs of the electric power industry. Because of the large size of the batteries, materials used for them need to be low cost, long lasting, and safe, as well as possess a moderate energy density. Having as high an energy density as possible is important to minimize the number of hardware components (and manufacturing cost) associated with the batteries, and thus the number of cells needed for the application. Using the appropriate high-capacity electrodes operated at 3.3 V, it is possible to have a Na-ion battery energy density of 210 Wh/kg. Such batteries may be able to supplant Li-ion batteries for large-scale grid-storage needs. The wide availability and abundance of Na for materials and the low price of Na ion batteries versus Li ion batteries provide one rationale for the development of new advanced chemistries for non-aqueous Na-ion batteries.

FY 2012 Results and Accomplishments

In FY 2011, we showed that layered transition metal oxides, such as $Na(Ni_{1/3}Fe_{1/3}Mn_{1/3})O_2$, provide excellent performance as cathodes in Na-ion batteries. In an effort to understand the stacking sequence of layered compounds and the contrast between oxides and sulfides, we turned to evaluating layered transition metal sulfides.

In FY 2012, we successfully made layered sodium sulfides and tested their properties as cathodes in Na batteries. Na_xVS_2 materials provide softer bonding to the Na cations, thereby readily allowing the sliding transformation of layers and therefore the promise of fast charge-discharge rates. For example, in Figure 1 we show the various stacking sequences of O3, P3, and O1. The O and P descriptors stand for octahedral and prismatic coordination of Na in the layers, respectively, and the number is the size of the unit cell in the form of stacked layers. The electrochemical voltage profile and high capacity of 200 mAhg^{-1} for the Na_xVS_2 in a Na battery are also shown at the bottom of the figure. The phase transformations are marked on the plot. Na_xVS_2 represents a new material for Na batteries and provides a good contrast to layered sodium transition metal oxides, which feature a stronger Na-O bonding environment.

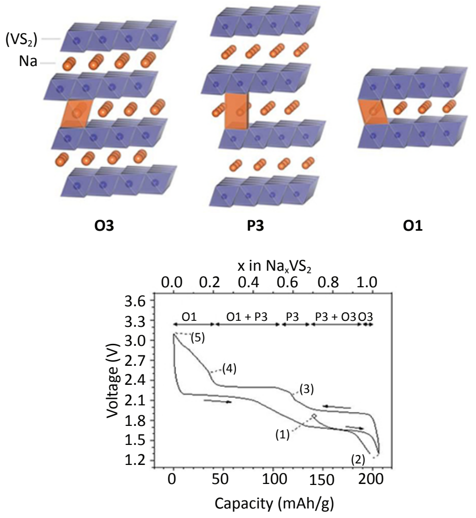


Figure 1. Top: Na_xVS_2 O3, P3, and O1 phase stacking sequences. Bottom: electrochemical voltage profile of a Na/Na_xVS_2 battery. Phase transitions are marked in the figure.

In addition, we have prepared physical vapor deposited (PVD) Sn thin films and studied their electrochemical reactions as high-capacity anodes with Na. In the Na/Sn electrochemical reaction, the greatest capacity in the material corresponds to the largest content of Na that can be formed in the binary alloy, which is the $Na_{15}Sn_4$ phase (formed as shown below). We observed this phase in *in operando* Na battery synchrotron x-ray diffraction measurements at the Advanced Photon Source.

$$\text{Equation 1: } 15\ Na^+ + 15\ e^- + 4\ Sn \rightarrow Na_{15}Sn_4$$

$Na_{15}Sn_4$ has a moderate material density (χ=2.4 g/cc) as compared to bulk tin (χ=5.77 g/cc), but a very high volumetric energy density of 6164 mAh/cc. In comparison, lithiated carbon (LiC_6) has a volumetric energy density of 818 mAh/cc and possesses a low packing density of less than 1 g/cc. In the fully sodiated phase, $Na_{15}Sn_4$, the volume expands by 424% (χ=2.4 g/cc). The repeated expansion and contraction during electrochemical cycling pulverizes the electrode particles, causing loss of electrical contact with the current collector and leading to capacity fade. Thin films may counter this pulverization because they contain enough porosity to accommodate the volume increase and, further, are in direct contact with the current collector for good charge collection.

The electrochemical voltage profile of Na/Sn (PVD thin film) is shown in Figure 2. The cycling is reversible to 50 cycles, and the capacity is nearly theoretical (~ 800 mAhg^{-1}). Such high capacities may lead to Na-ion batteries that are competitive in energy density to Li-ion batteries.

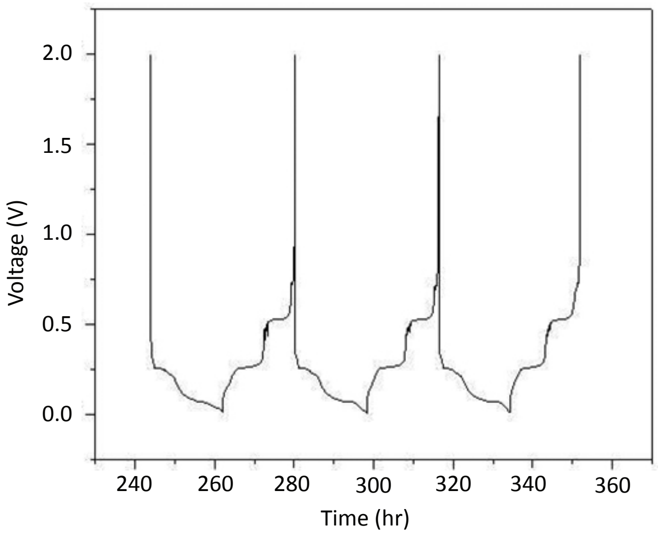


Figure 2. Voltage profiles of a Na/Sn coin cell under constant-current charge and discharge. The plateaus in the cycles represent various Na-Sn phases.

This work resulted in the following invention:

- Johnson, C.S, E. Lee, and Y. Kim, “Sodium Chalcogenide Electrodes for Sodium Batteries,” invention report submitted August 20, 2012. [ANL-IN-12-082].

Proposed Work for FY 2013

For FY 2013, we will evaluate other new materials that should have a strong impact on the performance of these batteries. We need to raise the voltage of the Na-ion cells to above about 3–4 V and beyond. To do this, we must turn to polyanionic cathode compounds that feature an inductive effect on the transition metal oxygen bond (TM-O) that will raise the redox voltage of the TM. In our proposed research on anodes, the approach is to develop novel intermetallic nanocomposite anodes, with a high surface area/volume ratio, that include a specially tailored cocktail of individual elements and intermetallic phases to enable sequential electrochemical reactions that are designed to reduce the volume expansion while increasing the volumetric capacity.

For example, our calculations suggest that an intermetallic alloy of SnSb in buffering Pb (70 wt.% SnSb, 30 wt.% Pb) will lower the volumetric changes to less than 131% (SnSb), 114% (Sb) and 53% (Sn) (as compared to 460% for pure Sn) for full electrochemical reaction with Na. The theoretical capacity of a 70% SnSb/30% Pb (SnSb@Pb) anode is 672 $mAhg^{-1}$, and even better, the volumetric capacity is much higher, at 8713 mAh/cc. These anodes will be coupled with our existing cathodes to form an advanced low-cost, long-life, safe, and stable Na-ion battery. Our Na-ion battery operating at ambient temperature will be attractive for safe and reliable grid storage.

Seminars

Slater, M., A. DeWahl, V. Maroni, S. Hackney, and C. Johnson (2012). “Composite Sodium-Lithium-Transition-Metal Oxides As Cathodes In Alkali-Ion Batteries.” University of Illinois at Urbana-Champaign, Urbana, IL, January 27, 2012.

Detailed and Reduced Chemical Kinetics of Green Fuels for Compression Ignition Engine Modeling

2011-140-R1

Raghu Sivaramakrishnan, Michael J. Davis,
Douglas E. Longman, and Sibendu Som

Project Description

Two needs — for an energy scenario dominated by alternative fuels derived from domestic sources and for stringent emissions compliance legislations for future transportation systems — have recently led the combustion research community to redirect its efforts to focus on clean-burning fuels and more efficient engines. Biodiesel is one of several alternative fuels that, when used alone or in blends with conventional petroleum-derived fuels, offers substantial emission advantages in compression ignition (CI) engines. Biodiesel is composed of mono-alkyl esters of long-chain fatty acids (C_{16}–C_{18}, saturated and unsaturated) derived from vegetable oils (soybean oil being a primary source in the United States) or animal fats. Despite the significance of these alkyl esters in alternative fuel scenarios, there have been very few fundamental and applied combustion studies of them. The focus of this project is to develop a high-fidelity CI engine model for the combustion of biodiesel fuel. It will represent a multidimensional computational study, in which detailed chemical kinetic models for biodiesel surrogates will be developed, reduced in size (number of species and reactions), and applied in predictive three-dimensional (3D) engine simulations.

Mission Relevance

This project is tied to DOE’s missions in energy and environment. It addresses the challenges that were the focus of a recent workshop convened by the DOE Office of Science under its Basic Energy Sciences Program and Office of Energy Efficiency and Renewable Energy under its Vehicle Technologies Program to identify basic and applied research needs and impacts in Predictive Simulations for Internal Combustion Engines (PreSICE) (http://science.energy.gov/~/media/bes/pdf/reports/files/PreSICE_rpt.pdf). This project also addresses the “grand challenge” of DOE’s Basic Research Needs Workshop (report available at http://science.energy.gov/~/media/bes/pdf/reports/files/ctf_rpt.pdf): the development of a validated, predictive combustion modeling capability that could have a significant long-term impact on the efficiency and emissions that would result from using evolving transportation fuels in advanced engines. This combustion modeling project is also relevant to the combustion and diagnostics program of the Air Force Office of Scientific Research, the Strategic Environmental Research and Development Program (SERDP) of the U.S. Department of Defense, and the combustion and propulsion programs of the National Aeronautics and Space Administration (NASA).

FY 2012 Results and Accomplishments

In FY 2011, we developed a reduced chemical kinetic model for our biodiesel surrogate (blend of n-heptane and methylbutanoate), applied it in 3D engine simulations, and found that the ignition delay was overpredicted by about 30–40% compared with the experimental data. In FY 2012, we focused on improving the reduced model by conducting sensitivity analyses under CI engine conditions and by updating the rates of key reaction steps. We also worked on analyzing and improving the mechanism reduction techniques. Three main accomplishments in 2012 were as follows:

1. We performed a series of 3D calculations to identify which chemical reactions are most important for ignition under CI engine conditions (heterogeneous). We chose the reactions on the basis of global sensitivity analyses of homogeneous systems.
2. We calculated the reaction rate parameters of the key reaction step ($HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, identified to be important for ignition in the engine modeling based on the analysis mentioned above) by using state-of-the-art quantum chemistry and reaction rate theory. We emphasized a complete description of the tunneling processes that can occur. The updated rates were used in CONVERGE for 3D engine simulations, and these results agreed more closely with the data from the experiments on ignition delays.
3. We compared directed relation graph (DRG -based reduction techniques systematically from two perspectives: accuracy and efficiency. We improved the efficiency of the original DRG method (60 times faster for a 3,299-species biodiesel mechanism) by applying sparse algorithms for building and sorting the graph edges.

Proposed Work for FY 2013

We plan to continue our work on uncertainty analyses in 3D simulations to identify the most sensitive steps for ascertaining engine performance. We will apply sparse regression techniques (e.g., Lasso, group Lasso, sparse group Lasso) to help in the global sensitivity analysis (GSA). We expect that 300–500 engine simulations will be needed for our reduced mechanism with 900 reactions, much less than the 20,000 simulations needed without the sparse regression. We also propose to perform on-the-fly reduction. The on-the-fly reduction scheme will be developed and tested first in zero dimensions and 1D with the CHEMKIN package and then extended to 3D engine simulations with CONVERGE.

Seminars

Som, S. (2012). “Recent Progress in CFD Modeling and Challenges.” *Indo-US Science and Technology Forum* workshop on “Liquid Atomization.” Indian Institute of Technology at Madras, Chennai, India, December. 19–20, 2011.

Som, S. (2012). “Compression Ignition Engine Modeling Activities at Argonne National Laboratory.” Politecnico di Milano, Milan, Italy, May 10, 2012.

Som, S. (2012). “Developing Predictive Internal Combustion Engine Simulation Capability for Next Generation Biofuels of Interest.” University of Wisconsin, Madison, WI, September 20, 2012.

Magnetomechanical Actuation of Membrane Channels and Cellular Signaling via Direct Energy Transfer

2011-147-R1

Valentyn Novosad and Elena A. Rozhkova

Project Description

Application of nanoscale magnetic materials allows the integration of inorganic material with biological molecules and therapeutics to achieve a combination of multivalent properties in one designer material. While most experimental results have been reported for applications of superparamagnetic materials, including their bioconjugates, interfacing of ferromagnetic nanomaterials with biomaterials is a novel approach. In contrast to hyperthermia modalities, we will explore the magnetomechanical actuation of membrane and cellular signaling via direct energy transfer. This is a completely different and novel pathway to achieve the cytotoxicity effect with magnetic nanomaterials.

We are investigating how lithographically defined magnetic particles can be used as mediators of cellular mechanotransduction for cancer therapy. Our data show that with the proper choice of magnetic particles, a magnetic field of extremely low frequency (a few tens of Hertz) applied for 10 min is sufficient to achieve statistically significant destruction of cancer cells *in vitro*. For comparison, in the case of commonly studied hyperthermia effects, magnetic fields with frequencies of hundreds of kilohertz are needed to achieve cell thermal ablation. In other words, the external energy supplied to the cell cultures in our experiments is ~100,000 times smaller than the most efficient hyperthermia use of magnetic nanoparticles to fight cancer known to date. Direct energy transfer and low operating field strength may create unprecedented treatment opportunities with low cost, a large working volume, and minimal invasiveness.

Mission Relevance

This project focuses on the understanding of mechanisms of intra- and intercellular energy transfer in support of DOE’s mission in basic science and innovation. Furthermore, the design of novel nano-bio hybrid materials is a cutting-edge research area that is expected to contribute greatly to emergent challenges connected with the exponentially growing societal demands for clean energy and upgraded medical and health technologies to combat disease.

Understanding and controlling the way cells communicate with each other is crucial for advancing therapy options. These options may not only improve the quality of life for an individual patient, but they also have a tremendous socioeconomic impact, since even small, incremental advances in reducing cancer mortality and disability will inevitably lead to a large health-care benefit.

FY 2012 Results and Accomplishments

Before FY 2012, we established the process of fabrication of gold-covered disk-shape particles with diameters ranging from one micrometer (standard contact optical lithography) and down to ~0.3 micrometers (deep UV projection lithography). Magnetically soft $Fe_{20}Ni_{80}$ alloy and polycrystalline iron materials were used as a magnetic core of the disks. All samples showed the spin vortex-like magnetic responses and very good magnet-mechanical coupling; however, the *in vitro* experiments were continued with micrometer-size FeNi particles, as they appeared less susceptible to agglomeration and easier to synthesize in large quantities and visualize by using optical microscopes. By comparing *in vitro* data obtained under different magnetic field conditions, we found that only low-frequency stimuli excitation resulted in statistically significant cell damage. Established cytotoxicity protocols included characterization of DNA damage, membrane leakage, and cell viability assays. These studies were further continued in FY 2012 with micrometer-size disks.

Thus, a currently used disk fabrication process employs a contact photolithographic patterning of a negative photoresist. Photoresist development yields a structure of 0.5-μm-tall, 1-μm-diameter pillars, which are then coated with three layers of metal by means of electron beam deposition. The central 60-nm-thick layer is permalloy, which defines the magnetic properties of the disk. The outer layers consist of 5-nm gold, which allows for biocompatibility and chemical functionalization of the disks to enable targeting to specific cell receptors and labeling the disks with, for example, fluorescent tags. Because of their large scattering cross section, the disks can be easily visualized under an optical microscope.

Figure 1A shows a pseudo-color image of the disks on the cell surface acquired in the confocal regime. To enable specific attachment of the disks to cancer cells, the disks were functionalized with IL-13a2R antibody, which targets the IL-13a2 receptor expressed on human glioma cells. Figure 1B illustrates the principle of magnetomechnical actuations of cancer cells by using ferromagnetic disks. A low-frequency alternating magnetic field induces high magnetomotive force, causing the disks to oscillate and stimulate the cell membrane. Current efforts are focused on mechanistic studies of cellular magnetomechanical-induced apoptosis (cell death). While details of a multi-step mechanism of magnetomechanical cell stimulation is yet to be fully understood, the experimental data clearly support the hypothesis about the mechanical origin of the apoptotic response. The stimulation elevates the intracellular calcium level, which suggests the recruitment of mechanosensitive receptors as a result of cell membrane stretching by oscillating disks. The natural lack of calcium metabolism in a cell makes it highly susceptible to elevated intracellular calcium concentrations, which, on prolonged exposure, may trigger the apoptosis. At the same time, acridine orange and ethidium bromide staining of magnetomechnically treated cells reveals the signs of apoptotic DNA damage.

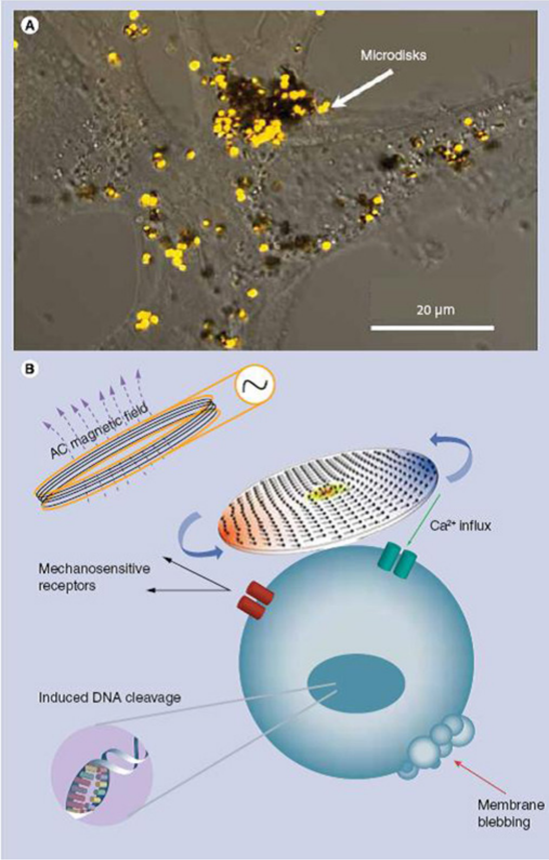


Figure 1. Ferromagnetic microdisks targeted to a cancer cell for magnetomechanical cell stimulation. (A) Confocal optical image of microdisks on the A172 glioblastoma cell surface. (B) The principle of magnetomechanical actuation of a cell membrane triggering apoptosis.

Figure 2 shows the confocal fluorescence images of the A172 human glioblastoma cells overlaid with their optical transmission images before and after the treatment with ferromagnetic microdisks in a weak low-frequency alternating current (AC) magnetic field. The enhanced green nuclear staining by acridine orange indicates that the cells are undergoing apoptosis. At the same time, the absence of orange nuclear staining suggests that for the given cell line, the magnetomechanically induced apoptosis does not necessarily involve the rupture of the cell membrane, since ethidium bromide does not enter the nucleus, at least in the early stages of apoptosis. Importantly, magnetic disks are not cytotoxic in the absence of the external field.

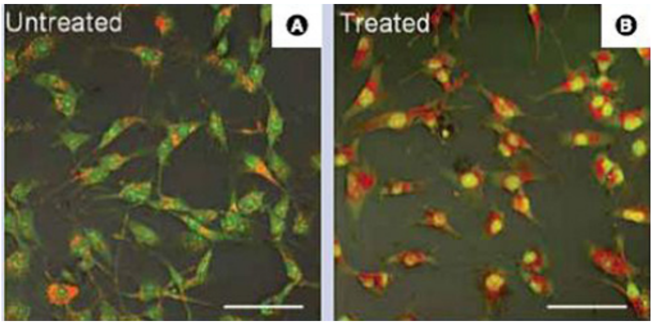


Figure 2. Acridine orange/ethidium bromide (14 μg/mL) staining of A172 human glioblastoma cells for assessing magnetomechanically induced DNA damage. Overlay of differential interference contrast and confocal fluorescence images of (A) control untreated cells and (B) magnetomechanically stimulated cells that were incubated with microdisks and then exposed to AC magnetic field (10 Hz, 100 Oe) for 15 minutes. The treated cells exhibit the signs of early apoptosis, as indicated by bright nuclear staining with acridine orange. Scale bar: 100 μm; 20× magnification objective.

Proposed Work for FY 2013

We have already established that the key signal messenger in magnetomechanically induced signaling was calcium. Questions remain regarding the mechanism behind this process. Increased levels of calcium ions, important messengers and regulators of apoptosis, can be connected with at least two possible pathways:

1. Influx from outer medium through induced ionic channels or temporary pores and
2. Release from intracellular molecular depots as a result of membrane mechanosensitive receptors induction.

Therefore, the important part of cellular studies at this stage will require precise quantitative measurements of extracellular calcium as a response to the application of AC fields. We will use inhibitors of calcium pumps (thapsigargin) and inhibitors of the mechanosensitive ion channels (e.g., gadolinium Gd3+ or specific peptides). Other membrane receptors — for example, purinergic receptors stimulated by adenosine triphosphate (ATP) — could also be involved in the calcium signaling in mechanically stimulated cells. At the same time, ATP has been shown to play a major role in calcium signaling between glial cells (for example, see A. Verkhatsky, R.K. Orkand, and H. Kettenmann, "Glial Calcium: Homeostasis and Signaling Function," *Physiol Review, vol.* 78, *pp.* 99–141, 1998). By blocking the purinergic receptors by using, for example, suramin, we could investigate their role in calcium signaling upon cell treatment with magnetic disks.

Seminars

Novosad, V. (2012). "Magnetism for Life." University of Colorado Springs, Colorado Springs, CO, February 24, 2012.

Novosad, V. (2012). "Multifunctional Magnetic Vortex Microdisks." Drexel University, Philadelphia, PA, November 11, 2011.

Rozhkova, E.A. (2012). "Smart Nano-bio Materials within Cellular Machinery." Loyola University, Chicago, IL, October 13, 2011.

Development of Wireless Data and Power Techniques for Large Instrumentation Systems

2011-153-R1

Zelimir Djurcic, Patrick De Lurgio, Gary Drake,
and Himansu Sahoo

Project Description

The objective of this project is to build a single detector module that operates using wireless power and sends data wirelessly. The goal is to eliminate the massive cable plants that are typical of large detectors, which could result in a reduction in cost, simplification of installation and repair, and a reduction in the dead mass of the detector. We want to ascertain the feasibility and practicality of such a device as a single detector module and as part of a large detector with thousands of modules. We chose a photomultiplier tube (PMT) as the base detector unit for this feasibility study because PMTs are widely used in large particle physics detectors. The system specifications assume the capability to measure single photoelectrons, which imposes requirements on bandwidth and sensitivity of the instrumentation. We chose a large 10-inch-diameter PMT, a Hamamatsu R7081, which has a single photoelectron rate of ~10 kHz. For many experiments, the single photoelectron rate dominates the event rate. For each event, we assumed that the data would consist of 6 bytes: 2 bytes of pulse height information and a 4-byte timestamp. At 10 kHz, this translates to 60 Kb (kilobytes), or 480 Kb/s (kilobytes per second). For a single detector element, these data rates are achievable for a wireless readout.

Mission Relevance

This project is relevant to DOE's mission in science and would contribute directly to that mission through the development of technology specifically applicable to measurements in high energy physics. On the basis of the results of this R&D project, we developed an all-wireless data acquisition system that could potentially be used to read out detector systems with a large number of channels. The goal was to design a practical, relatively low-cost, and reliable system that reduces the complexity of larger systems. The simplification of the infrastructure by the use of wireless techniques would also benefit detectors requiring increased mobility or decreased mass.

FY 2012 Results and Accomplishments

Prior to FY 2012, we considered different various technologies for wireless data transmission and wireless power transmission. For wireless data transmission, mobile/cellular technologies and wireless local area network technologies were considered. On the wireless power transmission side, optical and radio frequency (RF) techniques were considered. In selecting technologies, our preference was the use of inexpensive, off-the-shelf technologies that could be implemented relatively easily, and that could be considered as a viable implementation for the goals of this project.

Of the many available wireless data transfer technologies, 802.11n offers the highest data throughput and sufficient range for this application. This, combined with the ubiquity of hardware and the relative ease of implementation, made this technology the preferred option. The total data rate of a single-stream 802.11n link is approximately 65 Mb/s (megabytes per second). Based on the above considerations, in FY 2012 we built the demonstrator of the designed system.

Figure 1 shows a block diagram of the wireless demonstrator. The initial system that was built consists of four boards: generation high voltage for the PMT; front-end, including shaping and digitization of the PMT signal; digital board for processing the data and wireless data transmission; and a board for receiving wireless power and generating the different voltages needed by the system. It was designed to connect to a photovoltaic (PV) panel and send data wirelessly by using 802.11n in the 5 GHz band.

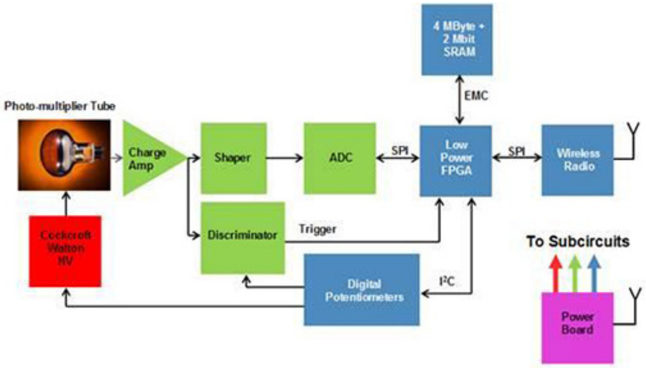


Figure 1. Block diagram of the wireless system.

With respect to the power transfer, we tested both optical and RF power transfer methods. The optical demonstrator that we built utilizes a high-power light-emitting diode (LED) that is collimated into an 8-in.-diameter beam and is received by a PV panel, as shown in Figure 2. The LED used is an OSRAM SFH4751 3.5-W optical output at 1 A input current to the LED. The LED wavelength is 940 nm, which matches the peak efficiency of the Delsolar 156 × 156-mm^2 PV cell used in the 312 × 280-mm^2 receiving solar panel. The complete detector system with PMT and electronics boards is shown in Figure 2. The LED with a collimator lens is not shown in the figure. In the tests performed, the distance between the PV and the detector was five meters.

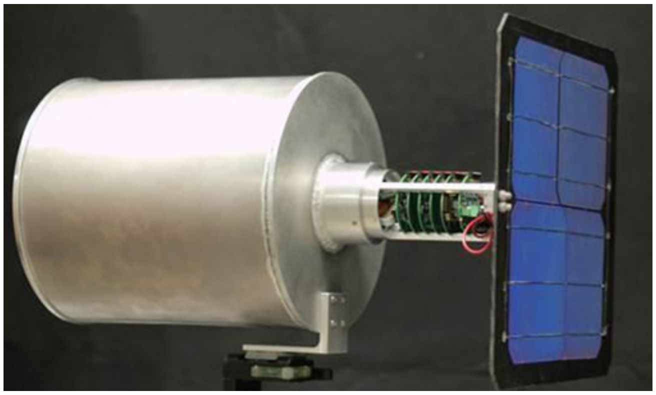


Figure 2. The completed detector system, with light-tight PMT enclosure and PV panel attached to a tripod (electronic enclosure open for reference.)

Ultra-Small Nanoparticles: A New Opportunity for Discovery of Catalytic Materials for Energy

2011-193-R1

Stefan Vajda, Larry Curtiss, Jeffrey Greeley, Michael J. Pellin, Subramanian Sankaranarayanan, and Randall Winans

Project Description

The goal of this project is to identify new catalytic materials in the intriguing, but not yet explored, 1–3-nm size regime by developing controlled assembly strategies that inherently combine the advantage of the high activity and selectivity of sub-nanometer building blocks. The primary challenges that must be overcome to meet this goal include (1) developing a full understanding through theory and experiment of the novel catalytic properties of ultra-small nanoparticles $(A_n)_m$ created from small clusters A_n, (2) determining the treatment conditions to control the assembly process for the formation of desired two- and three-dimensional ultra-small architectures, and (3) designing and testing ultra-small nanoparticles (USNP) with powerful new catalytic properties.

Mission Relevance

This project is relevant to DOE's missions in basic science and energy. Catalysis has clearly reemerged as a centerpiece in DOE-supported research, and it is anticipated that such research could meet the need for the production of classical fuels from resources that are available now but are not yet used, as well as the development of future alternative fuels and new materials for energy storage.

FY 2012 Results and Accomplishments

In the prior years, we performed experiments demonstrating that the final size and shape of the Ag aggregates could be controlled in the 1–3-nm size range as a result of choosing the initial size clusters (such as Ag_3 and $Ag_{15–19}$) and using various supports (alumina, ultrananocrystalline diamond [UNCD]). In the case of Co_{27} clusters supported on MgO, highly reactive 2–3-nm size nanoassemblies were formed, while their shape and catalytic performance varied under oxygen rich and oxygen poor conditions.

Using density functional theory (DFT), we studied O_2 dissociation and propylene epoxidation on catalytic sites of slightly larger Ag aggregates, Ag_{19} and Ag_{20} (in comparison with Ag_3 studied earlier), to investigate how size and spin of sub-nanometer aggregates affect their catalytic activities. We calculated O_2 dissociation on two representative sites of the most stable supported Ag_{19} — a site on top of the supported Ag aggregate away from the support, referred to as the “top site,” and a site on the interface of the Ag cluster and the alumina support, referred to as the “interfacial site.”

First, the energy profile for the O_2 dissociation reaction on the top site was calculated. The top site on a pentagonal pyramidal facet is very similar to that of the gas-phase Ag_{19}. The calculated reaction energy of −0.95 eV on the top site is noticeably lower (more exothermic) than on the gas-phase site; however, the reaction barrier of 0.46 eV is comparable to that of the gas-phase site. These results indicate that the support does not affect the barriers of O_2 dissociation on the Ag sites away from the support. Calculations suggest that the O_2 dissociation occurs preferentially on the interfacial sites rather than sites on the silver aggregate. We assume that after O_2 dissociation, oxygen migration to other sites involves a small barrier, as on a gas-phase cluster, where the two oxygen atoms most likely stay apart, as shown in Figure 1a, since these configurations are lowest in energy.

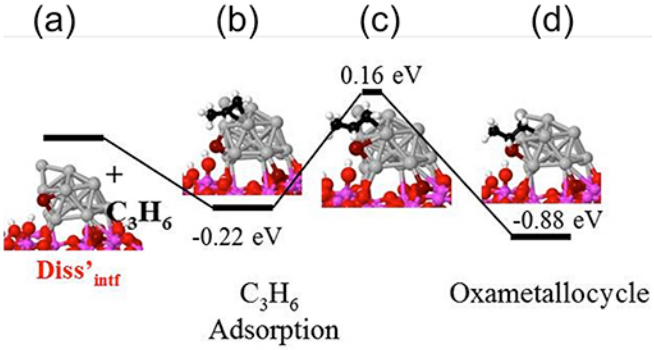


Figure 1. (a) Potential energy surface for propylene epoxidation on a Ag_{19} cluster supported on hydroxylated alumina surface: Dissociated oxygen bond to Ag_{19} cluster–$Ag_{19}O$ and gas-phase propylene, C_3H_6; (b) propylene adsorbed on $Ag_{19}O$; (c) barrier for formation of the reaction intermediate oxametallocycle; (d) and formed oxametallocycle. Silver atoms are shown in grey, oxygen in red, aluminum in pink, hydrogen in white, and carbon in black. Energies are relative to the initial state shown in (a).

Next, the initial steps were calculated for propylene epoxidation reaction by the oxygen on the supported Ag_{19}, and the reaction energy pathways are shown in Figure 1. The barrier for formation of the oxametallocycle is similar to that for the unsupported cluster. The lower barrier for oxygen activation at the interface between the silver USNP and alumina support and, subsequently, higher reactivity of alumina-supported catalysts in comparison with ultrananocrystalline diamond (UNCD) is in excellent agreement with the experimental observations performed on alumina- and UNCD-supported USNPs.

We also studied the effect of the amount of deposited silver trimer (Ag_3) clusters and the composition of the ambient gas on the size and shape of the silver USNPs. By increasing the metal loading, the general trend observed from *in situ* experiments was the formation of larger USNPs, while the presence of water vapor additive also affected the shape of the particles.

Proposed Work for FY 2013

Proposed work for FY 2013 includes the following:

- Complete studies of catalytic activity and selectivity of silver USNPs for oxygen addition as a function of aggregate size and presence of additives, such as water.
- Expand studies into the formation and chemistry of bimetallic USNPs.

Seminars

Lee, S. (2011). “Small Angle X-ray Scattering Characterization of Nanostructured Catalysts.” Advanced Photon Source: User Meeting, Argonne, IL, May 7–9, 2011.

Vajda, S. (2012). “Subnanometer and Nanometer Scale Materials: From Isolated Clusters to Cluster-Assembled Catalyst and their Properties.” Center for Interdisciplinary Nanoscience (CINaM) at University Marseille, Marseille, France, September 18, 2012.

Vajda, S. (2012). “In Situ Studies of Catalyst Designed at the Subnanometer to Nanometer: The Role of the Evolution of Particle Morphology and Oxidation State for Catalyst Performance.” European Synchrotron Research Facility (ESRF), Grenoble, France, September 15, 2012.

Vajda, S. (2012). “Catalyst Designed at the Sub-nanometer to Nanometer Scale: Size, Composition and Support Effects.” Interdisciplinary Center for Materials and Interfaces (CIMAINA), University of Milan, Italy, September 10, 2012.

Vajda, S. (2012). “Well-Defined sub-nm to nm Size Clusters in Dehydrogenation and Partial Oxidation Reactions: Cluster Size, Composition, Oxidation State, Morphology and Assembly Effects on Performance.” Leibniz Institute for Catalysis, Rostock, Germany, June 28, 2012.

Vajda, S. (2012). “(Sub)nanometer Clusters and Cluster-Assembled Materials: Composition and Catalytic Properties.” University of Southern California, Los Angeles, CA, April 9, 2012.

Vajda, S. (2012). “Catalytic Properties of Sub-Nanometer Size-Selected Clusters and their Assemblies.” University Palackeho Olomouc and Regional Nanocenter, Olomouc, Czech Republic, March 16, 2012.

Vajda, S. (2012). “Sub-nanometer Clusters as Building Blocks for (Multi)functional Nanoalloys.” Dalian Institute for Chemical Physics, Dalian, China, November 23, 2011.

Vajda, S. (2012). “Catalysis by Small Clusters and Nanoparticles: Bridging the Size Gap and Interconnecting Studies of Model and Practical Catalysts.” Shell Oil Co. Shell Projects and Technology (US), Houston, Texas, November 1, 2011.

Vajda, S. (2011). “Catalysis by Small Clusters and Nanoparticles.” INEOS, Naperville, IL, February 15, 2011.

Vajda, S. (2011). “Catalysis by Small Clusters and Nanoparticles.” Penn State University, State College, PA, January 20, 2011.

Vajda, S. (2011). “Catalysis by Small Clusters and Nanoparticles Under Realistic Reaction Conditions: I. Bridging the Subnanometer to Nanometer Size Range and II. Coupling the Studies of Model and Practical Catalysts.” Department of Chemical Engineering Colloquium, Universität Rostock, Germany, December 15, 2010.

Vajda, S. (2011). “Catalysis by Small Clusters and Nanoparticles.” Technische Universität, Munchen, Germany, December 13, 2010.

Vajda, S. (2011). “Catalysts Designed at the Subnanometer to the Nanometer Scale for Bond-selective Reactions: Bridging the Size Gap and Coupling Studies of Model, and Practical Catalysts.” Karlsruhe Inst. Tech. and Universität Karlsruhe, Karlsruhe, Germany, December 3, 2010.

Winans, R.E., S. Lee, B. Lee, S. Seifert, S. Vajda, L. Curtiss, J. Elam and M.J. Pellin (2011). “In-situ Studies of Nano Catalytic Reactions Using X-ray Techniques.” CNM/APS Workshop: Chemically Synthesized Nanoparticles for Catalysis, Argonne National Laboratory, IL, May 2–5, 2011.

New High Energy Rechargeable Li Batteries Based on Selenium and Selenium-Sulfur Composite (Se_xS_y) Electrodes

2012-012-N0

Ali Abouimrane and Khalil Amine

Project Description

The project objective is to develop novel cathode materials for high-energy-density rechargeable lithium batteries, with the utmost goal being an advanced energy storage system with high energy density that is low cost and very safe. Such batteries are essential for electric vehicles and plug-in hybrid electric vehicles. Their development requires breakthroughs in novel electrode materials, since the capacities of current commercial batteries — typically 120–160 mAh/g — are far below the demand of this application. In terms of high-energy-density batteries, Li/S and Li/O_2 batteries are attractive because they have the potential to provide 2–5 times the energy density of the lithium-ion batteries now on the market. However, they all have some limitations, such as poor cycle performance, large cell polarization, or low conductivity of sulfur (S). This project explores the potential of selenium (Se), a d-electron-containing member of group 16 with higher electrical conductivity than S, as an electrode material for rechargeable batteries. It focuses on conducting electrochemical performance testing of a series of new Se-containing materials and on understanding the mechanism of their electrochemical behavior through a high-energy x-ray scattering technique (pair distribution function [PDF]), *in situ* battery x-ray diffraction (XRD), and x-ray absorption spectroscopy (XAS).

Mission Relevance

This project is relevant to DOE’s missions in energy security and fundamental science. The signs of a potential new energy crisis have been warning us that our nation must develop alternative energy sources that can decrease our overwhelming dependence on fossil fuels. Energy storage is a key challenge that must be addressed to allow the use of efficient renewable energy applications. This project focuses on developing new energy storage materials with high energy density, which are necessary for electric vehicles and large-scale smart grid applications. In addition, a fundamental objective of this work is to understand the electrochemical processes of batteries and improve battery performance.

FY 2012 Results and Accomplishments

In FY 2012, Se and carbon (C) composites were successfully tested as cathode materials for Li batteries at room temperature and 55°C. Unlike the widely studied Li/S system, Li/Se batteries can be cycled to high voltages (up to 4.6 V) without failure. Extension of the cycling potential up to 4.6 V did not adversely affect the electrochemical performance of Li/Se-C, which sustains a capacity of 280 mAh/g over 80 cycles (100 mA/g, ~C/6: full charge or discharge in 6 hours, Figure 1). An important result is that this feature allows for the use of high potential windows, as opposed to the case for Li/S, in which charging beyond 3.6 V disables any further cycling. Because of their high densities and voltage output, these batteries offer greater volumetric energy densities than S-based batteries, which opens possibilities for new energy storage systems that will enable electric vehicles and smart grids.

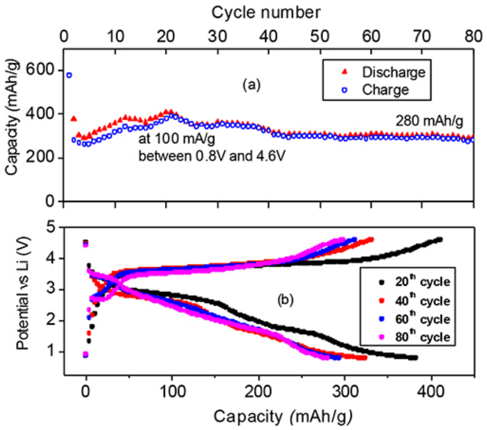


Figure 1. The cycling stability (a) and charge (rising)/discharge (falling) voltage profile curves (b) of Li/Se-C between 0.8 V and 4.6 V (100 mA/g current density).

The structural mechanisms for Li insertion in these electrodes were investigated by using PDF analysis. PDFs of the pristine and recovered Li/Se-C materials are shown in Figure 2. Refinement of a structure against the data obtained for pristine Se confirmed the trigonal structure, with chains of Se atoms linked by Se-Se bonds of 2.36 Å. Fittings to the data of the fully discharged material suggest the formation of an anti-fluorite-type Li_2Se phase. At intermediate points in the discharge (2 V, ~240 mAh/g), both Li_2Se and Se are present, in agreement with the occurrence of a single, first-order phase transition.

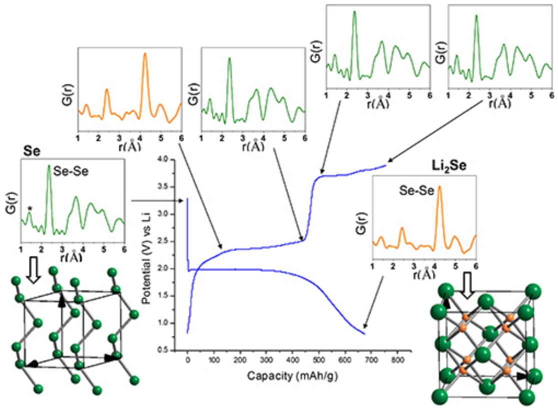


Figure 2. PDFs for the pristine Se-C electrode and for one upon recovery from various states of discharge/charge showing atom-atom distances. Structural representations of the Se and A_2Se (anti-fluorite) phases are shown.

In addition, preliminary investigation of the mixed chalcogenide system, SeS_2 and carbon composite, demonstrates that Se_xS_y-based electrodes can offer higher theoretical capacities than Se alone. In the current drive to discover and optimize materials for electrochemical energy storage, this new class of Se-containing materials offers a new, promising opportunity to enable using high-energy batteries for transportation and grid applications.

Proposed Work for FY 2013

For FY 2013, we will investigate other Se-containing materials, the objective being to further improve their specific capacity and optimize their cycle performance (by changing the electrolyte, altering the composite material treatment process, for example). Another important part of the work will be to perform characterizations to clarify the mechanism underneath through *in situ* battery XRD and XAS.

Developing New Ce-Based, High-Efficiency Light-Conversion Phosphors

2012-052-N0

Guokui Liu and Suntharalingam Skanthakumar

Project Description

Among the five rare earth minerals identified by DOE as of the greatest importance and at highest risk of inadequate supply, europium (Eu) and terbium (Tb) are mostly used in phosphors for lighting and display devices, whereas yttrium (Y) is used for phosphor hosts and in alloys and catalysts. We plan to develop a new series of cerium (Ce) -based photoluminescence phosphors without Eu, Tb, and Y for luminescent lamps and solid-state lighting devices.

To replace Eu and Tb as luminescent centers, Ce has two advantages for making better phosphors for photoluminescence purposes. First, the Ce^{3+} $5d^1$ energy levels are strongly dependent on the host material, and thus the Ce^{3+} emission arising from the 5d-4f electronic transition could be controlled in a wide spectral range from blue to red via the selection of lattice compositions. Doping Ce^{3+} into two different host materials is sufficient to substitute the current commercial tri-phosphors activated respectively by Eu^{2+} (blue), Tb^{3+} (green), and Eu^{3+} (red). Second, the $4f^1$-$5d^1$ transition in Ce^{3+} is parity-allowed, and the $4f^6$-$4f^6$ ($4f^8$-$4f^8$) transitions in Eu^{3+} (Tb^{3+}) are parity-forbidden. Therefore, the efficiency of a Ce^{3+} activated phosphor is expected to be much higher than that activated by Eu^{3+} and Tb^{3+}.

This project focuses on the synthesis of phosphors that are either capable of emitting fluorescence in the entire visible region or emitting light in green-red after absorption of light in the blue region. Using solid-state reaction methods with necessary modifications, we plan to synthesize and characterize a series of Ce^{3+} activated phosphors, including silicate garnets and nitrides with modified compositions. For instance, through variation of compositions in a general formula of $Ce_xCa_{3-x}Mg_ySc_{2-y}Si_3O_{12}$, we expect to obtain photoluminescence from 480 to 680 nm to meet color-rendering requirements for white light or color displays. These materials have crystalline structures in micrometer sizes. Efficiency of the phosphors will be enhanced through systematic optimizations of host compositions, Ce concentration, lattice structure, and synthesis conditions.

Mission Relevance

The proposed work is in line with DOE's energy technology programs sponsored by Advanced Research Projects Agency-Energy (ARPA-E) and the Office of Energy Efficiency & Renewable Energy (EERE), specifically on energy-efficient luminescent materials for solid-state lighting devices. Advances in design, synthesis, characterization, and theoretical analysis and modeling of phosphor materials for optical applications will benefit materials and technology developments for efficient use of energy.

FY 2012 Results and Accomplishments

During FY 2012, we sought host materials for Ce^{3+} to meet the spectral criteria of phosphors for creating white light, which includes synthesis and spectral and structure characterization.

A series of Ce phosphors, including $(Ca_{1-x}Mn_x)_2(Gd_{1-y}Ce_y)_8(SiO_4)_6O_2$, $Ca_{3(1-x)}Ce_{3x}Sc_{2(1-y)}Mg_{2y}Si_3O_{12}$, and $Mn^{4+, 2+}$ doped in $CaAl_{12}O_{19}$, were synthesized by using a modified solid-state reaction method in which precursors were made using a gel-combustion method. Precursors of the Ce-activated phosphors were annealed at different temperatures between 700 and 1,200^{o}C and under either carbon or N_2 (97%) + H_2 (3%) conditions.

Application of a gel-combustion method for making precursors was effective for obtaining much higher luminescence efficiency than from the phosphors synthesized by using conventional fusion of the oxides. Photoluminescence properties and crystalline structures were characterized to identify optimized compositions and luminescence centers that meet the criteria of phosphors to convert ultraviolet (UV) emission to white light.

The photoluminescence of $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ (CSS:Ce) is similar to that of $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) currently used in white light-emitting diodes (LEDs), except for a blue shift of the emission band about 10 nm. Under UV (300–370 nm) excitation, Ce^{3+} in $Ca_2Gd_8(SiO_4)_6O_2$ emits a broad band stretching from purple-blue (390 nm) to yellow (580 nm), and in $Ca_3Sc_2Si_3O_{12}$, Ce^{3+} emits from green (470 nm) to red (650 nm). The broad spectrum of Ce^{3+} in $Ca_2Gd_8(SiO_4)_6O_2$ consists of two bands; one peaked at 409 nm and another at 470 nm. Our x-ray diffraction results indicate that there is only one crystallographic phase in $Ca_2Gd_8(SiO_4)_6O_2$ doped with Ce^{3+} and Mn^{2+}. The two emission bands in 409 nm (blue) and 470 nm (green) are due to Ce^{3+} at two different sites, which increases the overall luminescence bandwidth to meet the spectral requirements. However, as shown in Figure 1, for generation of warm white light with correlated color temperature (CCT) below 4,000 K, both spectra are deficient in the red component. Co-doping of magnesium (Mn) with Ce was considered, along with composition modification for enhancing emission in red.

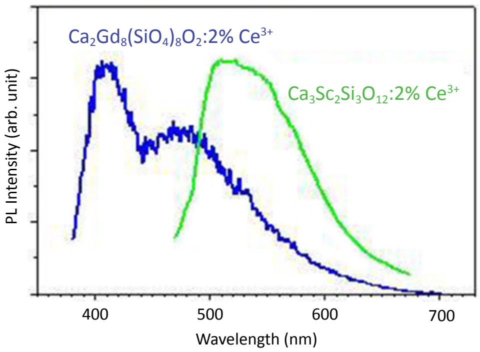


Figure 1. Photoluminescence spectra of $Ca_2Gd_8(SiO_4)_6O_2:Ce^{3+}$ and $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$. The blue emission spectrum was obtained with a pulsed laser; the green spectrum was excited by a continuous laser operating at 450 nm.

Significant progress was made in expanding the Ce^{3+} luminescence bands to obtain white light emission. Luminescence emission covering the entire visible region was obtained through systematic host variation or co-doping of Mn^{2+} and Ce^{3+}. Mn^{2+} substitutes Ca^{2+} very well in $Ca_2Gd_8(SiO_4)_6O_2$ and emits a broad red band centered at 590 nm and stretches to 700 nm. By co-doping of Ce^{3+} and Mn^{2+} in $Ca_2Gd_8(SiO_4)_6O_2$, we obtained an emission band continuously covering the entire visible region. As shown in Figure 2, in comparison with the emission spectra of General Electric's (GE's) triphosphors and a commercial white LED (using YAG:Ce phosphor to convert blue LED emission to yellow and red light), the emission spectrum of $Ca_{1.8}Mn_{0.2}Gd_{7.2}Ce_{0{\cdot}8}(SiO_4)_6O_2$ has much better spectral properties for creating high-quality white light with a color rendering index (CRI) greater than 90. CCT is tunable by controlling the Mn^{2+} doping.

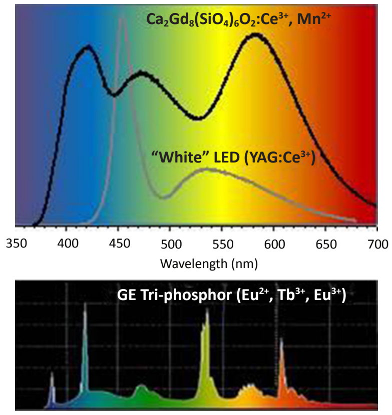


Figure 2. Photoluminescence spectrum of $Ca_2Gd_8(SiO_4)_6O_2$ co-doped with Ce^{3+} and Mn^{2+} compared with commercial white light LED and GE's triphosphor.

By using energy- and time-resolved and laser-induced luminescence measurements shown in Figure 3, we revealed the spectral contribution and luminescence dynamics of Ce^{3+} and Mn^{2+}, respectively. The red emission contributed by Mn^{2+} compensates very well the Ce^{3+} spectrum in the red region for creating warm white light. Because the decay time of the Ce^{3+} fluorescence is short (42 ns) and exhibits a single exponential behavior, as shown in Figure 3 (b), there is no evidence suggesting that the excitation of Mn^{2+} occurred through energy transfer from Ce^{3+}, which indicates that co-doping of Mn^{2+} does not sacrifice the quantum efficiency of Ce^{3+} emission. These results indicate that this system could be an ideal candidate for lamp phosphor without the rare earth elements of Eu, Tb, and Y. Further investigation of this photosystem, including excitation and energy efficiency measurements, are under way.

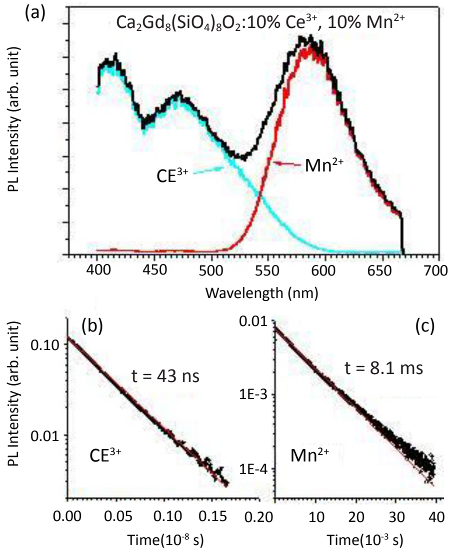


Figure 3. Emission spectra and luminescence temporal dynamics for Ce^{3+} and Mn^{2+} co-doped in $Ca_2Gd_8(SiO_4)_6O_2$. (a) The full profile of photoluminescence spectrum and the emission spectra of Ce^{3+} and Mn^{2+} obtained, respectively, by using gated photodetectors with different time delays after pulsed laser excitation at 355 nm. (b) Luminescence (410 nm) decay of Ce^{3+} emission. (c) Luminescence (520 nm) decay of Mn^{2+} emission in $Ca_2Gd_8(SiO_4)_6O_2$. Both decay curves are fit by a single exponential decay function (plotted in red).

We observed that the photoluminescence spectrum of CSS:Ce^{3+} is sensitive to variation of the host composition. By replacing a fraction of trivalent Sc^{3+} ions in $Ca_3Sc_2Si_3O_{12}$:Ce^{3+} with divalent Mg^{2+} ions, an intense emission band centered at ~400 nm appeared, whereas the Ce^{3+} emission band between 450 and 650 nm diminished significantly. In Figure 4, the emission spectrum was recorded as a function of the ratio between the concentration of magnesium (Mg) and Sc in $Ca_{2.82}Ce_{0.18}Sc_{2(1-x)}Mg_{2x}Si_3O_{12}$, with x varied from 0 to 0.6. It is known that the emission band between 450 and 650 nm is from Ce^{3+} in the phase of CSS. Thus, the new band centered at 400 nm is attributed to Ce^{3+} at a different phase formed by adding Mg in the composition. X-ray diffraction spectra shown in Figure 5 confirm the structure changes. Figure 5 (A) shows a CSS structure of little impurity structures, while the increase of Mg in the compound leads to the formation of impurity phases. The characteristic lines of the CSS structure reduce in intensity, and new lines that belong to a different phase(s) emerge as the concentration of Mg^{2+} increases. Structure analysis is currently being performed to identify the new phase(s) and to reveal the specific phase in which the Ce^{3+} ion emits in the purple-blue region. Compared with the spectrum of white LED shown in Figure 2, the spectrum of x = 0.1 shown in Figure 4 has the spectral profile and CRI similar to that of the commercial white light LED. By fine-tuning the ratio between the Sc and Mg ions, an optimized composition of $Ca_{3(1-x)}Ce_{3x}Sc_{2(1-y)}Mg_{2y}Si_3O_{12}$ will be achieved to convert UV light into the emission with the desired CRI and CCT properties for targeted applications. To develop a white phosphor with optimized composition to meet spectral and efficiency requirements, our current work also includes modification of the primary lattice of CSS with other cations such as La^{3+}, and co-doping of Ce^{3+} and Mn^{2+} in the same host matrix.

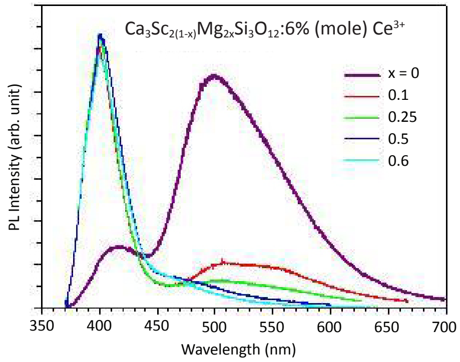


Figure 4. Spectral variation induced by composition modification. In $Ca_3Sc_{2(1-x)}Mg_{2x}Si_3O_{12}$, Ce^{3+} occupies two different lattice sites; one emits light of a purple-blue color and another emits green-red. The ratio of intensities of the two photoluminescence bands can be changed by replacing Sc with Mg.

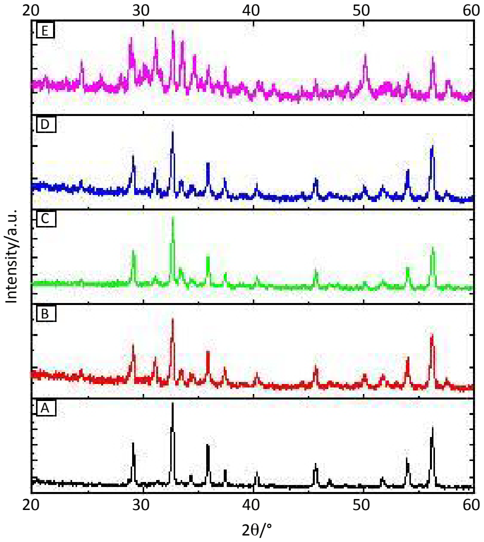


*Figure 5. X-ray diffraction spectra of $Ca_3Sc_{2(1x)}Mg_{2x}Si_3O_{12}$ indicate that in addition to the intrinsic crystalline lattice of CSS (marked with * in the plot), new phases are formed as the fraction of Mg is increased: (A) x = 0.1, (B) x = 0.25, (C) x = 0.4, (D) x = 0.5, (E) x = 0.6. All samples were annealed at 1,100°C in a 96.5% N_2 and 3.5% H environment for 3 hours.*

In seeking phosphor compounds in which co-doping of Ce and Mn were stabilized for white light emission, we realized that the oxidation state of Mn is sensitive to charge compensation in the host material. Mn^{4+} is stable in $CaAl_{12}O_{19}$:0.5%Mn sintered at 1,500°C for 3 hours in air. Under 450-nm light excitation, only red luminescence was observed, indicating all Mn ions are tetravalent (Mn^{4+}). However, when co-doped with a small amount of trivalent cations, such as La^{3+}, Mn^{4+} can be efficiently converted to Mn^{2+}. As shown in Figure 6, only green emission of Mn^{2+} was observed in $CaAl_{12}O_{19}$:0.5%Mn co-doped with La^{3+} in 3 mole % of Ca^{2+}. This result suggests another direction of controlling photoluminescence colors in potential phosphors.

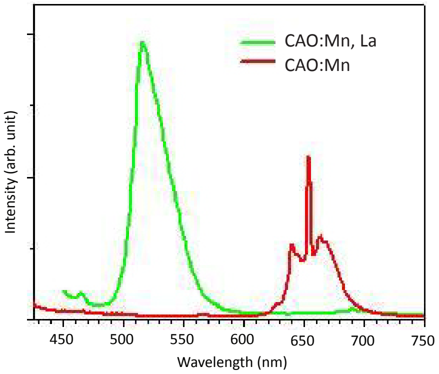


Figure 6. Green and red photoluminescence of $CaAl_{12}O_{19}$ doped, respectively, with Mn, and with Mn and La. In Mn doped material prepared in air, only Mn^{4+} is stabilized, whereas in the co-doped material, Mn^{4+} is converted to Mn^{2+}.

Proposed Work for FY 2013

We will continue our synthesis and characterization effort in identifying potential candidates for light conversion phosphors to meet the spectral and efficiency criteria. A new series of phosphors of nitridesilicates with basic composition of $M_2Si_5N_8$ (M = Ca, Sr, Ba) will be synthesized and characterized. Without any rare earth elements in their composition, this series is more attractive. To stabilize Ce^{3+}, charge compensators such as N^+ will be co-doped.

We will also focus on improving quantum efficiency. After the host materials are selected and optimized for meeting spectral requirements and absorption and emission wavelengths for white light emission, the major work will be improving phosphor efficiency. Efficiency enhancement will be achieved primarily through optimization of Ce^{3+} concentration, co-doping, and synthesis conditions. Luminescence efficiency will be measured with samples treated at various annealing temperatures and in different reducing environments. Phosphor efficiency will be measured in comparison with commercial phosphors activated by Eu and Tb and with the current LED phosphor YAG:Ce.

On the basis of the larger cross section in 4f-5d transitions versus 4f-4f transitions, we expect that the Ce^{3+} activated phosphors developed in the proposed work will have a higher efficiency than that of the current Eu- and Tb-activated phosphors. The target energy efficiency (photo-emission/photo-absorption) is 55–60% for UV excitation and 70–75% for violet (380–420 nm) excitation. The energy efficiency will be measured along with CRI and CCT with a spherical photodetector that measures the absolute photon energy or light intensity.

Charge imbalance in the CSS:Ce series and energy transfer between the Ce^{3+} and Mn^{2+} in the co-doped systems are anticipated obstacles to achieving high efficiency. Thus, they will be studied by using energy- and time-resolved laser spectroscopic methods and Advanced Photon Source facilities to reveal the local environments of the luminescence centers Ce^{3+} and Mn^{2+}. After the required spectral properties and conversion efficiency are achieved, synthesis methods and procedures for controlling materials properties will be optimized for large-scale production.

Development of a Close-Packed $LaBr_3$(Ce) Detector Array for Nuclear Physics Applications

2012-055-N0

Michael P. Carpenter, Michael Albers, Martin Alcorta,
Jun Chen, Filip G. Kondev, Darek Sewernyiak,
and Shaofei Zhu

Project Description

The development of new radiation detectors with properties superior to those of earlier devices has always led to big advances in basic and applied science. The most important progress in γ-ray counting technology has been the development of germanium (Ge)-based solid-state detectors, which have superb energy resolution and ever-increasing efficiency. Unfortunately, their time resolution is relatively poor (>5 nanoseconds) and they need to be kept at liquid nitrogen temperatures, which limits their use in many applications.

The goal of this project is to significantly advance γ-ray detector technology by developing an $LaBr_3$(Ce) detector array that operates at room temperature and combines the best energy resolution achievable by scintillator detectors with superior time resolution. An energy resolution of less than 2.0% and timing performance of about 30 picoseconds (ps) appear to be feasible. High efficiency will result from assembling a matrix of individual $LaBr_3$(Ce) detector modules. We will demonstrate the feasibility of building such an array by developing a module consisting of four $LaBr_3$(Ce) detectors arranged in a 2 × 2 matrix/wall configuration. The key issue is to maintain both the good energy resolution and excellent timing characteristics of this material as development moves from single crystal detectors to a multi-detector array.

Mission Relevance

The project is relevant to DOE's mission in science, although the benefits extend to DOE mission in national security. $LaBr_3$(Ce) detector technology would be the best option for building an advanced photon detector system that will be used in the Facility for Rare Isotope Beams (FRIB), a major location for nuclear physics research in the United States funded by DOE's Office of Nuclear Physics. A compact array of such detectors could be used in conjunction with the national tracking gamma-ray array GRETINA. In addition, applications of this work would interest a variety of private, federal, and international organizations concerned with assay and imaging of radioactive materials and nuclear smuggling. Among them are DOE (environmental remediation, waste management, nuclear nonproliferation), the U.S. Department of Defense (nuclear weapons effects), the U.S. Department of State (treaty verification), the U.S. Customs Service (nuclear smuggling), the International Atomic Energy Agency (nuclear nonproliferation), and the National Institutes of Health (medical imaging).

FY 2012 Results and Accomplishments

We did extensive testing by using two 1 × 1-inch $LaBr_3$(Ce) detectors in FY 2012 and are now preparing to test two 1.5 × 1.5-inch detectors under the same conditions. The tests include measurements taken in the laboratory to document the detector's performance with regard to energy resolution and efficiency and measurements taken by using the pair of detectors in tandem with Ge detectors to investigate timing characteristics. We measured an intrinsic time resolution of about 120 ps and an energy resolution of 2% for a 1-MeV γ-ray. By using these detectors, coupled with Argonne's Gammasphere, we measured the lifetimes of excited nuclear states down to 70 ps. Figure 1 shows the time spectra measured by using the detectors for several specific nuclear states and their deduced lifetimes. Results of these investigations indicate that the detectors will provide both the energy and timing resolution required. The final detector matrix will be made from crystals with dimensions of 1 × 1 × 1.5 inches.

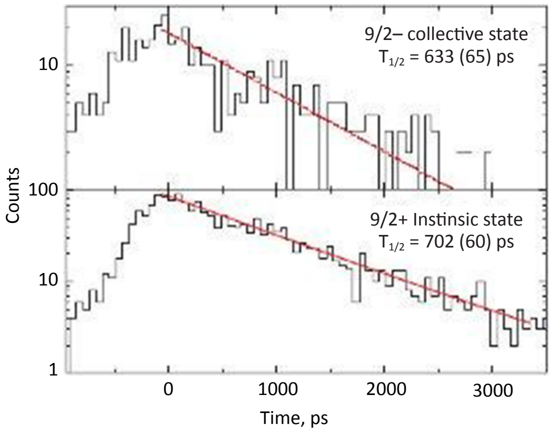


Figure 1. Time spectra determined from time differences taken between transitions before and after the excited state of interest, as measured by the two $LaBr_3$(Ce) detectors.

Proposed Work for FY 2013

We will acquire up to eight $LaBr_3$(Ce) detectors of the appropriate size and geometry, along with associated electronics and photomultiplier tubes, assemble a 2 × 2-inch module by using 1 × 1.5-inch crystals, and conduct a performance evaluation by using radioactive sources and in-beam measurements. Our plan is to utilize a micro channel plate (MCP) phototube commercially available from Planacon. These MCPs provide the timing performance required while maintaining energy resolution. Testing will include evaluating the performance of the crystals when singly attached to the MCP and when attached as a unit of four. Of particular importance is whether any degradation in timing and or energy resolution occurs when incident gamma-rays Compton scatter from one crystal to the next. The timing measurements will utilize a coincident gamma-ray source and a 1.5 × 1.5-inch $LaBr_3$(Ce) crystal coupled to a standard phototube.

Revealing Lithium-Based Battery Performance by *in situ* Characterization

2012-061-N0

Dean Miller

Project Description

The project is designed to improve our understanding of lithium battery operation by bridging the gap between macroscale diagnostics and nanoscale characterization. In particular, this research focuses on the characterization of lithium battery materials from the mesoscopic length scale to the nanoscale under operating conditions. The basic approach is to use *in situ* characterization of microscale and nanoscale batteries in operation to help determine what makes them work and, perhaps more importantly, what makes them stop working.

Mission Relevance

This project directly addresses DOE's mission to transform the nation's energy system — particularly in the area of electric vehicle technology — by promising to elucidate the underlying mechanisms of performance degradation in lithium-based batteries.

FY 2012 Results and Accomplishments

We successfully developed an approach to carry out electrochemical cycling of single Li-ion battery cathode particles that allows simultaneous imaging by scanning electron microscopy (SEM). In the approach, a single cathode oxide particle is attached to a nanomanipulator probe, which is then used to partially immerse the particle in a droplet of electrolyte covering an anode to form the microscale battery (Figure 1). Electrical attachments to the manipulator probe and the sample stage are connected to a potentiostat to complete the circuit and cycle the battery.

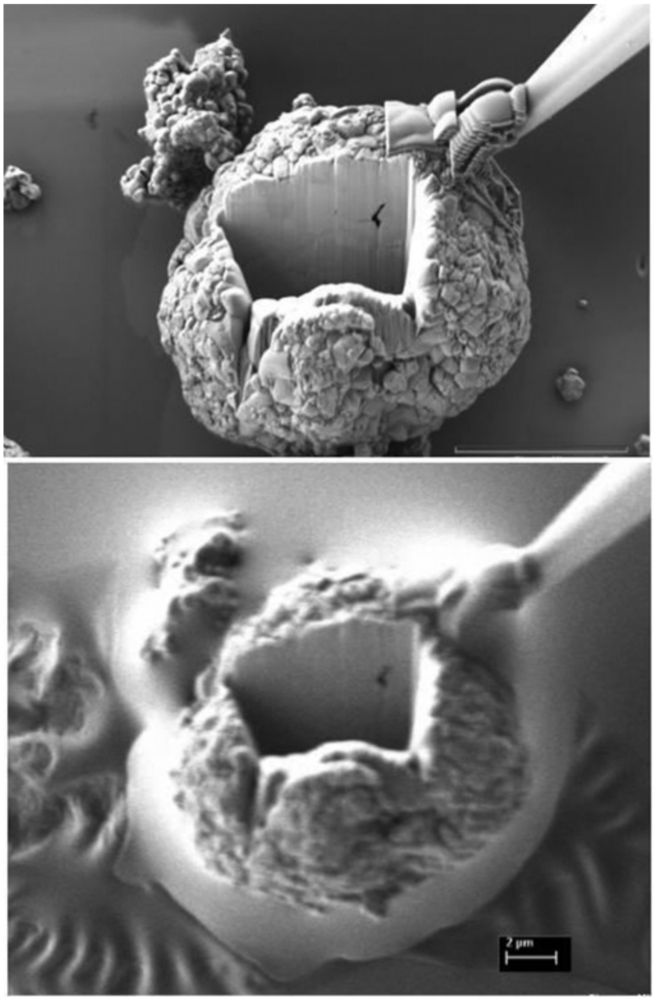


Figure 1. (Top) A $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particle attached to a probe. (Bottom) The same particle partially immersed in electrolyte ready for in situ *cycling.*

The type of information that has come out of these studies is illustrated in Figure 2, which shows a series of frames extracted from a video sequence captured live during electrochemical cycling. The two important features revealed by dynamic *in situ* imaging are the early onset of particle cracking and electrolyte penetration all the way into the interior of the particle. The role of electrolyte penetration into cathode particles has been debated, and this experiment clearly reveals this phenomenon can take place. Less well-illustrated in this series of still images — but clearly revealed in the video — is the step-like growth of fractures, indicating this is an elastically driven crack propagation rather than a chemical effect. This is an important observation. Previous studies had not clearly established intraparticle fracture in the early stages of electrochemical cycling. Some suggest chemical dissolution is the key parameter, but our studies in this work refute that hypothesis.

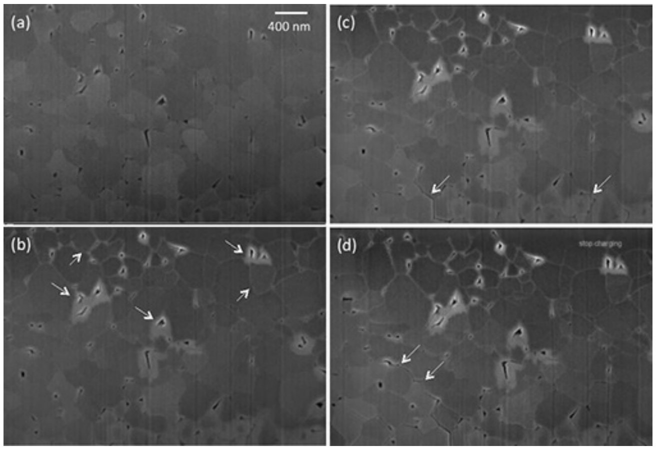


Figure 2. Series of still images from a live video collected during the first charge of an $Li(Ni,Co,Al)O_2$ particle. (a) The polished surface within a single particle in the as-prepared condition. (b) Surface about one-third of the way through, (c) about two- thirds of the way through, and (d) at the end of the charge cycle. Cracking and electrolyte penetration into the interior of the particle are indicated by the regions to which the arrows are pointing.

Examination of particles harvested from coin cells that were subjected to cycling confirm that this process also takes place in macroscale, practical batteries. Together, the observations suggest a mechanism for performance degradation based on the electrical isolation of grains within the cathode particles based on cracking. While grains in contact with the conducting binder medium may still contribute to battery performance, isolated grains within the interior of the particle may no longer contribute to capacity as a result of loss of electrical connectivity, despite enhanced ionic pathways due to electrolyte penetration into the grain.

It is commonly suggested that the loss of the mobile Li inventory is the dominant factor in the loss of capacity upon cycling for practical transition metal-oxide cathode Li-ion batteries. While it is very likely such a mechanism contributes to capacity loss in the case of $Li(Ni,Co,Al)O_2$-type materials, this work suggests other mechanisms may play an important role.

Proposed Work for FY 2013

Our work in FY 2013 will focus on developing a transmission electron microscopy (TEM) -based *in situ* capability to complement our SEM-level work. The TEM-based capability will allow *in situ* studies of single grains and nanoscale structural phenomena. Many processes that take place during battery cycling produce subtle changes in local structure and chemistry, and TEM-scale studies can provide critical insights into these processes. Overall, the combination of SEM- and TEM-based *in situ* approaches will allow us to link battery performance to structure from the macroscale to the nanoscale.

Graphene-Enabled Superlubricity: Vanishing Friction and Wear in Static and Sliding Contacts

2012-072-N0

Anirudha V. Sumant and Ali Erdemir

Project Description

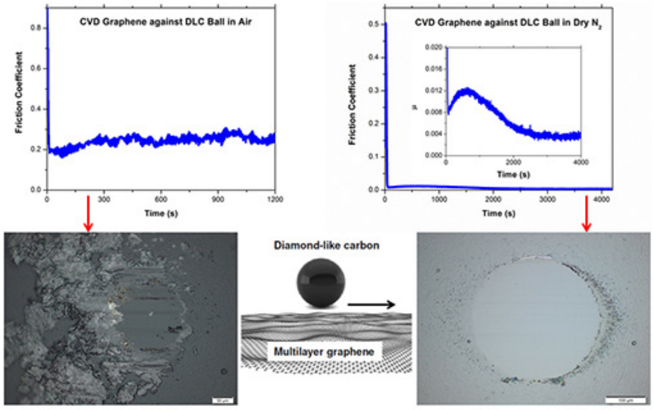
The main objective of this project is to understand the origin of the superlubric behavior of graphene, which our team recently discovered while conducting tribological studies on multilayer graphene films at the macro scale. This superlubricity, which we saw for the first time when graphene slid against diamond-like carbon (DLC) surfaces at macro scale at room temperature, is important from both scientific and technological points of view. This project involves systematic tribological studies from macro to micro to nano scales in which various material pairs are compared in controlled atmospheric conditions. We will use advanced surface characterization techniques to make detailed characterizations of the wear tracks in order to understand the surface chemistry of graphene.

Mission Relevance

This project is relevant to DOE's goal to find innovative ways to reduce energy consumption through fundamental research on materials. The total energy consumed in the United States and in Europe by industrial motor-driven systems (e.g., pumps, compressors, fans) is about 1.36 trillion kWh/year. It is estimated that these systems lose about 15% or 204 billion kWh/year as a result of motor inefficiency. About 20% of this loss, or ~41 billion kWh/year, is due to mechanical losses, and of this, roughly 20% or 8.2 billion kWh/year can be attributed to bearings. Assuming a conservative approach, a minimum reduction in energy loss of 30% due to the low friction offered by new materials would yield a potential energy savings of 2.46 billion kWh/year; this is equivalent to 420,000 barrels of oil. These numbers make it obvious that research to discover new materials that could reduce wear and friction is important. If such research was fully developed and demonstrated, it could have huge positive impacts on many mechanical and tribological applications that could lead to tremendous savings on energy.

FY 2012 Results and Accomplishments

We studied macro-scale tribological properties of different carbon-based tribo-pairs under different ambient conditions. We generated a comprehensive database by carrying out systematic wear/friction tests under various atmospheric conditions (air, dry nitrogen [N_2], hydrogen, in vacuum) with different tribo-pairs of interest. The tribo-pair tests included graphene versus graphene, graphene versus DLC, and graphene versus nickel (Ni). A comparison of the coefficient of friction (COF) and corresponding wear produced on the DLC-coated balls for the tests carried out in air and in a dry N_2 environment is shown in Figure 1. The tests demonstrated an extraordinarily low COF (0.003) and showed a significant reduction in wear for dry N_2. The fact that multilayer graphene, which is just few nanometers thick, can provide such low friction for a prolonged time (more than 5,000 cycles) with negligible wear is a groundbreaking result that establishes it as a new solid lubricant material that could be used in a number of tribological applications.



High wear debris on DLC-coated ball running against graphene

Less wear debris on DLC-coated ball running against graphene

Figure 1. Friction and wear behavior of graphene sliding against a DLC ball in air and in a dry N_2 environment, with corresponding images of the wear scar produced on the DLC ball.

A common thread in all the cases mentioned was the fact that the graphene was synthesized by using a thermal chemical vapor deposition (CVD) process, which was generally carried out at 950°C. We replaced the CVD graphene by solution-processed graphene (SPG), which was obtained by chemical exfoliation of the highly oriented pyrolytic graphite (HOPG). We repeated tribological studies on Ni substrates coated with SPG versus DLC-coated balls and observed a similar trend, demonstrating superlubric behavior under identical test conditions (i.e., typical COF = 0.005 in dry N_2).

An analysis of the graphene-coated Ni surface showed that the wear rate was more than two orders of magnitude lower than that of the uncoated Ni surface running against a DLC ball in a dry N_2 environment; this indicated a significant improvement in the wear resistance of the Ni surface with the presence of a graphene layer that was just a few nanometers thick. We applied the same concept in the case of steel against steel and demonstrated a reasonably low COF (0.15–0.2) and low wear when SPG was introduced. We observed that the graphene layer also prevented corrosion and thus reduced the wear rate at sliding contact interfaces. This feature is very important with regard to industrial use of graphene based lubricant and will help in eliminating oil-based lubricants, which produce toxic waste. We studied micro- and nano-scale tribological properties of different surfaces by using the atomic force microscopy (AFM) lateral force measurement technique.

In this case, a DLC-coated AFM tip was raster-scanned over HOPG, CVD-grown graphene, and fused silica surfaces.

Figure 2 shows relative changes in the lateral force experienced by an AFM tip with increasing load. At the nano scale, both HOPG and CVD graphene showed extremely low friction, which demonstrates their potential for developing low-friction surfaces in both microelectromechanical system (MEMS) and nanoelectromechanical system (NEMS) devices.

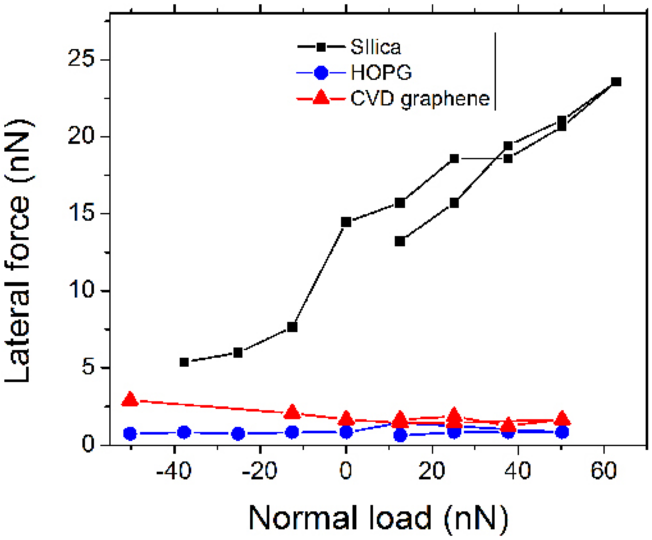


Figure 2. AFM lateral force measurements for DLC-coated tip against silica, HOPG, and CVD-grown graphene.

This work resulted in the following inventions/patents:

- Sumant, A., A. Erdemir, J. Choi, and D. Berman, "Superlubrication Graphene Films," invention report submitted August, 2011, and patent application filed July, 2012. [ANL-IN-11-056].

Proposed Work for FY 2013

To understand the wear mechanism of graphene-enabled superlubricity and the chemical and structural modification of the graphene and counterface surfaces during friction experiments, we will characterize the wear tracks produced on the graphene and counterface materials by using a range of spectroscopic techniques. Surface modifications in the carbon-bonding configuration on the graphene surfaces within the wear tracks will be characterized by Raman spectroscopy (ultraviolet and visible) at Argonne's Center for Nanoscale Materials.

In addition, we will use advanced surface sensitive characterization techniques, such as x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass-spectrometry (TOF-SIMS), to detect elemental and chemical changes that may have occurred in a few atomic layers of graphene and counterface surfaces. Together, both techniques will provide valuable information about the tribochemical modification on graphene surfaces, which is very important for understanding the mechanism of superlubricity. We will use data generated in the first two tasks to develop a comprehensive model by using molecular dynamics simulation and density functional theory.

Rechargeable Nanofluids Technology for Electrical Energy Storage

2012-087-N0

Elena V. Timofeeva and Dileep Singh

Project Description

This revolutionary electrical energy storage concept for transportation combines the best attributes of rechargeable solid-state batteries, flow batteries, and capacitors. It incorporates semi-solid, high-energy-density rechargeable, renewable, and recyclable electrochemical fuel in a flow system that decouples power from stored energy. Estimated high energy density (up to 1100 Wh/L) together with low system costs ($20–80 per kWh) would enable rapid, widespread adoption of electric vehicles.

This technology advances redox flow battery concepts, where energy is stored and released through a reversible electrochemical reaction between two electrolytes (dissolved red/ox active ions). Increasing the volume concentrations of electroactive nanoparticles dramatically increases energy density and allows the use of electroactive compounds with low solvability. The proposed technology has potential to become a liquid electrochemical fuel — an alternative to gasoline — which would further enable adoption of electric vehicles. Nano-sized particles and good electrolyte/nanoparticle contact in nanofluids contribute to fast response times, high charge/discharge efficiency, and extended fuel cycle lifetime. We are collaborating in this work with John P. Katsoudas and Carlo U. Segre from the Illinois Institute of Technology.

Mission Relevance

This project expands the scientific foundations for new and improved energy storage technologies, addressing one of DOE's major mission areas: energy security. Energy density in the proposed nanofluids exceeds the U.S. Advanced Battery Consortium's (USABC's) long-term electric vehicle battery goal of 300 Wh/L (200 Wh/kg), reaching 1100 Wh/L (620 Wh/kg at 60 vol% nanofluid) at a cost of $20–80 per kWh — significantly lower than USABC transportation goal of less than $250 per kWh. Because the technology incorporates electrode materials that are easy to separate from other battery components for disposal and recycling, its advancement may encourage the use of environmentally friendly electrolytes.

FY 2012 Results and Accomplishments

We formulated and tested two types of rechargeable nanofluid systems: (1) water-based graphite nanoparticle suspension (Figure 1) and (2) Li-ion electrolyte based nanofluids with intermetallic anode nanoparticles (Figure 2). We achieved stable suspensions of these nanoparticles in electrolytes by using appropriate surface modifiers that mediate the electron and Li+ ion transfer, while improving the miscibility of nanoparticles with electrolyte.

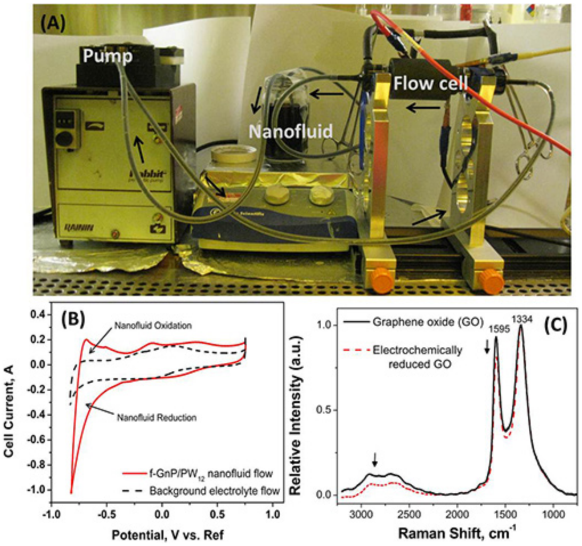


Figure 1. (A) Bench-scale flow cell for testing water-based nanoparticle suspensions in half cell configuration. (B) Cyclic voltammogram shows additional current for reduction/oxidation of nanofluid flow. (C) Raman spectroscopy of nanoparticles before and after electrochemical treatment shows changes in the peak ratio, which indicate partial reduction of graphene oxide to graphene.

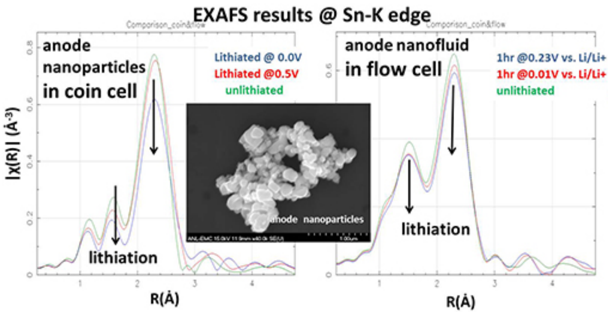


Figure 2. Fourier transformed x-ray adsorption spectra for intermetallic anode nanoparticles show that similar changes to the structure occur when nanoparticles are lithiated in conventional coin cell assembly (left) and in nanofluid flow cell (right). SEM image shows sizes of anode particle of 50–300 nm.

We selected a water-based system for the ease of handling and testing of nanofluids, even though they have low energy density. We are transferring knowledge gained in the water-based system to the Li-ion-based nanofluid with intermetallic nanoparticles being developed in parallel as the actual prospective high-energy-density formulation. We addressed many aspects of flow battery engineering, in particular, developing two flow cell designs, as well as a coin cell and a flow cell for *in situ* x-ray absorption spectroscopy (XAS) experiments. Currently, both of the cells are used for half-cell testing of nanofluid electrodes. Ultimately, we expect to engineer a complete flow battery cell as an enclosure to the "rechargeable fuel" pipeline.

We used a combination of electrochemical testing, Raman spectroscopy, and XAS to obtain electronic and atomic structural information on the materials. *Ex situ* XAS experiments demonstrated that both types of studied nanofluids can be charged/discharged upon passage through the flow cell. *In situ* XAS characterization is under way, which will facilitate comparisons between charging/discharging of the same electrode material in the flow cell and in the solid-state battery assembly. We will use this information to assess the kinetics and completeness of charge/discharge in both forms of batteries and to estimate efficiency. We made significant progress in formulating and electrochemical testing of rechargeable nanofluids, and we are progressing toward the milestone of *in situ* comparison testing of the same electrode material in nanofluid and coin cell battery assemblies by the end of FY 2013.

Proposed Work for FY 2013

We will continue to optimize the suspensions from red/ox active nanoparticle materials, with particular focus on stabilizing agents and optimized nanoparticle sizes for fast charge/discharge process. We are looking into other nanomaterials for anode and cathode nanofluids. Working with other Argonne battery research groups in the Energy Systems and Chemical Science and Engineering divisions, we will test these new nanofluid electrodes in flow battery configuration.

Electrochemical studies of rechargeable nanofluids in suspension electrode configuration will continue, with particular attention paid to optimizing the flow cell design. We plan to compare the electrochemical properties of suspension electrodes to the same electrode nanoparticles in a coin cell configuration and characterize prospective rechargeable nanofluid formulations with *in situ* XAS spectroscopy.

Novel Non-Carbon Catalyst Support for PEMFCs

2012-180-N0

Xiaoping Wang, Spencer Carey, Stacy DeCrane, Nancy Kariuki, David Lane, Jun Lu, Xiangyi Luo, Debbie Myers, and Tammi Nowicki

Project Description

The objective of the project is to develop a new class of durable, non-carbon supports for state-of-the-art platinum (Pt) and Pt-alloy cathode electrocatalysts for polymer electrolyte membrane fuel cells (PEMFCs) that will significantly improve their durability and performance. These new materials, based on transition metal silicides (TMSs), will be much more stable than the carbon blacks used in current PEMFCs. Furthermore, the silicides exhibit electrocatalytic activity, which potentially may lead to synergistic effects for cathode reaction. The scope of the research includes identifying the most stable silicide support candidates, a study of model systems to gain insight into the interaction with the catalyst, synthesis of silicide-supported Pt electrocatalysts with desired characteristics, and characterization of the activity and stability of these materials in simulated fuel cell environments.

Mission Relevance

This project is relevant to DOE's missions in basic science and energy. Improving the durability of PEMFC technology by developing durable catalyst support for PEMFCs is one of the missions of DOE's Fuel Cell Technologies program. Successful development of silicides as the catalyst support will help to meet DOE's target for the automotive application of reaching a degradation level for PEMFC performance of less than 40% over 5,000 hours of operation by 2015.

FY 2012 Results and Accomplishments

Seven TMSs were initially identified as potential candidates on the basis of their published stability and electronic conductivity. The chemical and electrochemical stability of these seven TMSs were further investigated to enable selection of the three best candidates. The chemical stability of the TMSs was determined by exposing the TMSs to 0.5 M sulfuric acid for 50 days, followed by analyzing the acid for dissolved metal and silicon and analyzing the resulting silicide phase structure by using high-energy x-ray diffraction (HE-XRD). The results showed that all of the TMSs experienced a loss of weight of less than 2%. There was minimal change in the phase structure of the TMSs, with the desired disilicide phase being the major phase. These observations indicate that the TMSs will remain stable in the acidic conditions of the PEMFCs. On the basis of these results, we selected the three TMSs with the lowest amounts of weight loss (<0.5%) for further study.

Next, the stability of the as-received and acid-treated TMSs toward potential cycling in the range relevant to PEMFC cathode operation were determined by using cyclic voltammetry. The results showed that acid treatment caused no significant change of the voltammetric features of the TMSs. Three TMSs with the highest electrochemical stability (or the lowest oxidation currents from 0.7 to 1.4 V) were identified, consistent with the chemical stability study.

The oxygen reduction reaction (ORR) activity of the TMSs before and after acid treatment was determined next, as ORR activity is a desired feature for a catalyst support. The results showed that all the TMSs are ORR active, and the activity is not affected by exposure to high potentials (≤1.4 V), as indicated in Figure 1. However, acid treatment significantly lowered their ORR activity, which could be attributed to changes in the surface composition or structure caused by acid treatment.

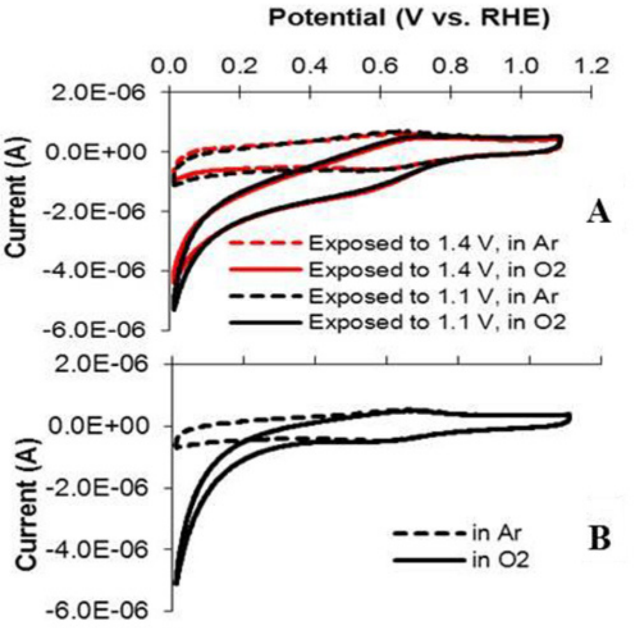


Figure 1. Typical examples of cyclic voltammograms obtained from transition metal silicides in the deaerated and oxygen-saturated 0.1-M sulfuric acid: (A) after exposure to ≤1.4 V, and (B) after acid treatment (B). (Note: RHE = reversible hydrogen electrode.)

Colloidal synthetic methods were used to deposit Pt catalyst nanoparticles on one of the three down-selected TMSs. In one method, Pt nanoparticles capped by nonpolar organic molecules- were synthesized and subsequently supported on the selected silicide. Analysis of the sample by transmission electron microscopy (TEM) showed that uniform Pt particles with a mean diameter of 5 nm were formed. However, the capped-Pt nanoparticles were aggregated into spherical assemblies and were separate from the support, indicating repulsion between the hydrophobic capped-Pt nanoparticles and the hydrophilic silicide surface. In another method, a hydrophilic perfluorosulfonic acid (PFSA) polymer-capping agent was used to facilitate interaction between the Pt nanoparticles and the silicide. TEM analysis showed improved Pt particle dispersion on the silicide by using this synthetic approach; however, the Pt loading was lower than the target (7 wt% vs. 20 wt%) resulting from the weak interaction between the support and the PFSA-capped Pt. Modification of the colloidal synthetic method is under way to enhance the Pt-support interactions.

Proposed Work for FY 2013

In our FY 2013 activities, we will seek to:

1. Improve the colloidal synthetic technique and explore alternative synthetic techniques to prepare silicide-supported Pt nanoparticles at >20 wt%.
2. Synthesize and characterize Pt nanoparticles supported on the other two silicides selected for further study.
3. Optimize the composition, structure, and interfacial interaction between the silicide support and the catalytic metal by using model systems.

4. Conduct x-ray spectroscopies at the APS to monitor the oxidation state and structural changes of the catalyst components and then correlate the findings with the silicide-supported Pt activity.

Curing Cancer with the Power of Fireflies

2012-181-N0

Tijana Rajh, Shankar Balasubramanian, Benjamin Blaiszik, Harry Fry, Matthew Massich, and Chunxing She

Project Description

Photodynamic therapy (PDT) is an emergent technology used for the treatment of cancers, psoriasis, and other autoimmune diseases. In this method, light energy is converted to chemical energy, creating highly reactive oxygen species (ROSs) that, under appropriate conditions, are highly disruptive to the metabolism of (cancer) cells and lead to cell death. However, current PDT technology is limited by its dependence on whether light can reach the treatment area, eliminating potential applications of PDT to treat tumors located in tissue that cannot be easily illuminated. To overcome this limitation, we have linked a light source that will travel alongside the therapy to the intended treatment location. Our approach involves functionalizing semiconducting titanium dioxide (TiO_2) nanoparticles with the light-producing protein *firefly luciferase*. Luciferase yields bioluminescence in the presence of its substrate, luciferin, and the highly energetic molecule adenosine triphosphate (ATP), which has recently been found to be present in a 100-fold excess at tumor sites. The TiO_2-luciferase conjugates will also be functionalized with antibodies that target them to cancerous cells specifically by binding known biomarkers expressed on the surface of cancer cells. The light from the luciferase then activates the semiconductor nanoparticles attached to them and results in efficient ROS production, inducing programmed cell death.

Mission Relevance

This project is relevant to key DOE missions in basic science. We believe that this approach can be regarded as a breakthrough in PDT technology because it eliminates the major limitation of the technology. The advantage of this approach is that it can be used for early detection — and early treatment — of cancers and autoimmune diseases. In addition, light created *in situ* can also be utilized to power a variety of *in vivo* light-driven devices deep in the tissue.

FY 2012 Results and Accomplishments

Our studies of the TiO_2-luciferase conjugates confirmed that the photon-emitting oxidation of luciferin by the enzyme luciferase is indeed able to transfer energy to the TiO_2 nanoparticle when luciferase is conjugated to the particle's surface. This energy transfer was confirmed by using multiple experimental methods. First, electrical current was measured for the TiO_2-luciferase nanoparticle system. The current was monitored before and after the addition of the substrate luciferin. No current was observed in controls lacking luciferin and ATP. Moreover, the current was detected following the addition of the luciferin and ATP in a concentration-dependent manner. Further, the energy transfer was confirmed by measuring the bioluminescence of the luciferase-luciferin reaction: compared with when the luciferase is free in solution, approximately 60% of the light emitted is quenched by the TiO_2 nanoparticles when the luciferase is covalently bound to the particle surface. This finding suggests that the light energy that is quenched when luciferase is conjugated to the TiO_2 nanoparticles is transferred to the particles to subsequently produce ROSs.

The efficient conversion of light energy to chemical energy in the form of ROS production is important because the ROSs induce cell death in cancerous tissue. Our research demonstrated that the TiO_2-luciferase nanoparticles are able to increase ROS levels (indicated by the red fluorescence) and induce cell death (drastic changes in cell morphology) in the A172 glioblastoma cell line (Figure 1). We also demonstrated that ATP can be used as a method of preferentially activating the TiO_2-luciferase conjugates to produce ROS only at the location of a tumor. At below 10-μM concentrations of ATP (i.e., similar to concentrations present in healthy tissue), very little luminescence indicative of ROS formation is emitted, whereas at concentrations of more than 100 μM (i.e., similar to concentrations found in tumors), significant luminescence is observed. These results are also consistent with measurements of current taken at various ATP concentrations.

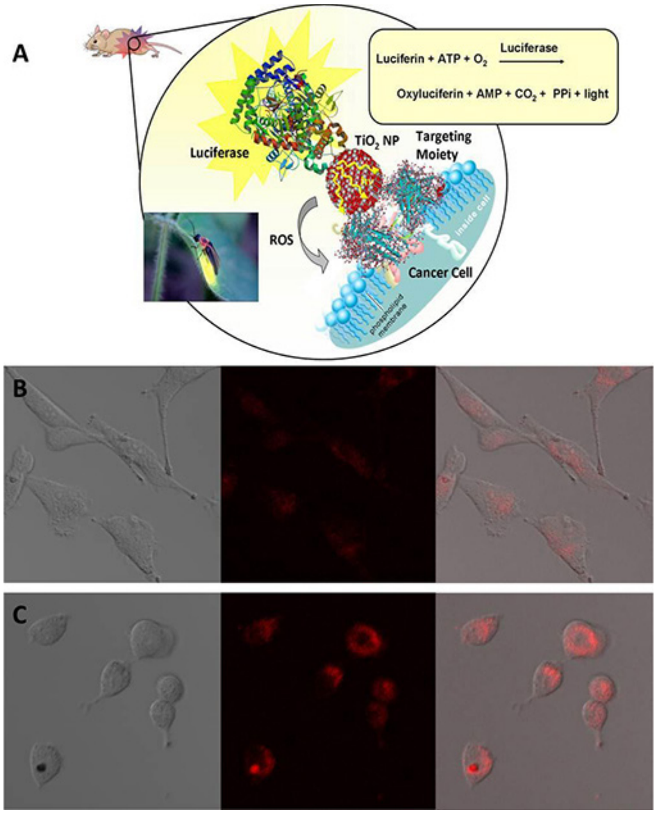


Figure 1: (A) Schematic depicting the mechanism of TiO_2-luciferase nanoparticle-induced tumor cell death in conjunction with laser confocal microscope images of (B) untreated A172 cells stained with Mitosox dye that emits red fluorescence when it interacts with superoxide; (C) A172 cells following 2 hours of treatment with the TiO_2-luciferase nanoparticles. Confocal images are composed of an optical image, shown on the left; a photoluminescence image, shown in the middle panel; and an overlay of the optical and photoluminescence image, shown on the right.

This work resulted in the following invention:

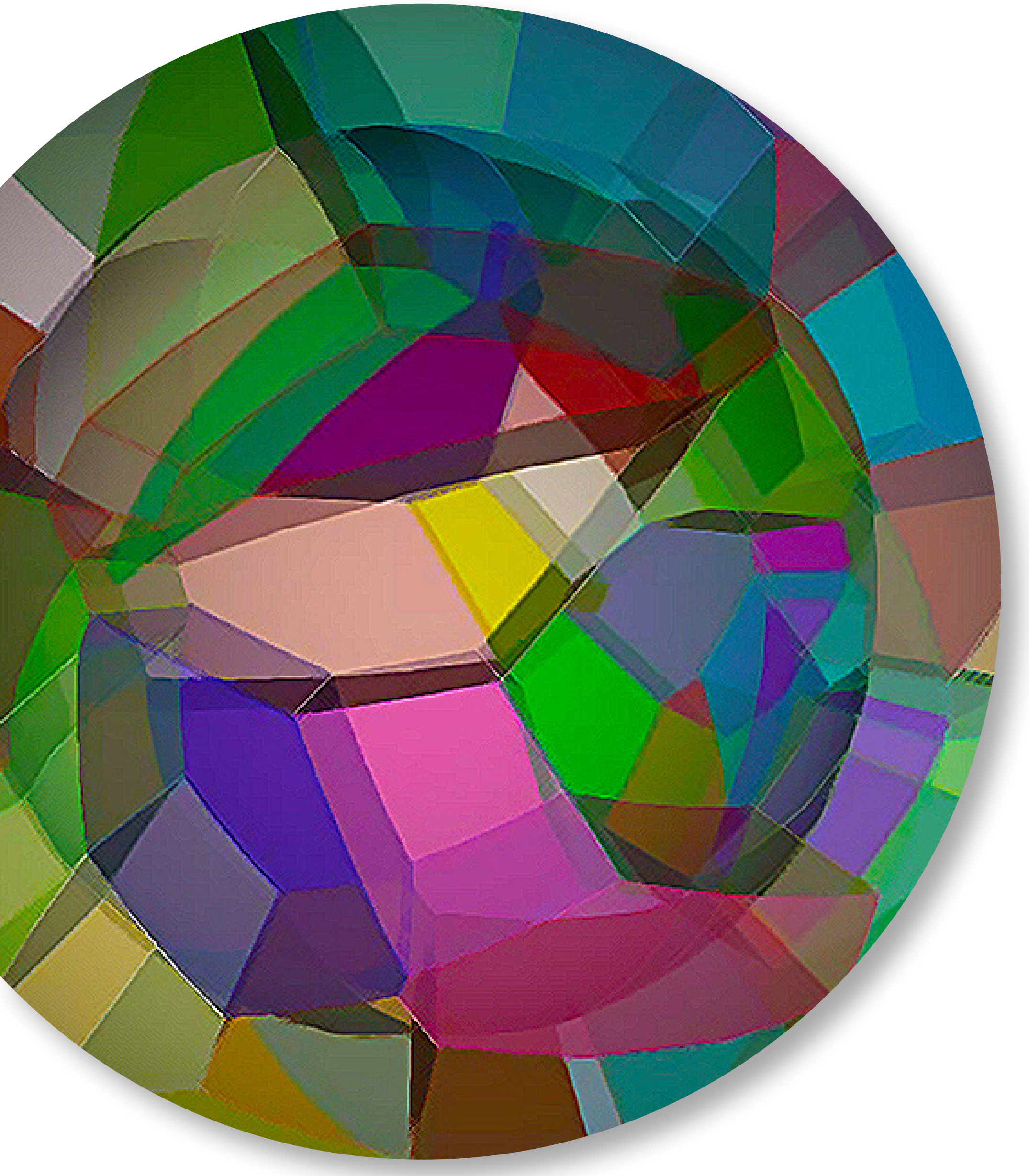
- Rajh, T., N. Dimitrijevic, H. Fry, E. Rozhkova, and B. Grzyowski, “Use of Metal Oxide Nanoparticles for Cancer Cell Lysis,” invention report submitted December 2010. [ANL-IN-10-079]

Proposed Work for FY 2013

The next major objectives of this project will consist of optimizing the antibody targeting of the TiO_2-luciferase nanoparticles to accomplish successful binding of cultured cancer cells and to further characterize the extent and type of cell death that is being induced. Once these goals are achieved, we will then study the effectiveness of our system to reduce tumor size in a mouse xenograft tumor model.

FY2012
annual report

CLIMATE AND BIOGEOSPHERE INTERACTIONS



Development of a High-Throughput Approach to Soil Physical and Chemical Characterization in Tandem with Soil Metagenome Analysis

2010-119-R2

R. Michael Miller, Jack Gilbert, and Julie Jastrow

Project Description

Recently, we demonstrated that using a subsystem approach to soil metagenomics offers possibilities for understanding soil metabolic processes at a continental scale. We used the subsystem classification of MG-RAST (metagenomic RAST Server [http://metagenomics.nmpdr.org]) to identify distinct metabolic clusters in soils on the basis of biome type. These metabolic subsystem clusters appear to be influenced by climate, vegetation, and soil characteristics. The subsystem pathways for the respective clusters indicate that the quality of the soil's organic residues and other factors (e.g., soil texture, pH, and base cations) are major drivers. They also suggest that a more refined measure of the soil's organic substrate composition is needed to better identify the drivers that influence the soil metagenome subsystem. Therefore, a characterization of the chemistry of soil fractions could provide critical information about the quality of SOM (soil organic matter) pools with various turnover times, which could, in turn, help elucidate the mechanisms controlling SOM cycling. We have recently determined that information can be acquired on SOM composition by using mid-infrared (mid-IR) spectroscopy, since it can characterize the quality of soil (i.e., mineral and organic matter composition, as well as its decomposability) with regard to its potential for high throughput.

What differentiates this study from the few studies that have been conducted on soils using mid-IR is our intent to identify the appropriate scale that a soil trait integrates with the MG-RAST soil metagenome metabolic subsystems. Although mid-IR spectroscopy has the potential as a means for high-throughput soil analysis, its true potential is with the information contained within the spectra on soil organic matter and mineral content quality. Incorporation of such spectral information with soil metagenomic data should allow for a greater understanding of those factors that drive microbial community composition and how microbial community composition influences process.

Even though mineral content and soil organic matter are the known primary soil components that drive the spectral quality within the mid-IR region, the science is still in a phase where structural assignments based on organic matter quality is in an annotation phase. Ideally, by using mid-IR spectroscopy, it should be possible to characterize soil organic matter in a manner that has potential for identifying those organic matter compounds that influence microbial composition and especially the metabolic profiles that they represent.

A major goal of the study is to determine whether mid-IR spectroscopy can be used as a high-throughput means for determining basic soil characteristics. More specifically, can mid-IR spectroscopy be similarly used as a means for identifying soil carbon pools that respond to disturbances associated with climatic change and land-use practices? A secondary goal is to determine ways of utilizing the spectra in a manner that could be integrated with microbial properties of a soil, especially in tandem with soil metagenomic analyses. Also, for annotation purposes, spectral libraries need to be created from known organic matter input sources to soils. These inputs are primarily from either plant litter or root systems and associated mycorrhizal fungal hyphae.

Mission Relevance

This project is relevant to DOE's missions in science and the environment. One of DOE's primary missions is to anticipate the environmental consequences of energy use. In the area of climate change research, a major goal is to understand carbon cycling. Because soils are the largest reservoir of carbon (due to the vast amount of carbon sequestered in soil organic matter), there is a need to better quantify carbon stocks, including their vulnerability to such factors as climate change and land-use. Similarly, there is a need to determine what form the carbon is in and its subsequent vulnerability to microbial activity.

FY 2012 Results and Accomplishments

In previous years, we reported on the need for establishing proper protocols for handling of soil samples. Considerable effort was directed at determining how soil preparation can influence spectral quality. To avoid process-created noise, we established protocols for handling and preparing soils before obtaining mid-IR spectra. We identified the importance of particle-size (and, hence, the need for optimal grinding of a soil) and established protocols for when to use a background of KBr. The success of the technique relies on the availability of an adequate calibration model for each system under study and so rather large data sets are needed.

Several larger issues need to be resolved for the general use of mid-IR, including the scale of calibration (local, landscape, regional, or continental); a need to examine different approaches to integrate spectral information with soil characteristics, including soil metagenomic data; and annotation of spectral regions associated with various classes of biomolecules (e.g., carbohydrates, lipids, and proteins). We found that mid-FTIR can be a useful tool for high-throughput and routine characterization of organic matter quality for soils from a range of different ecosystems. For example, 119 soil samples from permafrost regions in Alaska, ranging latitudinally from the Arctic Ocean coastal plains to the southeastern rainforests of Ketchikan, can easily be separated by using principal component analysis (PCA). We found that the PC 1 axis can account for 52% of the variation, with separation of samples being based on carbon content. Separation also is determined by the amount of partially decomposed organic matter, such as lignin, polysaccharides, aromatic compounds, aliphatics, carbonyls in esters, proteins, and amides. PC 3 explains 9% of variation and is driven by the amount of soil carbonates, while PC 2 accounts for 21% of the variation and consists of site-specific characteristics. These findings support our previous findings that resulted from using soil samples from the National Ecological Observatory Network (NEON), which represents a continental gradient. For the NEON samples, we found that the PC 1 axis accounts for 80% of the variability, with the strongest predictor being soil organic carbon.

Preliminary analysis incorporating the NEON soil metagenomics dataset with the mid-IR spectra indicated that more than 70% of the variation can be accounted for by the first principal component, although interpretation is not straightforward and requires a better understanding of the various metabolic pathways driving the relationship with the various spectral regions.

Significant advances were made in characterizing root and fungal cell wall contributions to soils by using mid-IR. The arbuscular mycorrhizal fungal hyphal matrix mid-IR spectra are some of the first for this group of fungi (Figure 1). Because these fungi are root associated, we wanted to determine if these hyphae could be identified in a background of roots. We used pure hyphae and diluted it with switchgrass root samples to determine if we could readily identify root-associated fungi. The best results were obtained by taking the first derivative of the spectra. There were three spectral regions where there was a clear difference between the pure hyphae and roots. We found that a detection limit of around 25% hyphae is needed in order to separate the hyphal signal from the root signal.

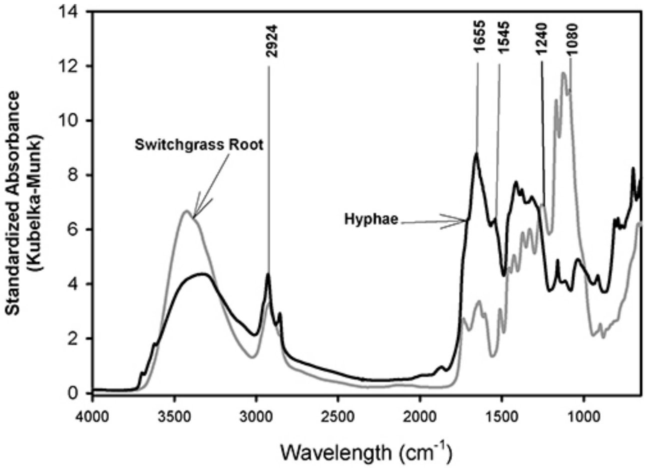


Figure 1. Comparison of mid-IR spectra of biomass from switchgrass roots and hyphae of arbuscular mycorrhizal fungi. The primary differences for the two spectra are found in the regions of absorbance (Kubelka-Munk units) showing characteristic vibrational bands for amides at around 1,655 and 1,545 cm^{-1}, for lipids at 2,900 and 1,240 cm^{-1}, and carbohydrates at 1,080 cm^{-1}.

The primary outcome of the study indicates that soils can be uniquely characterized by their mid-IR spectra. Our preliminary observations indicate that the integration of soil spectra with soil metagenomic data is possible. We have initiated the development of a library of various components of soils, including spectra of roots and associated mycorrhizal fungi along local, regional, and continental gradients. As annotation of the mid-IR spectra improves, the technique offers a nondestructive means for simultaneously determining a soil "signature," as well as a possible means for quantifying differences in soils for labile soil carbon and nitrogen pools, which are key parameters in understanding SOM dynamics.

Accelerating the MG-RAST Metagenomics Pipeline

2010-131-R2

Narayan Desai, Ewing Lusk, and Folker Meyer

Project Description

MG-RAST is one of the premier metagenomics analysis platforms in the world, serving more than 8,000 users. Each day, more than 500 people use MG-RAST and its analysis tools. MG-RAST has analyzed more than 60,000 metagenomes, accounting for over 16 terabase pairs (Tbp) of data. A majority of the data sets are from 1 to 20 gigabase pairs (Gbp) in size, although a large number of 200-Gbp jobs have begun to be seen. Processing for these jobs takes the central processing unit 1,000–5,000 hours from start to finish. Since the beginning of 2012, current-generation high-throughput sequencer data sets have increased in size to 600 Gbp. This explosive growth in data volume is rapidly creating a crisis in data analysis; sequencing technology is outpacing even Moore's law.

These data sets provide a key opportunity to deeply understand the impact of bacterial communities on life, medicine, and the environment. Obtaining such an understanding of these communities' interactions, capabilities, and structure has made MG-RAST a critical asset to microbial ecologists. However, without infrastructure improvement, the current MG-RAST pipeline cannot accept the new data sets. To support the continuing efforts of the metagenomics community in the United States and worldwide, the MG-RAST pipeline needs to be redesigned to handle large data sets, interface with exotic hardware, and be flexible enough to adapt to the changing requirements of the research communities.

Mission Relevance

This project is relevant to DOE's missions in science and the environment. Traditionally, gene-sequencing technologies have only been applicable to organisms that could be isolated and cultured. This restriction limited the use of these technologies to a very small percentage of the natural biosphere.

Metagenomics is an approach to analyze the microbial communities present in samples of genetic materials gathered from the environment, often from soil. Metagenomic analysis provides insight into microbial communities highly relevant to issues of climate and bioenergy.

Large-scale metagenomics provides insight into the abundances of organisms, functions, and proteins in the natural environment, leading to applications in bio-energy and remediation and enabling bio-prospecting. High-quality, high-performance metagenomics analysis tools are critical to fully understanding the carbon cycle and links between microbial communities and climate effects.

FY 2012 Results and Accomplishments

The primary scope of our work was to improve the analysis throughput of MG-RAST. In the first two years of the project, we achieved 10X improvements; in FY 2012, we achieved a 7X improvement. (Thus, we improved the analytical throughput by a factor of 700 over the three project years.) The improvements have made MG-RAST the clear leader in metagenomic data analysis worldwide. It now supports more than 8,000 users. In the project's last month (September 2012), we analyzed nearly 2,400 user jobs that made up nearly 1.1 Tbp of data; in contrast, in the project's first month (October 2009), we analyzed 162 jobs that made up 6.36 Gbp of data. This growth gave MG-RAST the competitive advantage to dominate the metagenomics analysis landscape.

Over the course of the project, we applied a number of techniques to improve the throughput of MG-RAST. We developed (1) a workflow management system that was scaled to allow us to run our analysis computations across a larger number of nodes and (2) new analysis algorithms that decrease the computational costs of analyzing a given amount of data. We also built methods to allow users to reuse the analysis results of other users, improving the benefit of our computational investment in data set analysis.

Our work resulted in a number of good outcomes. It enabled us to participate as the metagenomics component of the DOE KBase project, build a unique data repository of large quantities of metagenomics datasets, and build scalable tooling to support large-scale bioinformatics data analysis.

We have created the largest archive of metagenomic datasets in the world, with environmental metadata in many cases. The datasets are driving developments aimed at large-scale cross-comparisons of proteins and communities across the planet and at more robust methods for comparing datasets (avoiding the annotation biases of all existing databases).

We also developed a data management system called Shock as a part of this project. Shock was adopted by the KBase project for large dataset management. It is also being deployed at several other institutions. This package provides the fundamental infrastructure that will change the landscape of large-scale sequence data management; it supports federation, rich metadata, and provenance information, which should improve the reusability of expensive computational results. All of this work represents the first steps toward a data ecosystem that will radically improve the ability of the research community to share and reuse data products, thereby reducing the individual costs of computation.

High-Throughput Reconstruction of Metabolic Models for Organisms with Applications in Energy, Bioremediation, and Carbon Sequestration

2010-139-R2

Rick Stevens, Christopher Henry, and Folker Meyer

Project Description

Since the first prokaryotic genome was sequenced in 1995, extensive effort has been invested in the construction of genome-scale models of bacterial metabolism in order to better understand how the cell converts simple molecules into DNA, RNA, proteins, and complex lipids. These models are useful for a variety of important applications:

- Predicting the media conditions that will enable an organism to be cultured in the lab;
- Predicting and controlling the interactions between different organisms in a microbial community to improve carbon sequestration in the environment;
- Designing metabolic engineering strategies to reshape the metabolism of a cell to produce biofuels, commodity chemicals, and pharmaceuticals; and
- Improving crop yield by identifying organisms that best contribute to soil fertility.

Unfortunately, because of the extensive manual curation and computation that is required to build a new genome-scale metabolic model, the pace of new model reconstruction is dwarfed by the pace at which new complete genome sequences are emerging. In the past 10 years, 40 genome-scale metabolic models have been published, while 1,000+ genomes have been sequenced.

Fortunately, new methods have emerged that enable automation of various steps in the model reconstruction process, which we have implemented and integrated into an automated model reconstruction pipeline, the Model SEED pipeline. Now that this pipeline exists, we have the opportunity to put it to work building genome-scale models for organisms that are important for applications of interest to the DOE, including cellulose degradation, metal reduction, bioremediation, biosolar energy, climate change, energy production, carbon sequestration, and soil sustainability. We are also exploring options for migrating the most computationally intensive steps of our pipeline to large-scale computing environments (clouds and clusters).

Mission Relevance

This project is relevant to DOE's missions in science and energy. The genome-scale metabolic models produced as the main product of this research drive forward numerous DOE objectives: cellulose degradation, metal reduction, bioremediation, biosolar energy, climate change, energy production, carbon sequestration, and soil sustainability. Experimental biologists will benefit from these models, as they provide a means of analyzing existing experimental results and optimizing the design of future experiments to maximize learning. The proposed scale-up of the model pipeline will enable reconstruction of models for all sequenced prokaryotes, including many pathogens. This work will benefit National Institutes of Health (NIH) researchers studying methods to fight these pathogens. Because we will be establishing the technology and infrastructure required to maintain these models with the most up-to-date information, these models will not be a one-time advancement but will be an enabling resource for the entire research community.

FY 2012 Results and Accomplishments

In FY 2010, we released a website for the automated reconstruction, optimization, and analysis of genome-scale metabolic models: http://seed-viewer.theseed.org/models/. Since the initial release of this site, it has been applied to construct over 17,000 genome-scale metabolic models for over 2,000 unique users. This resource has rapidly become the source of draft metabolic models for the scientific community worldwide. In total in FY 2010, we built models for over 1,000 distinct organisms, including organisms of interest to the DOE. We also transitioned portions of our Model and Biochemistry database to SQL, making it possible to rapidly expand this database to accommodate significant growth in the number of models available for analysis, and we constructed a web-based API (application programming interface) for our model data, facilitating the distribution of model computations over the cloud, as well as enabling users to access model data programmatically.

In FY 2011, we demonstrated the improved scalability of our Model SEED pipeline by applying it to construct 3,500 new genome-scale metabolic models, effectively producing a model for every complete prokaryotic genome sequence available in 2011. This effort brought the total number of models available in the Model SEED pipeline to 11,000. To build our 3,500 models, we developed infrastructure to run the Model SEED pipeline on the new Beagle supercomputer, now available at the Argonne/University of Chicago Computation Institute. To facilitate the process of validating these models, we gathered experimental data for numerous organisms. These include gene expression data for 29 genomes, including many genomes of interest to bioenergy. These data were integrated into our SQL database and made available for use over our web-based API. We analyzed these data to identify portions of the metabolic network that are universally active or inactive. We also gathered additional gene essentiality and biolog phenotype data for four genomes: *E. coli*, *B. subtilis*, *S. oneidensis*, and *C. difficile*. We applied our models to the analysis of these phenotypes and used the results to correct model errors. We also constructed a database for these phenotype data, and we are working with experimental groups to enable them to contribute data directly to this database. We continued to improve our web-based API tools, including a tool for applying the models to the simulation of gene expression experiments.

In FY 2012, we continued our efforts to construct new subsystems in the Model SEED pipeline. This effort focused on catabolic pathways, CO_2 fixation, isoprene biosynthesis, and methanogenesis. A major focus was placed on electron transport chain and fermentation pathways. Our goal was to construct high-quality core models of all microorganisms, capturing central carbon pathways, fermentations, and ETC (electron transport chain). These models actually address many of the needs of metabolic engineers working on biofuels and bioremediation, and they represent a substantial increase in quality over automatically generated genome-scale models. They also address our needs in understanding metal reduction, as ETC pathways to metals have been elucidated through this work. We also developed a distributable version of our modeling software, backed by a revolutionary new document-based database design, enabling the rapid and free interchange of models between collaborators and with the research community. The new system also tracks complete history and provenance on all models, an essential capability that facilitates the bookkeeping required to track how models are adjusted throughout the research process. Finally, we developed new model optimization techniques aimed at identifying the reactions that must be added to enable any reaction associated with an annotated gene to function. This work provided a mechanism to build truly complete models, to identify missing functions in the annotation, and to identify functions that are incorrectly annotated and have little support for their presence in the organism.

Seminars

Henry, C. (2012). "Unraveling Biological Complexity with Computation." Northwestern University, Evanston, IL, January 11, 2012.

Henry, C. (2012). "Enhancing the SEED Framework for Curation and Analysis of Genomic Data and Genome-scale Metabolic Models." DOE GTL Grantees/Contractors Meeting, Washington, D.C., February 1, 2012.

Acceleration of Cloud Microphysical Retrievals for Climate Models

2010-194-R2

Edwin Campos and Douglas Sisterson

Project Description

This project is driven by the assumption that significantly improved climate models are needed to address important scientific and policy questions, and that the development of analytical and visualization tools and software is essential for understanding environmental and climate changes.

New science, uncertainty quantification, and computational tools are needed to promote understanding of the central issues of climate change science. With a better understanding of the atmospheric processes that are relevant to climate, it is then possible to increase the fidelity and applicability of regional climate and biogeospheric simulations to levels that enable informed policy.

Toward a better understanding of the atmospheric processes that are relevant to climate, the general objectives are threefold: (1) to adapt and enhance existing codes, developing new software for analysis and display; (2) to create advanced visualizations of multi-sensor observations of clouds and precipitation; and (3) to validate and refine multi-sensor cloud microphysical retrievals.

Mission Relevance

The main deliverables of this research are multi-instrument data products representing key cloud processes. These have the potential to reduce the time required for developing the sophisticated cloud modeling parameterizations needed to significantly improve climate models. Therefore, this research activity is relevant to key DOE missions in the environment. It also aligns with the DOE-SC discovery mission to understand relationships between climate change and Earth's ecosystems, driving predictive understanding of the Earth's systems and potential impacts of climate change.

FY 2012 Results and Accomplishments

We began the project in late FY 2010 by modifying original computer codes used in the weather domain (previously used in Canada for the 2010 Winter Olympics) in order to analyze and retrieve geophysical variables needed for climate modeling. Using a multidisciplinary approach, we were able to effectively adapt, modify, and create computer code for analysis and display of remote-sensing observations (weather radar, wind profiler, ceilometer, and radiometer), as well as ingest and analyze limited instrument datasets from the Atmospheric Radiation Measurement (ARM) Program's Climate Research Facility (ACRF).

New software was then developed (in the interactive data language (IDL), able to run on any personal computer) for analysis and visualization of cloud properties (particularly tropospheric profiling) by using Atmospheric Radiation Measurement (ARM) remote sensors. The software is able to input various dataset types from the ARM Climate Research Facility installations at different sites around the world.

An algorithm to estimate the Planetary Boundary Layer height from observations by the UHF wind profiler radars at the ARM Southern Great Plains site was developed and remote-sensing analysis to study scale-dependence of cloud model parameterizations, using ARM datasets from the North Slope of Alaska and the U.S. Southern Great Plains was initiated. This work was done in collaboration with the FASTER project Principal Investigator at Brookhaven National Laboratory. FASTER is a DOE Earth System Modeling effort (with about 30 participants) to better represent those cloud processes that occur at scales smaller than current climate model resolution.

The lead investigator participated in the NASA International Field Campaign, GCPEx, as Principal Investigator for cloud analyses with a Microwave Profiling Radiometer. This instrument was operated last January in coordination with other co-located remote sensors and aircraft missions over Ontario, Canada, to study winter clouds and precipitation.

Proposed Work for FY 2013

Proposed work for FY 2013 includes the following:

- Validate cloud-microphysical retrievals by using multi-instrument datasets.
- Engage with the ARM community on developing value-added data sets for climate modeling test and validation.

Seminars

Campos, E. (2010). "Cloud Processes Over the 2010 Winter Olympic Venues as Analyzed from Combined Remote-Sensing Observations." Environmental Science Department, Brookhaven National Laboratory, Upton, NY, September 29–30, 2010.

Campos, E. (2011). "Multi-scale Remote Sensing of the Atmosphere: Profiling." Invited Seminar, Department of Atmospheric Sciences, University of Illinois at Urbana-Champaign, IL, July. 13, 2011.

Campos, E. (2011). "Vertical Velocity from Clear-air Radar Targets." Vertical Velocity Focus Group – Break-out Session, DOE Atmospheric-System-Research Science-Team-Meeting, San Antonio, TX, March 30, 2011.

Campos, E. (2012). "Monitoring the Planetary Boundary Layer with Profiler Radars." Science Team Meeting of the Atmospheric System Research Program, US Department of Energy, Arlington, VA, March 12–16, 2012.

Collis, S.M., E. Campos, K.B. Widener, N. Bharadwaj, and P. Kollias. (2012). "X-band Radars for Climate Science." X-Band Weather Radar Workshop, Technical University of Delft, Delft, Netherlands, November 14–17, 2011.

Simultaneous Ecological Assessment and Characterization of Novel Proteins from a Soil Microbial Community

2010-195-R2

Jack Gilbert

Project Description

Communities of microbial organisms play a major role in earth's biogeochemical cycles. Until recently, however, studying those microbial communities presented major technical challenges, leaving us with a poor understanding of microbial systems. But with the advent of second-generation DNA sequencing technology, we can now study microbial systems *in situ* by sequencing their genomes (metagenomics) and by studying the gene expression in those communities (metatranscriptomics). Although we can generate large quantities of data, interpreting the data relies on existing biological knowledge captured in a variety of databases. A major source of uncertainty stems from our inability to identify proteins of identical function from metagenomic data alone. The need to identify those *isofunctional* proteins (and to study the overall diversity of proteins) has become much more acute — as well as more realizable — with advances in metagenomics.

At present, metagenomic and metatranscriptomic approaches suffer from a significant lack of knowledge regarding the function of many of the putative proteins identified. The problem is that there are hundreds of thousands to millions of unknown sequences — and only three ways of assigning function to these proteins. The first and most reliable way is to clone the gene, express it in another cell, and see what function it may impart. Unfortunately, not only is this process very slow, but also, one must know in advance the function of interest in order to demonstrate or recognize it. To circumvent this problem, researchers compare the protein to already characterized proteins, either by sequence or structure. Comparison by sequence is the currently accepted method; a complication of this method is that many proteins having different sequences perform the same function. Hence, structure is currently the easiest route to annotate the function, because if two proteins have the same structure, they are very likely to have the same function.

To identify which proteins to focus on from the millions of targets, the researcher must determine which proteins are important in the ecosystem of choice. It is therefore necessary to apply next-generation sequencing to produce an ecologically relevant, statistically designed experiment — for example, the examination of a soil ecosystem. From such a study, one can determine the top 1,000 most relevant targets. Moreover, promising targets from this analysis can be further analyzed and protein structures confirmed by using the high-throughput protein crystallization facility at Argonne. Once we have such protein structures, a protein-folding homology search can be run to determine the putative function of that protein. These data can then be fed back into the ecological data to determine what impact this information has on our ability to interpret metagenomic and metatranscriptomic analyses.

Mission Relevance

The genetic and protein information acquired during this study is of direct relevance to the DOE missions in renewable energy, environmental analysis, remediation, and basic science. In the area of energy production, we have already seen the use of synthetic organisms that could have major ramifications for renewable energy from photo bioreactors. Identifying key genes in the process, and using metagenomics to determine what genes can produce more efficient proteins for these desired processes, are objectives of this research. Environmental analysis and remediation will be improved by metagenomic and metatranscriptomic analyses, permitting exploration of environments for genes and proteins of interest. Identified targets could be used for remediation purposes, and characterization of different environments will have dramatic impacts on how we view, for example, uranium cycling in contaminated sites. Fundamentally, this research will produce a paradigm shift in microbial ecology and ecological theory by exploring microbial life from the microbes' perspective. We also want to help define how microbes exist in communities and how they interact with plant life. In soil ecosystems, this has direct relevance to rhizosphere and leaf-based community interactions and plant productivity, all of which are highly relevant for agriculture.

FY 2012 Results and Accomplishments

Prior to FY 2012 we set up the infrastructure and sequencing center required to process the initial samples, as well as performing the sample acquisition from initial collaborators to create the first 5,000–10,000 samples. We also worked with collaborators at the University of Colorado, Boulder, to generate a public database service and set up a metadata curation system.

We processed more than 22,000 environmental samples, making the Earth Microbiome Project (EMP) the largest coordinated bacterial community ecology study to date. Currently, the EMP exists as the most comprehensive assessment of microbial ecological dynamics in the history of microbiology. In addition, we embarked on a specific characterization study for unique proteins in plant-microbe associations — focusing on those proteins necessary for microbe-microbe interactions in different plant tissues, as well as plant-bacterial interactions associated with flowers, fruits, and roots in different plant species. This key shift is designed to explore the niche structure associated with different bacteria in different environments and to target the proteins of unknown function that are essential for the development and maintenance of these interactions.

Proposed Work for FY 2013

We will continue to analyze more environments in FY 2013, with the hope of exploring the 16S rRNA community structure of a further 10,000 environmental samples. In addition, the exploration of unknown protein functions in plant-associated and soil-associated ecosystems will continue, with further characterization of hundreds of protein targets.

Seminars

Gilbert, J. (2011). “Lecture Notes: Beyond the Genome: Creating Predictive Models of Microbial Communities.” Oregon State University Expert Series, Corvallis, OR, April 21, 2011.

Gilbert, J. (2011). “Lecture Notes: The Earth Microbiome Project.” Special Session, Waterloo University, Canada, April 15, 2011.

Gilbert, J. (2011). “Lecture Notes: Marine Microbial Metagenomics: Lessons Learned from a Coastal Observatory.” CAMERA Inspirational Lecture Series-UCSD, San Diego, CA, January 2, 2011.

Toward Understanding Cloud Processes and Uncertainty Modeling in Next-Generation, High-Resolution Climate Models

2011-052-R1

Yan Feng, Mihai Anitescu, Emil Constantinescu,
and Robert L. Jacob

Project Description

Cloud processes in global climate models (GCMs) are highly parameterized and often tuned to obtain the Earth’s radiative balance and global mean temperature. As a result, clouds constitute the single largest source of uncertainty in terms of radiative forcing (i.e., the change in net downward radiation at the top of the atmosphere) and climate feedback. In addition to the uncertainties associated with physical processes, the climate system has an inherent stochasticity, and errors associated with predictions cannot be faithfully simulated in a deterministic modeling framework. The dynamic nature of uncertainty itself needs to be taken into consideration. Improving modeling of cloud processes — especially the interactions of clouds with aerosols (naturally emitted or human-induced airborne nanoparticles) — is a priority for the coming decade.

In this project, we are evaluating and quantifying the uncertainties associated with cloud processes in a high-resolution Community Atmospheric Model (CAM) using observations. We are also developing and testing new physical representations of aerosol and cloud microphysics. The proposed new treatment of cloud physics and the error modeling will focus on improving the climate model’s predictions of precipitation on a regional scale. Such an interdisciplinary approach poses novel and critical challenges for the climate modeling, mathematics, and high-performance computing communities.

Mission Relevance

This project is relevant to DOE’s environmental mission. In the next decade, DOE, the National Science Foundation (NSF), and the U.S. Department of Agriculture are projecting that developing next-generation climate models and quantifying uncertainty in GCMs will be major emerging areas of climate science research. The outcome of this research will provide interdisciplinary engineers and scientists with the sophisticated tools they need to generate reliable decadal and regional climate projections with reduced uncertainty — projections that can be used in making important policy decisions.

FY 2012 Results and Accomplishments

Our FY 2011 evaluation of CAM that employed observations found that the sensitivity to aerosols of the occurrence of precipitation and of cloud liquid water content is probably overestimated in the model. This bias could be closely linked to the heating effect caused by aerosol absorption of incoming solar radiation. Such heating leads to a reduction in cloud cover through evaporation and suppression of the upward motion required for cloud formation. On the basis of a new aerosol scheme developed in FY 2011, we examined the enhanced solar absorption by a class of organic carbon aerosols known as brown carbon, which originates from fuel combustion and from biogenic compounds emitted by soil and vegetation. Until now, the climate impact of brown carbon has not been considered in any GCMs, but we found that it contributes +0.25 Wm^{-2} (or about 19%) of the total solar absorption by human-induced aerosols. The radiative impact of brown carbon at the top of the atmosphere is a warming effect (+0.11 Wm^{-2}) like that of greenhouse gases (GHGs), while the effect at the surface is cooling (-0.14 Wm^{-2}) — opposite of the effect of GHGs. If not included, these estimated effects can impose a significant source of uncertainty in global climate simulations of clouds and precipitation, especially over biomass-burning and biofuel-combustion regions (Figure 1).

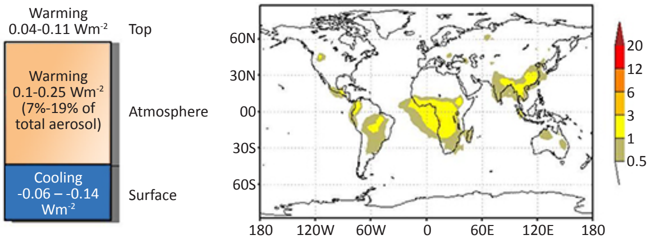


Figure 1. Left: Annual and global mean atmospheric warming and surface cooling (in W m^{-2}) caused by light absorption by organic brown carbon aerosol. Right: Spatial distribution of atmospheric warming (in W m^{-2}) by brown carbon. Over the regions dominated by biomass or bio-fuel burnings, the warming due to brown carbon is over 1 W m^{-2}.

Partnering with outside institutes, we developed an iron-heterogeneous chemistry scheme for dust and improved dust source functions. We found that these improvements could significantly alter the soluble iron deposition rate from atmosphere to ocean; increases in the deposition of soluble iron in desert dust since 1870 have likely resulted in the uptake of ~4 parts per million (ppm) +/-100% more CO_2, by perturbing the ocean biogeochemical cycle as a nutrient to marine biota. Neither these aerosol biogeochemical processes nor the subsequent activation of marine biogenic aerosol to form cloud droplets have been included and quantified in the Earth System model.

Our progress in uncertainty quantification included development of a strategy to generate consistent parameter perturbations constrained by physical laws or assumptions. The new strategy allows us to reduce the instabilities that accompany perturbations and improve sampling efficiency. We are implementing it on a single-column version of the CAM, driven by the Atmospheric Radiation Measurement (ARM) Climate Research Facility data sets during the Tropical Warm Pool — International Cloud Experiment (TWP-ICE) . One of the striking findings in this case study is related to solving the differential equation of stratiform precipitation in the model through Picard iterations. By default, only two iterations were carried out regardless of the residual size. We found that by increasing the sub-time steps from 2 to 10, up to 10-mm/day differences in 3-hour precipitation rates were obtained; typical precipitation rates range from 20 to 100 mm/day.

Proposed Work for FY 2013

To continue our progress in model development, we are working with the CAM developers from Pacific Northwest National Laboratory to implement the new brown carbon parameterization in CAM. This will allow us to quantify the resulting changes in cloud cover and impact on precipitation in the climate simulations. We are also working with the CAM developers to implement an aerosol heterogeneous chemistry scheme and to improve dust aerosol simulations in CAM. These improvements will allow us to quantify the cloud forcing that is attributable to dust and pollution aerosols through the ocean's biogeochemical cycle in the Earth System model. We will also continue development of the parameter calibration framework; integrate the new radar data, which could distinguish large-scale precipitation from convective precipitation; implement the physically based cloud microphysics for convective clouds that will allow us to calibrate the total precipitation; and apply the calibrated parameters in the large-scale model sensitivity studies. Quantification and reduction of uncertainty in regional-scale cloud and precipitation processes will be the main focuses of the DOE Regional Climate Modeling program.

Evaluation of Microtopography Effects on the Terrestrial Biosphere and Hydrosphere under Regional Climate Change

2011-129-R1

Beth Drewniak, Satish Balay, Todd Munson, Barry Smith, and Y. Eugene Yan

Project Description

The next generation of land surface models is expected to be coupled to climate models and used to evaluate the feedback between the terrestrial biosphere and the atmosphere. Expanding the capability of the models to account for soil microtopography will improve the modeling of the hydrology and carbon cycling of the land surface system. We intend to introduce land use changes at the subgrid level, a large-scale component of microtopography. We propose to introduce an evolving land surface as a result of changes from human influences as well as changes resulting from climate. With this approach, we will be able to (1) model variability at the subgrid scale, (2) understand the interactions between land use shifts and climate, and (3) evaluate the impacts of subgrid variability on carbon cycling. The approach and tools developed in this proposed work will be applicable across multiple land surface models.

The Community Land Model (CLM) maintained by the National Center for Atmospheric Research (NCAR) has a subgrid hierarchy that allows up to six landunits to exist on each gridcell: ice, lake, wetland, urban, vegetated, and crop. In this project, we will expand the model capability to allow changes in landunits, driven by an input dataset or by calculation of climate-induced changes in a given landunit. We will design a set of rules that will be used to inform CLM how the landunit transitions should take place such that both prescribed and prognostic transitions can be modeled simultaneously.

Mission Relevance

This work is relevant to DOE's environmental mission. It will provide tools and methodologies to evaluate the effects of land use and land change at a regional scale, while improving the capability for representing subgrid variability. The improvements in the land surface models will help to develop the next-generation coupled Integrated Assessment (IA) and Earth System Models (ESM), the result being an improvement in representation of land surface heterogeneity and subgrid soil biogeochemistry.

FY 2012 Results and Accomplishments

We focused our effort on the further development of the CLM. The first changes to the model began in FY 2011 and concluded in FY 2012. We began in FY 2011 to add transient landunit capability to CLM4. CLM has a subgrid hierarchy that divides each gridcell into landunits, with each landunit containing one or more soil columns, and each soil column contains multiple plant functional types (PFTs; or the corresponding subgrid level for the non-vegetated landunits). These are all tracked in the model by their weight by using filters to eliminate calculations over zero-weighted portions of the gridcell. To allow land types to expand or contract, we modified CLM4 such that each gridcell is allocated memory as a placeholder for zero-weighted landunits, soil columns, and PFTs in a gridcell. We determined that the demanding memory requirement did not significantly slow the model run time.

Next, we developed a function that calculates weight changes for each landunit, soil column, and PFT at a yearly interval, based on several of the CLM initialization functions for the subgrid hierarchy formation. This function was completed in FY 2012. A dataset containing changes in vegetation and cropland landunits was created for initial testing of the re-weight module. Initial testing showed the code was successful in calculating changes in landunit weight on the gridcell; however, since the conservation subroutine is not in place, we cannot fully test the reweight function. An NCAR software engineer is revising the code to eliminate redundant subroutines and organize the workflow.

The level of interest in the CLM community led to a discussion of current challenges, which include initializing landunits that were not previously present on a gridcell and tracking changes between landunits that do not have the same state variables (i.e., variables describing the state of the landunit, for example, soil organic carbon is not defined in a glacier landunit). As a result, we designed a method to inform CLM how the landunit transitions should take place. Ongoing collaboration with NCAR through a wiki is ensuring that this new capability is applicable for all landunit types and processes.

Part of the code includes a mini transition matrix, which will aid in the initialization of new or expanding landunits on a gridcell. The mini transition matrix provides reference information for variables that are not compatible between landunits (e.g., soil carbon, nitrogen, etc.) via a lookup matrix of transfer values. As the model evolves, this matrix will be expanded to a spatial grid, particularly for variables that might have appropriate resolution. An example of the matrix is:

$$\mathrm{S} = \begin{bmatrix} s11 & \dots & s1n \\ \dots & sij & \dots \\ sn1 & & snn \end{bmatrix}$$

In the transition matrix, each s_{ij} determines the initialization of a transition from land use type i to land use type j. We are in the process of creating a list of all potential state variables that should be handled with this approach. The change in most state variables in an expanding landunit would be updated by using the weighted average of the shrinking landunits.

Proposed Work for FY 2013

During FY 2013, we will finalize the design of the above code, which will aid with the conservation function for water, energy, and biogeochemistry, and we will implement the new means of initializing landunits in a gridcell. Once the code is fully capable, we will begin to test it with sample changes in land use to determine how the model performs. Finally, we will integrate it with the climate model to determine the behavior of landunits with changing climate.

Will Linking Ultra-Large-Scale Metagenomics with Models Representing Biogeochemical Cycling Improve Existing Carbon Flux Models?

2011-196-R1

Folker Meyer

Project Description

Microorganisms are the key players dominating the major biogeochemical cycles. Nevertheless, microbial processes cannot be parameterized with carbon flux models, leading to considerable uncertainty in these models. Because the extreme diversity in soil microbial communities prevents many direct molecular assays based on databases of *known* (i.e., cultivable) microorganisms, we will leverage metagenomic data to design a set of directed molecular probes to inform the existing models and reduce their uncertainty.

This study is enabled by recent advances in microbial ecology and metagenomics at the intersection of biology, bioinformatics, and computer science. In particular, ultra high-throughput

DNA sequencing enables inventory of not only the microbial species present but the metabolic functions encoded in complex microbial communities. We can use these data as input to a dynamic systems-based model and thereby identify key enzymes involved in microbial metabolisms critical in biogeochemical cycles.

Mission Relevance

This project has direct relevance for the DOE Biological and Environmental Research (BER) missions exploring carbon/nitrogen cycling and carbon sequestration processes in soils, as well as biogeochemical processes contributing to contaminant biotransformation and immobilization. This research is in a unique position to start bridging the gap between molecular and field scale. If we are able to do so successfully, we can positively impact the efforts to devise regional climate models by providing a set of cost-effective "field site" molecular probes that will provide deep insights into the carbon-flux state of soils. The project has potential for improving numerous project designs across the DOE national laboratory system and, hence, will be relevant to DOE's environmental mission.

FY 2012 Results and Accomplishments

Most soil processes, including microbial diversity, are extremely variable across spatial scales. The destructive and labor-intensive nature of traditional soil sampling and processing methods has hampered broad investigation of spatial heterogeneity in soils. Thus, we have characterized the microbial community structure over centimeter-scale gradients as a first step in developing the proposed molecular probes.

We previously collected in FY 2011 an unprecedented 750 soil cores to characterize the drivers of spatial structure in microbial diversity and an additional 480 cores to quantify soil moisture at the scale of the microbial populations. We also capitalized on the ongoing experiments at the Sustainable Bioenergy Crop Production Research Facility at Fermi National Accelerator Laboratory (Fermilab). Using an innovative "micro-core" approach that allowed us to characterize the soil high spatial resolutions, we collected 25 soil samples from 10 × 10-cm grids (Figure 1A) at five points along a 36-m transect in each of six 36 × 20-m plots (fertilized and unfertilized treatments). On the basis of the cores collected, we made several field observations that established the degree of resource patchiness at the site. For instance, soil moisture for all samples obtained ranged from 18% to 37% when we sampled, but most of the variability was restricted to only one of the three blocks. Additionally, soil CO_2 efflux from the sampling sites also varied. Many studies have shown strong correlations between CO_2 flux and moisture. Interestingly, there was only a marginally significant relationship between flux and soil moisture during our field campaign, suggesting that other factors, such as microbial community structure, may be important predictors of flux.

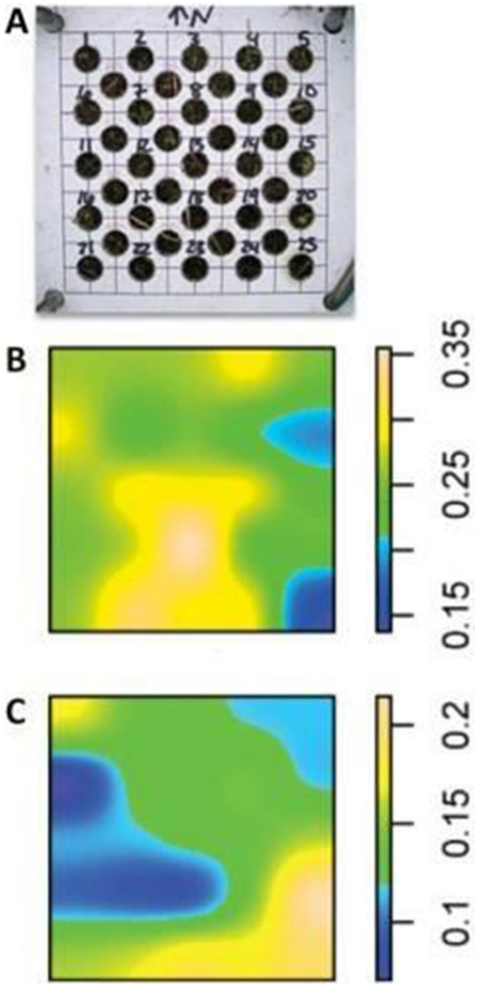


Figure 1. (A) Spatial structure of Verrucomicrobia from soil collected in two 10 × 10-cm areas, including the sampling scheme, with 25 soil microcores arrayed in 100 cm², and the relative abundance of Verrucomicrobia in (B) unfertilized and (C) fertilized soil. Yellow and blue areas indicate high and low relative abundance, respectively, of the Verrcomicrobia phylum relative to other microbial groups.

Targeting a broadly occurring gene found in all microorganisms (encoding ribosomal RNA [rRNA], a gene important in the production of proteins), we generated inventories of the microbes found in each sample. Using the Illumina MiSeq DNA sequencing instrument at Argonne's IGSB-Next Generation Sequencing Core, we produced over three million DNA reads and then analyzed them with a standard analysis pipeline (QIIME). Overall, we found that Verrucomicrobia was the dominant bacterial phylum in our inventories. The data indicated that fertilization significantly promoted bacterial diversity and were statistically significant (probability value $P = 0.0109$, sample size $n = 6$), although the magnitude of this difference was relatively small (Shannon index was 8.35 in fertilized and 8.7 in unfertilized plots) and was mostly driven by a reduction in Verrucomicrobia diversity in the fertilized plots ($P < 0.01$, $n = 6$).

Few of the grids exhibited significant spatial structure, and the relative abundances of bacterial phyla tended to change abruptly over length scales < 2 cm. For example, Verrucomicrobia relative abundance ranged from approximately 25% to 50% over the space of a single 10-cm grid (Figure 1B). Furthermore, less than 20% of the grids had significant spatial autocorrelation, and those that did had a "Moran's I" (a metric of autocorrelation) near zero. These results suggest that patterns in microbial community structure are not predictable based on spatial proximity. The observed degree of spatial variability within the 10-cm grids presents issues for fine-scale experiments, but it was easily overcome by good replication in addressing ecosystem-scale questions.

Proposed Work for FY 2013

Our microcore sampling strategy provided a map of soil microbial communities at an unprecedented spatial resolution; we have now prioritized measuring soil pH and permanganate oxidizable carbon (POXC), which can both be carried out on small sample volumes. We expect that these two tests will give us insight into the spatial variability in the microbial communities (i.e., small, abrupt gradients in pH or POXC should correlate with relative abundances of various microbial taxa that are influenced by the uneven distribution of plant roots, organic detritus, or other features).

We additionally will use information gleaned from our rRNA-based data to select a subset of samples for shotgun metagenomic sequencing. From these data, we will build a model that will track the differential change in specific carbon and nitrogen metabolites within and between each sample. By comparing the resulting data to environmental parameters co-collected at this site, we will be able to make predictions over time and space. In this way, we can generate a microbial weather map for the spatial and temporal fluctuation in assemblage structure and function-derived metabolite turnover in this system.

High-Performance Computation: Developing and Testing a 3-D Regional-Scale Climate Model in the Ganges Valley, India

2011-216-R1

John Krummel, Yan Feng, and Veerabhadra Rao Kotamarthi

Project Description

The Ganges Valley Aerosol eXperiment (GVAX) began a one-year observation period by using the DOE Atmospheric Radiation Monitoring (ARM) mobile facility at Nainital, India, in July 2011. This major field study involves multiple DOE laboratories and U.S. and Indian research institutes. Radiative flux; cloud properties; convection; and the physical, chemical, and optical properties of aerosol are being measured to develop core data sets for scientific analysis. The observational data range from surface measurements that yield point and profile data sets to a few selected aircraft-platform-based measurements. These measurements must be placed in a larger, regional context in order to relate the observations to a particular dynamic state of the atmosphere and to develop hypotheses that explain observed phenomena.

The aim of this project is to develop and test a three-dimensional (3-D) regional-scale climate model; the project will generate the conditions required to develop such a regional context, which will facilitate the GVAX field experiment in climate research. Baseline simulations of a 3-D, regional-scale model will provide the necessary analytical support for scientific studies conducted under GVAX. The 3-D model will be a test bed for high-performance computing data storage and visualization.

Mission Relevance

This project is relevant to DOE's missions in basic science and the environment. The modeling results for air pollution and meteorological fields will become one of the central "data" products archived at the DOE ARM web sites. The large volumes of model outputs generated can also be used to test or assess the feasibility of using cloud computing systems, such as Magellan. The project will demonstrate capabilities in operating a 3-D regional climate model and managing a large volume of forecast data sets, thus making regional model forecasting a regular part of the mobile ARM facility support. In addition, the project is relevant to a recent request by DOE's Climate Change Prediction Program for proposals to develop regional-scale resolving models and modeling activities designed for integrated assessment modeling.

FY 2012 Results and Accomplishments

In FY 2011, we configured and set up the latest version of the 3-D Regional-Scale Climate Model, WRF-Chem 3.3, on the Argonne Fusion clusters. The regional model was then scaled up to running on 200 processors. The WRF-Chem model embedded with the new MOZCART chemistry module was used to study air pollution and regional climate over South Asia for the first time. Operational daily forecasts for the GVAX experiment have been performed since July 2011.

In FY 2012, we successfully completed the daily forecasts through March 2012. During the forecast period, the regional model was run on 200 processors daily, producing about 180 gigabytes (GB) of data products each day. We developed a new online data and visualization server (http://atmos.anl.gov:8080/las) by using the National Oceanic and Atmospheric Administration (NOAA) Live Access Server (LAS) to handle on-the-fly visualization and basic analysis of the large data set. This tool allows field experimentalists to visualize, and/or download, the forecast data and make flight plans.

With researchers at the University of California, San Diego, we successfully used the regional model forecasts of weather and air pollution, as well as the online LAS visualization tool, in another National Science Foundation (NSF) -funded CARDEX (Cloud Aerosol Radiative Forcing Dynamics Experiment) field campaign (in March 2012). Following the GVAX field experiment, we coupled the regional climate model with the NOAA re-analysis meteorological fields (assimilated with observations and available with a delay of days after real time) and completed the eight-month climatology diagnostic runs. In contrast to the operational forest products, the WRF-Chem regional model climatology simulations, initialized with re-analysis data, are useful in interpreting observations and providing physical understanding of observed parameters. Figure 1 shows the regional model-simulated aerosol optical depth (AOD), a measure of the atmospheric abundance of nanometer-size particles that reflect incoming solar radiation, compared with the GVAX surface observations and satellite observations. By capturing the observed geographic distribution and seasonal cycle of such aerosol content in the atmosphere, the regional model demonstrates the capability to simulate the climate effects of these airborne particles, emitted mainly from local industrial and agricultural activities.

Proposed Work for FY 2013

We demonstrated that 3-D weather and forecasts models are essential for *in situ* field experiments, especially aircraft observations; we are working to make this regional-scale model an operational product that is available to the DOE ARM program. With researchers in the aerosol group at Pacific Northwest National Laboratory, we will pursue about operating regional aerosol and cloud forecasts for the GOAMAZON experiment that will be conducted by DOE. We will also test the regional-scale climate model on the Blue Gene/P supercomputer at Argonne, which will allow us to use this model for long-term and large ensemble-member regional-scale studies. In response to one of the main focus areas of the DOE climate modeling program, we will continue running the WRF-Chem model in the diagnostic mode (driven by the re-analysis fields instead of forecast fields) to study air pollution and regional climate and compare our results with the GVAX and CARDEX observations.

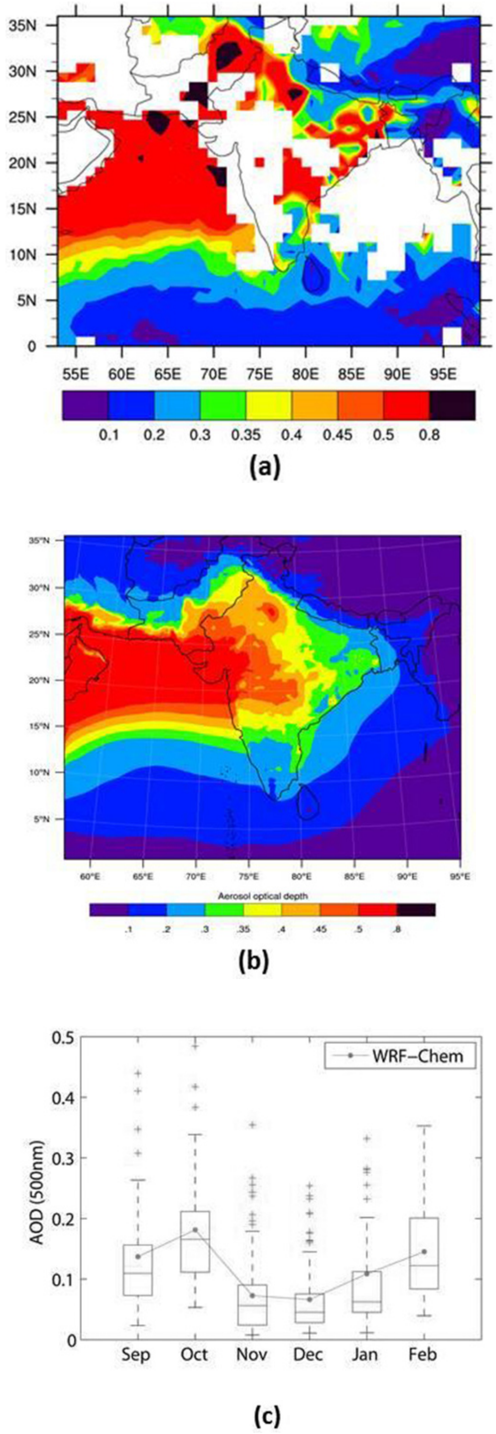


Figure 1. (a) August 2011 satellite observations and (b) regional model simulations of the AOD, a measure of the atmospheric abundance of nanometer-size particles that reflect the incoming solar radiation. (c) Regional-model (WRF-Chem) simulated AOD from September 2011 to February 2012, at Nainital, India, compared with the ARM multi-filter rotating shadow-band radiometer (MFRSR) surface observations during GVAX (box-whisker plots).

Knowledge Discovery in Microbial Community Composition and Metabolite Turnover Using Satellite Remote Sensing Data

2012-016-N0

Jack Gilbert, Peter Larsen, Oleg Roderick, and Ilya Safro

Project Description

The molecular characterization of a microbial community's structure is essential for exploring the life support system of planet Earth. In the past five years, the application of direct sequencing of genetic information from environmental samples has revolutionized our understanding of microbial dynamics and, more importantly, of the functional metabolic pathways that mediate the recycling and transformation of all inorganic and organic compounds in every ecosystem.

In the field of metagenomics — the sequencing of DNA extracted from every organism in a community at once — we are developing several products that revolutionize the exploration of the microbial function and that are directly relevant to understanding microbially mediated remediation, carbon turnover, and the potential for microbial biofuel production. We have used metagenomic data collected from the surface waters of oceanic provinces and terrestrial soil sites across Europe and America to develop two techniques: (1) predictive relative metabolic turnover (PRMT) and (2) microbial assemblage prediction (MAP). The techniques use environmental information to predict the consortia of microbial species present and the functional capacity of turnover metabolites (e.g., lipids, carbon dioxide, pollutants). The environmental parameters can be obtained from satellite remote sensing data. By defining the relationships between the parameters and the microbial dynamics, researchers can extrapolate a community's composition and metabolite turnover through space and time.

Although the tools and prediction methods are currently the most sophisticated in the field, they require further development to reach their full potential. The prediction process could be taken to a new level of scientific discovery by leveraging the high-performance computing resources at Argonne, designing and implementing advanced mathematical inference and knowledge discovery tools, and applying them to experimental data — the goal of this project is to develop global microbial weather maps that can forecast and hind-cast microbial activity, which will thus focus our search for relevant microbial biochemistry. Our techniques enable the prediction of thousands of metabolites in a single system; we want to increase that capability to tens of thousands of metabolites in thousands to millions of systems over hundreds of time points. The calculations required to do this need high-performance computing.

The questions we want to answer are an integral part of the microbiology challenge for current specialists, and addressing these problems at different scales of resolution requires exascale computation.

Mission Relevance

The project is relevant to DOE missions in science and environment. DOE scientists can use the predictions of surface-level communities to identify areas where microbial consortia capable of specific activities associated (e.g., with remediation) exist. Another DOE area of interest is exploring microbial dynamics in tundra ecosystems and refining the regional- and local-scale predictions of carbon turnover associated with surface microbial communities. The use of the tools has been recognized by BER as having the potential to help focus research efforts by highlighting areas with a high probability of error in these models. These areas could be subject to further research or site-directed research (e.g., next-generation ecosystem experiments [NGEE]).

FY 2012 Results and Accomplishments

In FY 2012, we explored the implementation of MAP/PRMT for an increasingly high-throughput framework (Figure 1) and were working to improve the accuracy of predictions and the ability of the tools to handle larger data sets. We also worked on automatic learning and extrapolation tools that have better speed, computational tractability, and analytical accuracy than previous approaches. The existing and new strategies are compared in Figure 2. To prepare for problems at extreme computational scales (ultimately, exascale), we looked for opportunities to parallelize certain aspects of the data analysis — in this instance, we were able to improve the parallelization of the Bayesian network generation tasks by using an approach that involves boosting relatively low-quality Bayesian networks obtained in parallel over very short times and combining them into one strong candidate. Thus, we improved the use of Banjo alone with regard to score and time, and we also removed, through parallelization, a bottleneck in the prediction process that did not allow large data sets with a large dimension to be processed.

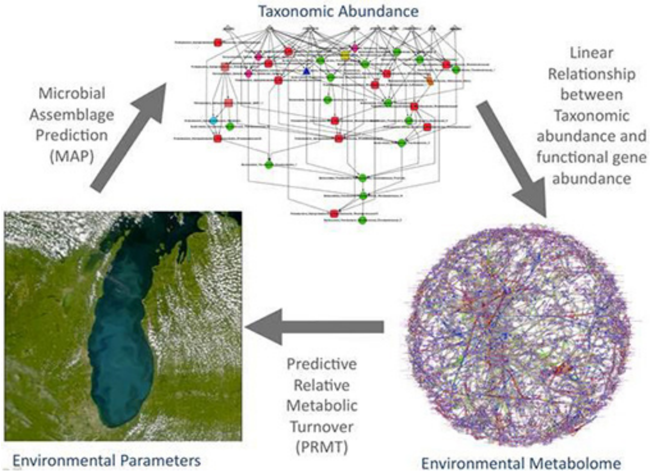


Figure 1. Interconnectivity between measured or modeled environmental parameters, MAP, and PRMT.

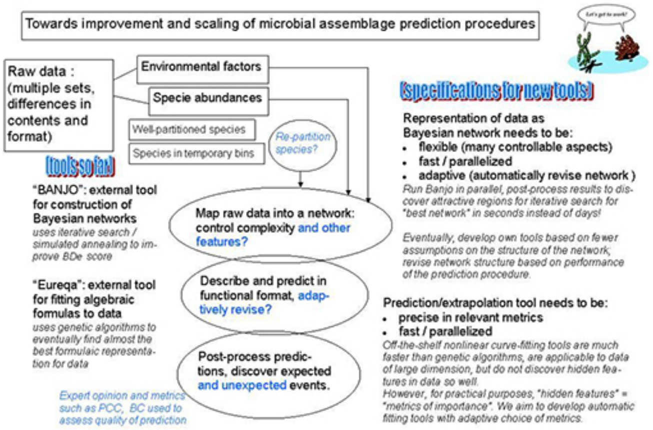


Figure 2. Workflow for analytical development of improvements to the Microbial Assemblage Prediction (MAP) model environment for improved speed, accuracy, and interpretation of microbial community sequence data.

To summarize the results of this year's work:

- We researched a number of options for representing biological data in mathematical models.
- We developed and partially tested mathematical tools for better predictions of microbial abundances in data sets of large magnitude.
- We developed tools and practices that are sufficient to achieve proof of concept for problems involving hundreds of variables.

Proposed Work for FY 2013

We do not expect to align the methods with MGRAST but do plan to implement a new model that works on a global scale. Specifically, we will apply the advances made in Year 1 to predict microbial community structure by using data from the DOE Earth Systems Model and Community Land Model.

Carbon Flux from Thawing Permafrost: Development of a Predictive Model Linking Microbial Activity and Biogeochemistry with Carbon Metabolism

2012-074-N0

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Project Description

The potential impact of climate warming in permafrost regions is a source of uncertainty in climate model predictions. Current global models predict terrestrial source/sink dynamics of greenhouse gases based on vegetative growth responses to environmental forcing factors, assuming that changes in the amount of organic carbon stored in soils can be predicted by these responses. These predictions are based largely on observations in temperate and tropical ecosystems, which do not apply to permafrost-affected soils. This project assesses the feasibility of developing predictive systems models derived from an understanding of the biogeochemical constraints on microbially mediated carbon metabolism as a means for upscaling decomposition processes occurring at sub-millimeter scales to the larger scales required to model the impacts of climatic change. Our objectives are to (1) develop and test a laboratory mesocosm system for evaluating the impact of key environmental drivers on microbially mediated carbon transformations and mineralization rates in permafrost-affected soils and (2) evaluate the potential for using multidisciplinary data to develop biogeochemical system-level models capable of predicting carbon fluxes caused by changing environmental drivers in permafrost regions.

Mission Relevance

This project is relevant to DOE's missions in basic science and the environment. A primary goal for DOE's environmental mission, and the basic science that supports it, is to develop the predictive understanding of Earth's climate and environmental systems needed to make informed decisions on energy use and production. Soils of the northern circumpolar region store one of the planet's largest reserves of carbon. Warming is expected to increase microbial activity, decompose perennially frozen organic deposits into CO_2 and CH_4, and return carbon sequestered for tens of thousands of years to the global carbon cycle. The amount and rate of release of these greenhouse gases from thawing permafrost and the extent to which their release will accelerate climatic change are largely unknown.

FY 2012 Results and Accomplishments

In 2012, we

- Obtained soil samples from three different soil horizons at three sites spanning a latitudinal gradient of arctic tundra ecoregions;
- Characterized these samples, standardized the sample handling, and developed analytical protocols appropriate to the unique and often problematic features of Arctic soils;
- Improved capabilities for storing, subsampling, and manipulating frozen soils and acquired/installed the instruments needed to automate measurements of mesocosm carbon fluxes;
- Designed/assembled an incubation system to maintain precise low temperatures for the mesocosms;
- Characterized the carbon chemistry of organic matter in the soil samples using solid-state ^{13}C nuclear magnetic resonance spectroscopy; and
- Generated inventories of the microbes in each sample by targeting a broadly occurring gene found in all microorganisms (encoding ribosomal RNA).

The soil horizons represented include: (1) the surface organic horizon of the seasonally thawed active layer, (2) the mineral horizon of the active layer, and (3) the mixed (cryoturbated) organic and mineral horizons of the upper permafrost. Analyses of the carbon chemistries of the samples (Figure 1) indicate that the active organic layers of all sites are more dominated by *O*-alkyl structures consistent with polysaccharides typically found in fresh plant and microbial tissues (e.g., cellulose, chitin), whereas the permafrost soil generally has a higher proportion of alkyl structures (considered to be a more biologically stable form of organic carbon in soils). Principal coordinates analysis (PCoA) of the datasets (Figure 2) illustrates microbial community composition differs between permafrost and both active layer horizon types across the three sites.

Proposed Work for FY 2013

In 2013, we plan to

- Design, prioritize, and conduct mesocosm incubation experiments encompassing a gradient of environmental conditions and responses required for a predictive model;
- Monitor CO_2 and CH_4 fluxes throughout each experiment and characterize the biomass and metagenomes of microbial communities, soil carbon forms, and geochemical properties at initial, intermediate, and completion times for each experimental cohort; and
- Explore the use of Fourier transform infrared spectroscopy and non-resonant inelastic x-ray scattering for further characterizing carbon chemistries.

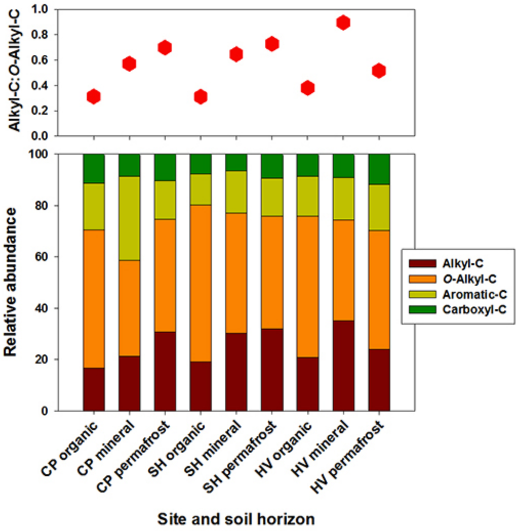

Figure 1. The lower portion of the graph shows the relative abundance of four organic carbon types as characterized by solid-state ^{13}C nuclear magnetic resonance in the active layer organic, active layer mineral, and permafrost soil horizons at three tundra sites (CP, SH, and HV). The top portion of the graph shows the ratios of alkyl-C to O-alkyl-C for each horizon, which are used to assess decomposition stages; higher ratios indicate a more decomposed state. The ratios shown suggest the degradation state of organic matter in the samples varies with soil horizon and across sites, which should provide the gradients needed to facilitate predictive model development.

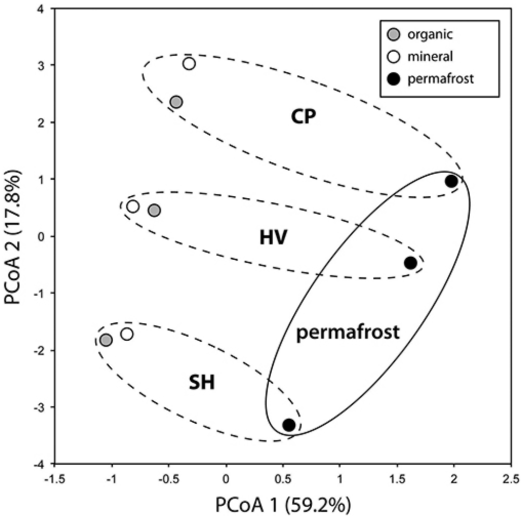

Figure 2. PCoA analysis of the datasets illustrates a clear separation in microbial community composition between permafrost and both active layer horizon types along the first PCoA axis. The second PCoA axis also suggests that a microbial community gradient exists across the three tundra sites (CP, SH, and HV).

Modeling the Interactions of Biophysical, Biogeochemical, and Microbial Dynamics in Permafrost-Affected Soils: from Pore Scale to Regional Scale

2012-205-N0

Zhaosheng Fan

Project Description

High-latitude regions contain approximately 30–60% of world's terrestrial soil organic carbon. Over the past decades, mean annual air temperatures in high-latitude permafrost regions have increased by 0.2–0.3°C per decade and will probably increase another 4–7°C by 2100. Because of their huge carbon stocks and great warming potential, boreal and tundra ecosystems have great potential to drive important interactions and feedback with the Earth's climate.

The objective of this work is to improve our quantitative and predictive understanding of high-latitude soil carbon cycling and its potential role in altering greenhouse gas concentrations in the atmosphere and thus, global climate. To achieve this goal, we will develop mechanistically based mathematical models to represent and simulate the fundamental and important interactions of soil physical, hydrological, geochemical, biogeochemical, and microbial community dynamics. We will then use the developed models to investigate the mechanisms controlling high-latitude soil carbon dynamics and better evaluate the relationship between high-latitude regions and the global carbon cycle.

Mission Relevance

This project is relevant to DOE's mission in basic science and the environment. One of DOE's primary missions is to provide quantitative and predictive understanding of how terrestrial ecosystems can affect atmospheric greenhouse gas concentration changes due to the large carbon stocks in these ecosystems. There is a need to understand the relationship between changing climate and terrestrial ecosystems. The outcome of this work will help to improve projections of the role of high-latitude ecosystems in the context of climate change.

FY 2012 Results and Accomplishments

We developed a mechanistically sophisticated process-based model to simulate the coupled physical, hydrological, and biological processes. The fundamental properties and processes considered in the model include spatial variations in soil physical properties, soil water flow and carbon movement, microbial dynamics (e.g., microbial growth, metabolism, and death), physical and chemical protection of soil carbon, and biogeochemical dynamics. We then used the model developed to examine the factors that control the soil carbon dynamics in two high-latitude black spruce ecosystems, one with permafrost and one without permafrost. We used high-temporal-resolution (i.e., hourly) field observation data (including soil temperature and moisture) at different soil depths to drive the model.

The results show that soil carbon in these two black spruce forest soils is strongly controlled by parameters associated with the soil carbon quality and microbial community dynamics, highlighting the urgent need to better discern those key parameters in future experiments and represent soil microbial dynamics in the existing ecosystem models. Water movement carried fresh carbon to the deep soil, which has the highest soil carbon stock, such that it stimulated decomposition of deep and old soil carbon as a result of the introduction of fresh carbon from the top soils with young soil carbon. Depending on soil drainage conditions, thawing of permafrost due to climate change may significantly affect surface topography (formation of thermokarst), either by enhancing drainage or by impounding water due to surface subsidence. Our results suggest that soil carbon stocks in sites with the formation of thermokarst are more vulnerable to climate change.

Proposed Work for FY 2013

The task for FY 2013 is to expand our current soil models by including more fundamental properties and processes that are poorly represented in the existing earth models. We plan to examine the contribution of fungal-, microbial-, and vegetation-derived carbon to soil organic carbon and to investigate what factors control those contributions. Since our model results suggest that quality of soil carbon is the most important factor controlling the vulnerability of high-latitude soil carbon to climate change, the contribution of carbon derived from different sources to total soil carbon will provide us with critical information about the quality of soil carbon across different ecosystems and its response to climate change.

We will develop a process-based model to better simulate the release of carbon dioxide and methane from soil–water systems. Carbon dioxide and methane are the two most important anthropogenic greenhouse gases. The improved model will help us to better understand soil carbon dynamics in peatland and wetland ecosystems and their responses to climate change (e.g., hydrological and vegetation change).

Developing, Improving, and Testing Methods for Predicting Spatial and Vertical Distributions of Soil Organic Carbon at Regional Scales

2012-206-N0

Umakant Mishra and John Krummel

Project Description

Perennially frozen soils of the northern circumpolar region (19 million km^2 or 16% of the global soil area) store the largest quantity of soil organic carbon (SOC) in the terrestrial biosphere. Polar regions will likely experience much higher temperature increases (3.2–3.5°C by 2100) than temperate or tropical regions over the next century. Therefore, high-latitude SOC stocks, which are preserved in large part because of low temperatures, are potentially vulnerable to the global carbon cycle.

Lacking high-latitude observations, global estimates of SOC stocks substantially underestimate permafrost-affected SOC. Current estimates of SOC stocks in permafrost-affected soils have been made by stratifying the study area, averaging point observations of SOC stocks within each stratum, and multiplying by the areal extent of that stratum. Observations rarely extend below the upper meter of the soil profile, even though high-latitude soils often contain considerable deep SOC. Consequently, estimates of total SOC stocks in high-latitude regions remain highly uncertain; current assessments suggest that the total amount of frozen carbon in permafrost soils could be equal to or even double the amount of carbon presently in the atmosphere. Recent studies have also recognized the need for more accurate assessments of the spatial heterogeneity of SOC stocks in permafrost-affected soils. This study

- Estimates spatially resolved SOC stocks to bedrock, distinguishing active-layer and permafrost-layer stocks, on the basis of geospatial analysis of soil profile observations and spatially referenced environmental variables for permafrost affected soils;
- Quantifies the prediction errors and uncertainties associated with the estimates; and
- Investigates the environmental controls that determine regional-scale SOC stocks.

Mission Relevance

This research is relevant to DOE's missions in science and the environment. DOE and other agencies now demand tighter coupling and iteration between empirical studies and model development — where the uncertainties in model predictions will identify priorities for new observations and experiments used to improve and test new models. This study will produce spatially distributed estimates of permafrost SOC stocks, which are important for development and testing of Earth system models (ESMs). Outside of DOE-BER, agencies such as NSF (the National Science Foundation), NASA (National Aeronautics and Space Administration), and USDA (the U.S. Department of Agriculture) (as well as private foundations) are prioritizing research related to climate change, coupled natural and human systems, ecosystem services, and land-use/land-cover change impact on SOC stocks.

FY 2012 Results and Accomplishments

We collected environmental datasets (such as digital elevation models, land cover types, long-term average annual temperature and precipitation, and bedrock and surficial geology data) from various sources for the state of Alaska. These included data for 422 geo-referenced SOC profiles from the National Soil Survey Characterization database. We also began collecting these datasets from the entire Northern circumpolar region, which we will use to develop new and improved predictions of the spatial variability of SOC stocks at 90-m spatial resolution across the Northern permafrost region.

We also began investigating the spatial heterogeneity, environmental controls, and prediction accuracy for SOC stocks across geospatial models and ESMs. We will compare SOC estimates from four geospatial approaches and four ESM estimates to evaluate the spatial heterogeneity of SOC stocks for Alaska (Figure 1). We will evaluate environmental controls of soil wetness, near-surface air temperature, and net primary productivity on SOC stocks across geospatial model and ESM estimates. This study will show how the environmental controls that govern accurate predictions of SOC stocks change as a function of the spatial resolution used by different models.

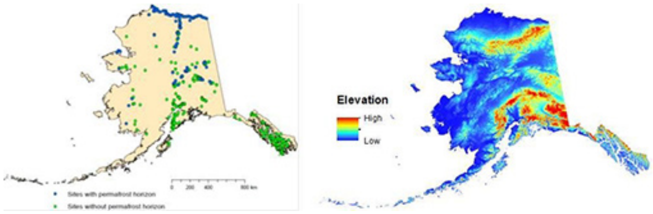

Figure 1. SOC profile observations (left) and digital elevation model (right) that will be used to predict SOC distribution across Alaska.

Proposed Work for FY 2013

We will predict the (1) spatial variability and environmental controls of active-layer, permafrost, and whole-profile thickness across Alaska at a 60-m spatial resolution and (2) potential loss of permafrost thickness under anticipated warming due to the moderate emissions scenario proposed by the Intergovernmental Panel on Climate Change. We will also document current knowledge about the characterization of soil carbon in permafrost-affected soils and potential vulnerability to changing climatic conditions. This effort will outline future research challenges and opportunities for scientists working to improve estimates of the quantity and decomposability of carbon stored in permafrost-affected soils. We will also continue to collect environmental datasets from the Northern circumpolar region.

Environmental Proteomics

2012-207-N0

Carol S. Giometti

Project Description

While the metagenome sequence provides a view of the potential metabolic activity of an ecosystem, the hypotheses and models derived from such sequence information should be validated by confirming that the predicted processes exist. The intent of the project is, therefore, to focus on ecosystems for which the soil chemistry is characterized and the metagenome sequence is readily available in order to develop the techniques needed to extract and identify the proteins present in the soil matrix. The hypothesis guiding the research is that protein activities harbored in soil structures and which regulate the organic carbon decomposition efficiency can be extracted and linked to specific gene sequences present in the corresponding metagenome sequence. The objectives of the project are to:

1. Investigate methods for the efficient extraction of proteins from soils and sediments with varying structures and complexities and
2. By using metagenomics RAST (MG-RAST), enable the linking of metagenome sequences with the peptide sequence in the context of soil samples of interest.

Mission Relevance

Climate change is a subject of international concern, and the management of carbon is central to developing and implementing approaches to mitigating the long-term effects of global warming. A core mission within DOE Biological and Environmental Research (DOE-BER), through both its Biological Systems Science and Climate and Environmental Research Divisions, is to support studies of the molecular processes involved in the terrestrial carbon cycle as well as the related topic of biofuel sustainability. This project supports that mission. In order to mitigate changes to the natural carbon cycle processes, we must first understand those processes and how they are regulated.

FY 2012 Results and Accomplishments

This project began quite late in FY 2012. A literature survey was done and data analysis was completed in order to be able to deliver a poster presentation on the topic. MG-RAST tools were explored, and a proteomics dataset from soil samples collected at Fermi National Accelerator Laboratory (Fermilab) was used to get an initial view of how proteomics data can be interfaced with current MG-RAST tools.

Proposed Work for FY 2013

During FY 2013, our focus will include the following:

- Demonstrating that detectable amounts of protein can be extracted from soils of varying composition by using peptide mass spectrometry and
- Doing a technical evaluation of proteomics tool development for implementation in MG-RAST.

FY2012
annual report

DIRECTOR'S GRAND CHALLENGE

Beyond Li-Ion Battery Technology for Energy Storage

2010-185-R2

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Project Description

The energy potential of lithium (Li) metal approaches that of gasoline, but today's battery manufacturers have not yet unlocked it. Today's Li-ion batteries may provide acceptable power for hybrid electric vehicles (HEVs) and all-electric vehicles (EVs), but they do not provide sufficient range. This limitation and the absence of a battery-charging infrastructure have limited public interest in EVs, particularly for long-distance travel. A breakthrough in Li-air battery technology could greatly increase the possibility of extending the electric range of these vehicles while reducing battery cost and weight. Successful implementation of nonaqueous Li-air cells has been hampered by four problems that have limited electrochemical performance: (1) the nonaqueous electrolytes are unstable at high potentials and easily oxidized by the oxygen released during charge, thereby seriously limiting cycle life; (2) during discharge, the solid and insoluble lithium peroxide (Li_2O_2) and/or lithium oxide (Li_2O) products are deposited on the surface or within the pores of the carbon cathode, clogging the pores and restricting oxygen flow; (3) poisoning of the lithium electrode due to oxygen crossover destroys the integrity and functioning of the cell; and (4) commonly used cathode catalysts, such as manganese dioxide (MnO_2) or Mn metal, do not access the full capacity of the oxygen electrode or enable sufficiently high rates.

To tackle these challenges, this project is focusing on resolving the severe limitations of the electrolytes and electrode catalysts in present-day Li-air cells. The goal is to enable a Li-air battery system with exceptionally high energy density and reversibility. We are using approaches that combine innovative advanced research on electrode, electrolyte, and catalytic materials, extensive computer modeling, and advanced characterization techniques.

Mission Relevance

The major benefit of this research will be the development of a reversible Li-air battery that provides many times the energy density of state-of-the-art Li-ion batteries for powering EVs. Designing and discovering new materials for the Li-air technology are relevant to the DOE mission of developing new energy technologies to contribute to U.S. energy security. The technology can also benefit many Department of Defense military applications that require very high energy density, such as satellite, EV tank, and military vehicles for silent watch and operation. Customers will be the automotive industry, satellite industry, and the military. Also, if the technology is successful for large batteries, it can be easily scaled down for consumer electronics applications.

FY 2012 Results and Accomplishments

There are many challenges in developing energy storage based on lithium oxygen redox couples, but the most important task is to discover an electrolyte system that is stable with respect to reduced oxygen species. Without a solvent system that can reset chemical attack by lithium superoxide Li_2O_2, and the electrochemical potentials required to oxidize these species back to oxygen, it is difficult to advance understanding of the Li-O_2 system. To tackle the challenge of discovering stable electrolytes for the oxygen reduction reaction, we employed several approaches, theory, and electrochemical analysis and synthesis.

Initial work focused on using propylene carbonate (PC) as the organic solvent for the electrolyte, since a report by Bruce et al. [T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, P. G. Bruce, *J. Am. Chem. Soc.* 128, 1390 (2006).] indicated lithium air was a suitable electrolyte. This was proven to be false; the PC was decomposed by the reduced oxygen species. We learned that caution is needed when dealing with a chemical reaction system and overinterpreting data. We also discovered that PC was vulnerable to attack by superoxide. We shifted our effort to ether-based solvents for the formation of electrolytes.

We investigated the decomposition pathways of dimethoxyethane (DME) by the chemical reaction with the major discharge product, Li_2O_2, by using theoretical methods. We carried out the computations by using small Li_2O_2 clusters as models for potential sites on Li_2O_2 surfaces. The computations suggested that decomposition of ethers can occur on certain sites on the Li_2O_2 surfaces involving hydrogen abstraction and subsequent reactions with oxygen, which leads to oxidized species such as those on the surface of Li_2O_2 (Figure 1). The most favourable site is a Li-O-Li site that may be present on small nanoparticles or as a defect site on a surface. Minor decomposition could also occur on other types of sites with a similar reaction mechanism. This electrolyte decomposition (electrolyte with hydrogen atoms) may influence the crystal growth, nanomorphologies of the discharge products, and charge overpotential.

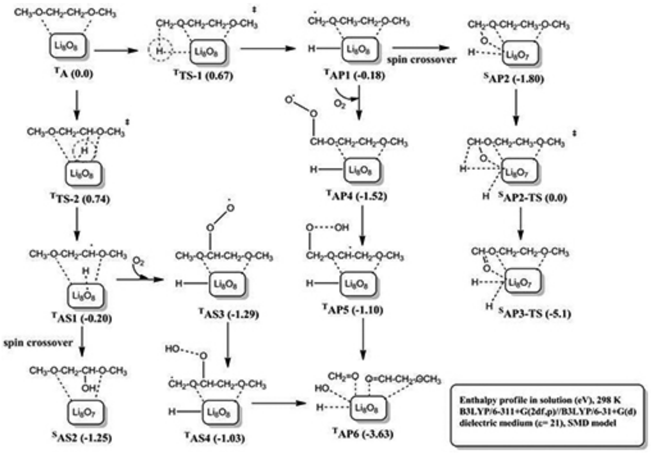


Figure 1. Predicted enthalpy profile in solution (enthalpies of reactions and enthalpy of activation) for various reaction steps during the decomposition of DME by triplet $(Li_2O_2)_4$ cluster at the B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d) level of theory. All energies are given in eV, w.r.t. initial reactants the lowest energy $(Li_2O_2)_4$-DME complex. The superscripts T and S represent the triplet and singlet states. The transition state labels TS1 and TS2 correspond to the hydrogen abstraction from primary (CH_3) and secondary (CH_2) carbon atoms, respectively.

On the basis of the apparent enhanced stability of the ether electrolytes, much of the experimental work shifted to using polyether-based electrolytes (Figure 2). Initial data indicated that 1NM3 and tetraglyme (Figure 3) would be suitable solvents for the electrolyte. Our initial theory calculations indicated that 1NM3 is much more stable than PC. Preliminary work using these solvents indicated that cells can be cycled at low potentials for long periods. For 1NM3 solvent, with a silane-based structure, much higher energy efficiency and lower charge overpotential were achieved. For another ether-based solvent, TEGDME, a longer cycle life was achieved (over 50 cycles with limited capacity voltage profiles). These data had great promise, in that much lower potentials on the charge cycle tended to indicate that the oxide oxidation reaction was much more facile in this electrolyte. However, as the investigation proceeded, it became apparent that the electrolyte was not stable in the reactions. Infrared investigation of the electrolyte showed significant changes. The new vibrational signals were in the region associated with C=C modes. In fact, a simple electrochemical test that involved “charging” the cell, which had never been exposed to oxygen, achieved potentials similar to those obtained when the cell was run in Li-O_2 mode. This result points out the complexity of the chemistry in this system. While O_2 evolution is occurring in the charge cycles, solvent decomposition competes effectively at the same potential. A comprehensive investigation of the electrochemical stability of the electrolyte solutions was carried out. Many factors that influence their stability were identified. The investigation indicated that water is a much more important impurity than previously thought. It is generally thought that small amounts of water (<10 parts per million) cause hydroxide formation in the presence of lithium but are not significant in the overall reaction scheme. A systematic investigation of the role of impurities suggests the possibility of transition between $1e^-$ and $2e^-$ oxygen reduction reaction (ORR) products. During this detailed electrochemical study, the existence of superoxide as the initial oxygen reduction product was confirmed, and the gaseous decomposition products were identified by using differential electrochemical mass spectrometry (DEMS).

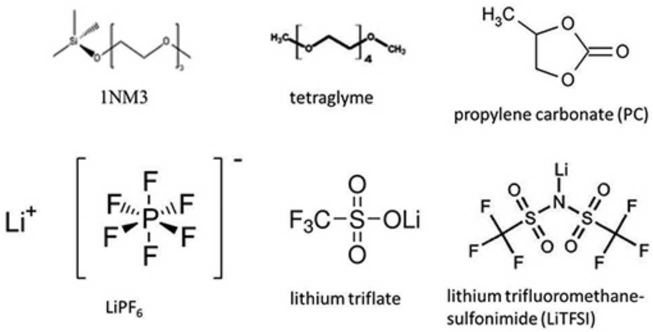


Figure 2. Chemical structures of solvents and salts that make up electrolyte solutions.

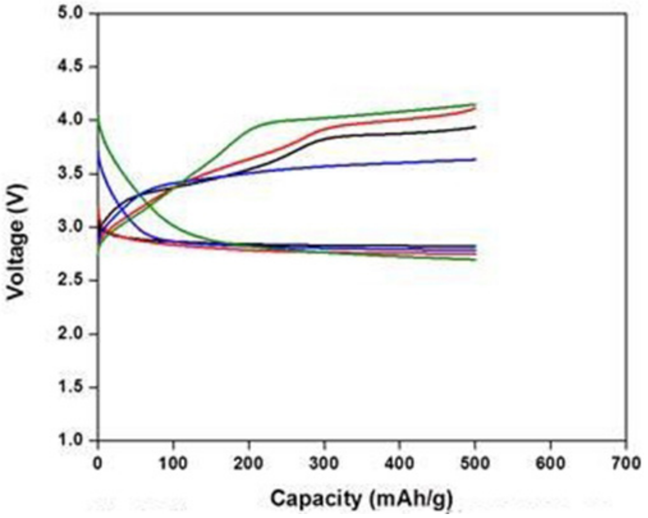


Figure 3. First and tenth cycles of 1NM3-$LiSO_3CF_3$ or TEGDME-$LiSO_3CF_3$ electrolyte with limited capacity of 500 mAh/g at a constant current density of 100 mA/g (MnO_2/C cathode). (The plateau of charge curve in the 1NM3 electrolyte dropped to 3.5 V after 10 cycles, and the overpotential for TEGDME became large after 10 cycles.)

Moreover, the complexity that the lithium metal added to the solvents’ stability had been underestimated. We identified major interactions with the solvent, O_2, and the Li metal that complicate the chemistry. We carried out an experimental study (*in situ* and *ex situ* XRD [x-ray diffraction], FTIR ([Fourier transform infrared] spectroscopy) and computational study (density functional theory [DFT]) of the electrolyte decomposition at a lithium anode using the tetraglyme electrolyte. The results indicate that the crossover of O_2 from the cathode to the anode in Li-air cells causes different decomposition reactions to occur at the Li anode than those that occur at a Li anode in a Li-ion battery. The evidence indicates formation of LiOH as well as carbonates at the anode in a Li-O_2 battery with a tetraglyme-based electrolyte, as shown in Figure 4. In contrast, ether reactions with lithium metal result in the formation of CH_3OLi, CH_3Li, and polymeric layers. The DFT calculations provide a mechanism for decomposition involving reduction of the electrolyte followed by O_2 from crossover from the cathode. The effect of the Li-O_2 anode ether/O_2 reactions on the cycling performance depends on the cell configuration (electrode loadings, oxygen pressure, etc.). This study provides evidence that controlling reactions of ethers at the lithium anode through suitable membranes or passivation films will be important for achieving good performance of Li-O_2 cells based on ether electrolytes.

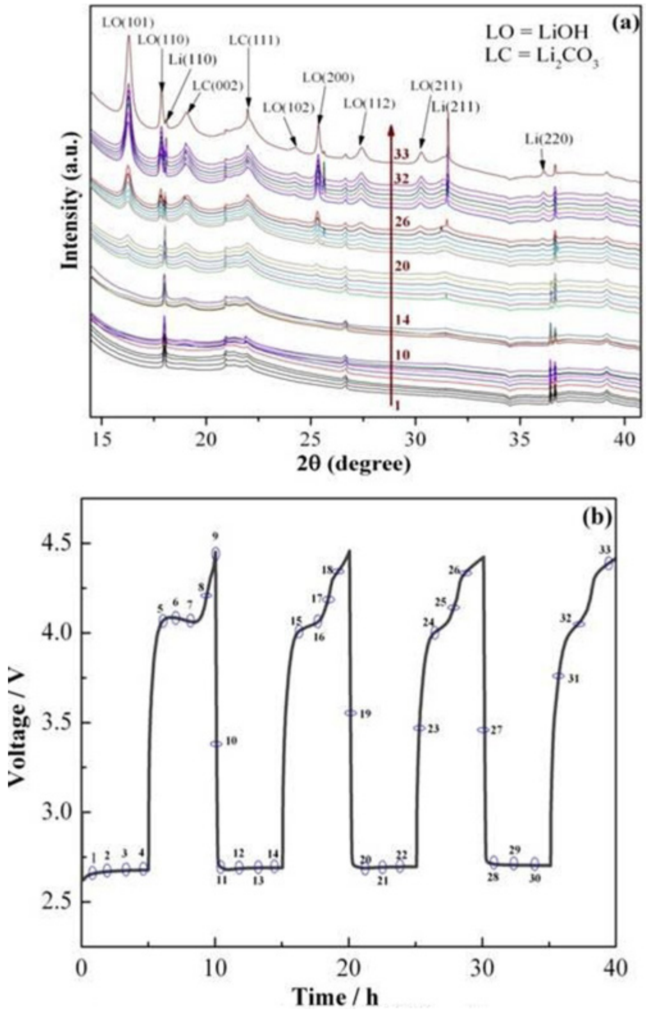


Figure 4. (a) In situ *XRD patterns of Li anode and LiOH formation during the operation conditions, and (b) corresponding voltage versus time profiles. Numbers on XRD data correspond to those on voltage profile.*

The nature of the oxygen reduction product is as important as the stability of the electrolyte. The reliable identification of the lithium oxides species Li_2O_2 is vital to the study of Li-O_2 batteries. Previous x-ray diffraction studies of Li_2O_2 resulted in Féher and Föppl proposing two disparate structures [for a discussion of these structures see Chan, M.K.Y., E.L. Shirley, N.K. Karan, M. Balasubramanian, Y. Ren, J.P. Greeley and T.T. Fister (2011). "Structure of Lithium Peroxide." Journal of Physical Chemistry Letters **2**(19): 2483-2486.]. We used a combination of first principles spectra computed using the Bethe-Salpeter equation, measured inelastic x-ray scattering data, and DFT total energies obtained from hybrid functionals to assess the difference between the two proposed structures. We found that all the spectroscopic and first principles results pointed to one (Föppl's) proposed structure as the appropriate one for Li_2O_2. Our work provides important benchmarks for the identification of this crucial discharge product.

The single electron reduction product is a superoxide, which is a very active oxidant and is only detected as a short-lived intermediate in the electrochemical process. The superoxide species can react in a number of different ways: electrochemical, reduction to peroxide, disproportionation to oxygen and peroxide, or solvent oxidation. Understanding these different reaction pathways and the factors that influence them is critical in under-rating the Li-O_2 system. For example, a key question regarding the oxide oxidization reaction was "How can nonconductive Li_2O_2 enable the electronic conductivity required for the electrochemical reaction?" A detailed investigation of the nature of the Li_2O_2 produced during the oxygen reduction reaction revealed surprising data. The magnetic properties of the Li_2O_2 discharge product formed in an ether-based electrolyte were investigated by using experimental and theoretical techniques. SQUID (superconducting quantum interference device) measurements show evidence of paramagnetism in the Li_2O_2 discharge product after contributions from the carbon cathode material are subtracted. This result was unexpected because Li_2O_2 is generally assumed to be nonmagnetic.

Magnetic measurements were also carried out on commercial Li_2O_2 to see if it also showed the presence of a magnetic moment. Both SQUID and EPR (electron paramagnetic resonance) measurements indicated that the commercial Li_2O_2 also has a magnetic moment. The commercial Li_2O_2 contains nanoparticles that range from 200 to 500 nm, compared to about 30 to 70 nm in the discharge product. A comparison of the EPR spectra of Li_2O_2 and LiO_2 provided evidence that the spin was due to a "superoxide" -type structure in the powder sample, although it is distinct from bulk LiO_2 both with regard to its structure and its much smaller number of spins. Density functional calculations provided an explanation of the observed magnetism; they found that "superoxide-like" O_2 surface groups with unpaired electrons exist on some *stoichiometric* Li_2O_2 crystalline surfaces and on nanoparticle surfaces, as shown in Figure 5. The number of spins predicted by theory is approximately consistent with the magnetic measurements of discharged Li_2O_2 product and the commercial product. The presence of magnetism in the Li_2O_2 discharge product, reported here for the first time, may play an important role in the charge and discharge chemistries of Li-O_2 batteries. The superoxide-like O_2 surface groups with spin could enable an electronic conductivity mechanism needed for reversible formation and decomposition of the Li_2O_2.

Further studies, under a private industry CRADA agreement as well as under Energy Frontier Research Center support, are under way to establish the dependence of the observed magnetism in Li_2O_2 on the type of electrolyte and cathode material used, as are computational studies of electrolyte decomposition on the superoxide-like surface sites.

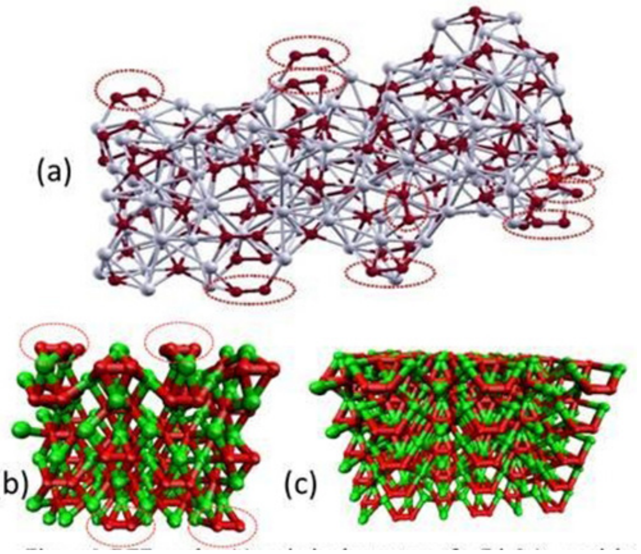


Figure 5. DFT results: (a) optimized structure of a $(Li_2O_2)_{54}$ particle in a high spin state (10 unpaired spins) with red circles denoting superoxide-like structures, (b) optimized lowest energy (100) Li_2O_2 surface structure (high spin S=1 state) with red circles denoting superoxide-like structures, (c) optimized lowest energy (110) Li_2O_2 surface structure (low spin S=0 state).

One approach to improving the high overpotentials observed in the charging reactions of the Li-O_2 cells is to employ a catalyst to lower the activation energy for the rate-determining step. Catalysts may have the added advantage of accelerating the desired reaction enough that undesirable side reactions may become unimportant. Our initial studies using cyclic voltammetry on gold, platinum, and glassy carbon indicated the existence of structure sensitivity indicative of oxygen-substrate interaction dependence. There are clear differences for the reduction potential for O_2 on these different substrates (i.e., catalysts are occurring). It is difficult to find an effacement catalyst for the reaction you want to promote. Lithium-metal oxides with a high formal Li_2O content have been explored as electrocatalysts for rechargeable nonaqueous Li-O_2 cells. Activation occurs predominantly by Li_2O removal, either electrochemically or chemically by acid treatment.

To understand the relatively large capacities and reversibilities gained when these electrocatalysts were employed, detailed structural characterization was performed at Argonne's Advanced Photon Source. We also employed a first principles DFT computation study to understand the chemistry of these systems. We sampled configurations of Li and Li_xO_y insertion into two polymorphs of MnO_2, α- and ramsdellite (R). The results indicate that the equilibrium voltages of Li and Li_xO_y insertion into α-MnO_2 are comparable and similar to the equilibrium voltages for Li_2O and Li_2O_2 formation, which implies the possibility of MnO_2 acting as a Li_xO_y-storage material during cycling in Li-O_2 cells. We also showed that equilibrium voltages of Li_xO_y insertion into α-MnO_2 occur between two phases of Li insertion into α- and R-MnO_2, providing a mixed-valence $Mn^{3+/4+}$ environment for the bulk of the Li-O_2 reaction, which may be of significance for the catalytic properties.

Li_2O removal from Li_5FeO_4 has also been investigated with DFT, showing the formation of nanoporous and amorphized Li-Fe-oxides as the removal progresses. The resultant energies give a reasonable range of voltages when compared to the experimental results.

Our DFT results (Figure 6) were also used to interpret characterization experiments, such as high-energy x-ray diffraction data, XANES (x-ray absorption near edge structure) data, and EXAFS (extended x-ray absorption fine structure) data. The comparisons allow us to suggest the atomistic changes underlying the measured structural changes and contribute toward an understanding of the mechanism of action of these electrocatalysts. For example, by corroborating DFT calculations with x-ray diffraction data, we showed that relative volume changes for Li insertion into hydrated and Li_2O-stabilized MnO_2 can be reproduced to within 10% accuracy. We can therefore use such volume changes to suggest the compositions of the electrocatalysts at various stages of discharge/charge. This behavior is being explored in a continuation of this project through the Center for Electrical Energy Storage (CEES) at Argonne, a DOE Energy Frontier Research Center (EFRC).

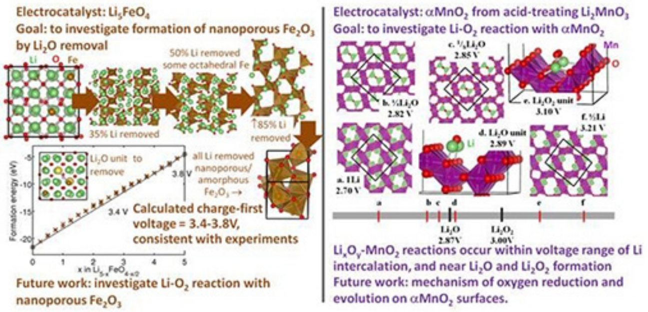
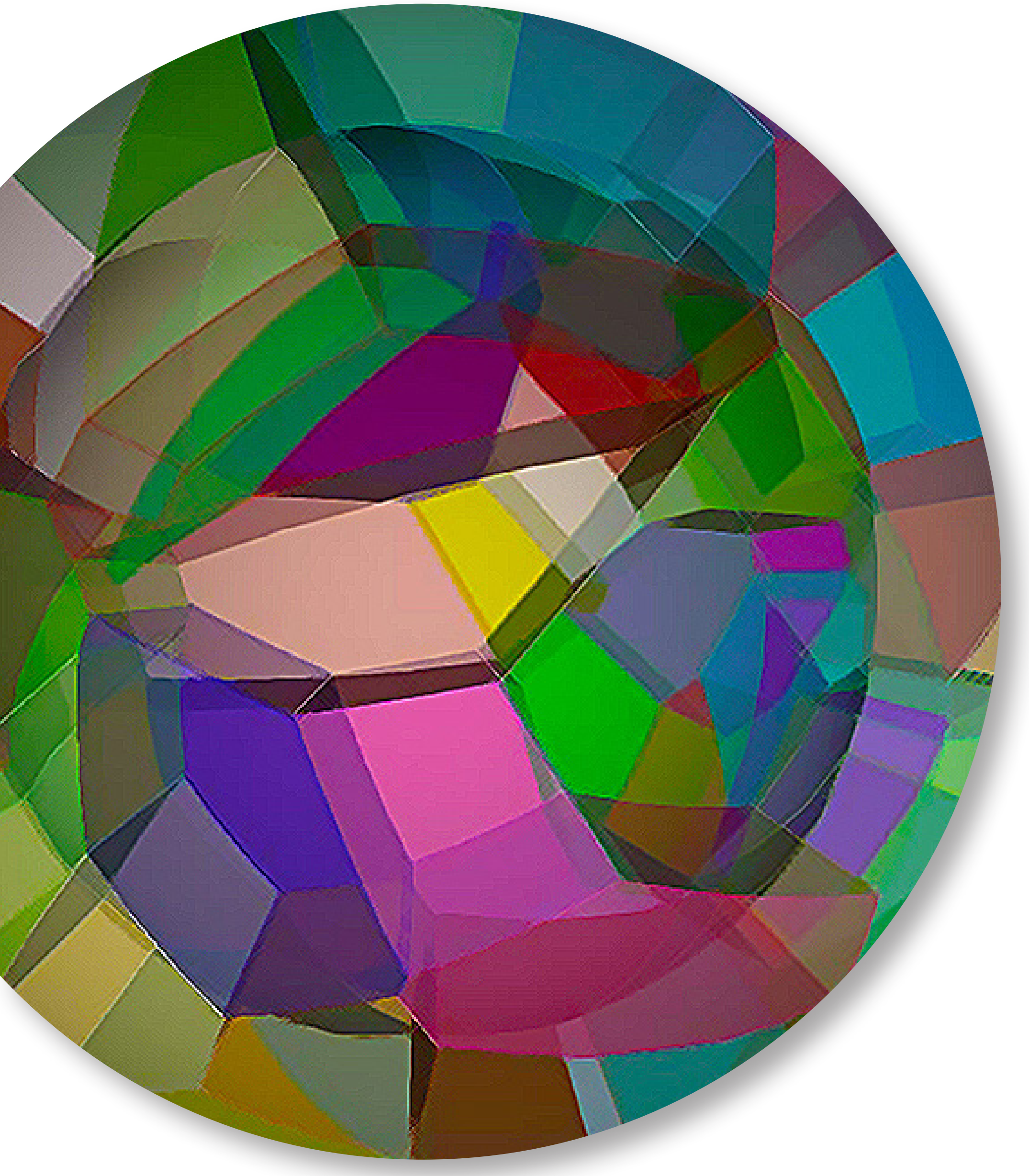


Figure 6. DFT has been used to investigate Fe/Mn oxide as electrocatalysts.

FY2012
annual report

EXASCALE COMPUTER SCIENCE AND APPLICATIONS



Open GATS: An Open Unified Framework for Global Address and Task Space Computing in the Exascale Era

2010-199-R2

Pavan Balaji, Jeffrey Hammond, Ewing Lusk, Nick Romero, and Rajeev Thakur

Project Description

Computing research has produced a rich variety of mature parallel programming models and runtime systems, each with its individual capabilities demonstrated on DOE applications. To take full advantage of the massive parallelism of emerging multi-petascale and exascale systems, these applications need to use the capabilities of multiple models together. A well-known example is an MPI (message passing interface) application that needs to use a threading model within a node to better exploit the shared memory and many cores on the node. However, emerging applications and extreme-scale machines require a richer and more complex interleaving of programming models. For example, how can multimodule applications primarily based on UPC (unified parallel C) or CAF (coarray Fortran) use math libraries written in MPI, such as PETSc, that have had hundreds of programmer-years of development invested in them? Similarly, how can an application written in global arrays (GAs) use load-balancing tools written in Charm++? Can the threading infrastructures of Charm++ and OpenMP coexist within the same application, over the limited resources available on the node? For promoting software reuse, especially for expensive high-performance computing (HPC) software, it is also important that someone can reuse an existing module or library in a new application, irrespective of the programming model in which it was written. The overall goals of this project are as follows:

- Design and investigate an integrated model that provides the capabilities of message passing, as well as global address and task sharing, in an environment where all three models can be used concurrently.
- Formulate a model that will allow applications to take full advantage of exascale hardware using scalable and flexible operating system capabilities.
- Investigate how data-intensive applications can take advantage of advanced input/output (I/O) and storage capabilities built for exascale systems.

Mission Relevance

Carrying out all of DOE's missions (in energy, the environment, and national security) and the science supporting them requires advanced computer-based modeling and simulation on the fastest supercomputing systems. A goal of the Advanced Scientific Computing Research (ASCR) program in DOE's Office of Science is to reach a computing capability of 1 exaflop/second by the end of this decade; this is also known as exascale computing. This project is directly related to this goal, and it includes new exotic architectures and requirements for new methods for programming on these architectures. This project is aimed at initial research that would allow us to propose further relevant topics in this area.

FY 2012 Accomplishments and Results

Over the past few years, we made a lot of progress toward a unified runtime system for exascale computers, in terms of both building the necessary programming interface requirements to sustain this effort and meeting the immediate technical challenge of integrating new functionality into a common infrastructure. Improvements included the following:

- Active messages and topology awareness extensions to the MPICH implementation of MPI,
- Shared memory communication extensions to the MPICH implementation of MPI,
- Improvements for hybrid programming with MPI and threads, and
- Hybrid programming with MPI and GAs

We also made improvements to the OSPRI (one-sided primitives) framework, which allows us to study basic interoperability requirements of one-sided communication models with message-passing models.

This work allowed computational chemistry applications (such as NWChem) to use, for the first time, the entire capability of MPI and scale on the Argonne Intrepid Blue Gene/P system and the University of Chicago Beagle Cray XE6 system. We are also now demonstrating the benefits of our model with other applications in computational biology and molecular dynamics. Some details on our accomplishments follow.

Active messages and shared memory communication extensions: Many large-scale applications have emerged recently and become important in such areas as bioinformatics and social networks. They are often data-intensive and involve irregular communication patterns and complex operations on remote processes. Active messages have proven to be an effective way to parallelize such nontraditional applications, but most current active message frameworks are low-level and system-specific, do not efficiently support asynchronous progress, and are not interoperable with two-sided and collective communications. We presented the design and implemented an active message framework inside MPI to provide portability and programmability, and we explored challenges in asynchronously handling active messages and other messages from the network and shared memory. We tested our implementation with a set of comprehensive benchmarks. Results indicate that our framework has the advantages of overlapping and interoperability, while introducing a modest overhead.

Topology improvements to MPICH: The MPI standard offers a set of topology-aware interfaces that can be used to construct graph and Cartesian topologies for MPI applications. These interfaces have been used mostly for topology construction and not for performance improvement. To optimize performance, we used graph embedding and node/network architecture discovery modules to match the communication topology of the applications to the physical topology of multi-core clusters with multi-level networks. Micro-benchmark results indicated considerably improved communication performance when weighted and network-aware mapping was used. The implementation can also improve the applications' communication and execution times.

Hybrid message passing and shared memory communication: Hybrid parallel programming with MPI for internode communication, in conjunction with a shared-memory programming model to manage intranode parallelism, has become a dominant approach to scalable parallel programming. While this model provides a great deal of flexibility and performance potential, it forces programmers to deal with the complexity of using two parallel programming systems in the same application. We introduced an MPI-integrated shared-memory programming model that is incorporated into MPI through a small extension to the one-sided communication interface. We demonstrated the integration of this interface with the upcoming MPI 3.0 one-sided semantics and described solutions for providing portable and efficient data sharing, atomic operations, and memory consistency. We described using the new interface in the MPICH implementation and demonstrated an average improvement of 40% in the performance of the communication component of a five-point stencil solver.

OSPRI enhancements: OSPRI provides the necessary communication functionality to implement GAs, which is an important instantiation of the PGAS (partitioned global address space) programming model, with significant buy-in from the computational chemistry community. The software design of OSPRI was modeled after MPICH because (1) MPICH is extremely robust software that has been vetted by all major high-performance computing vendors and (2) this approach will streamline the process of formally integrating OSPRI into MPICH as Argonne implements the unified software stack. In FY 2012, we made more progress in understanding OSPRI's various performance characteristics compared with those of the ARMCI model and the MPI RMA (remote-memory access) model. OSPRI consistently achieved the best performance of all the one-sided models. The basis for this was the OSPRI device design, which is more tailored to leadership-class architectures (like Blue Gene/P) and makes better use of hardware resources. OSPRI also optimizes for noncontiguous operations using the low-level active-message capability provided by DCMF, the low-level communication application programming interface (API). The fact that OSPRI is more optimized for Blue Gene/P than ARMCI does not mean it is less optimized for other architectures — it does mean, however, that OSPRI can always be better optimized for the hardware because of the MPICH2-derived device design, which allows for maximum code reuse with targeted replacement when a special implementation is warranted.

Proposed Work for FY 2013

We propose to demonstrate:

1. MPI interoperability with high-level global address space models such as CAF,
2. MPI interoperability with high-level tasking models such as Charm++, and
3. MPI-interoperable active message functionality in applications (possibly computational biology applications, and other applications as necessary).

Seminars

Balaji, P. (2012). "Is Exascale End-of-the-Line for Commodity Computing?" Florida State University (FSU), Tallahassee, FL, January 27, 2012.

Balaji, P. (2012). "Advanced Parallel Programming with MPI." Center for Scalable Application Development Software (CScADS) Workshop on Leadership Computing Platforms, Extreme-scale Applications, and Performance Strategies, Snowbird, UT, July 24, 2012.

Balaji, P. (2011). "Fault Resilient Computing with MPI." Institute of Computing Technologies, Chinese Academy of Sciences (ICT-CAS), Beijing, China, August 23, 2011.

Balaji, P. (2011). "Is Exascale the Last Frontier for Commodity Computing?" Queen's University, Kingston, Canada, March 17, 2011.

Balaji, P. (2011). "Hands-on Introduction to Parallel Programming with MPI." Shenzhen Institute of Advanced Technology (SIAT), Shenzhen, China, September 9, 2011.

Balaji, P. (2011). "Is MPI Relevant at Exascale." Institute of Software, Chinese Academy of Science (CAS), Beijing, China, November 29, 2010.

Balaji, P. (2011). "Is Hybrid Programming the Next Step in the Evolution of HPC." Institute of Computing Technology, Chinese Academy of Sciences (CAS), Beijing, China, December 2, 2010.

Balaji, P. (2011). "Will Existing Programming Models Evolve for Exascale Systems or Die." Center for Development of Advanced Computing (C-DAC), Pune, India, December 23, 2010.

Balaji, P. (2011). "Trends in One-sided Communication Models." Institute of Software, Chinese Academy of Science (CAS), Beijing, China, January 10, 2011.

Runtime Support for Integrating MPI and Accelerator Programming Models for Exascale Systems

2011-038-R1

Rajeev Thakur, Pavan Balaji, and Ewing Lusk

Project Description

The overall challenge of this project is to design a mechanism that will allow both new and existing applications to be programmed for upcoming heterogeneous architectures. More specifically, we need a mechanism that is not only efficient and easy to program but also provides a natural transition path, so that existing applications can use future systems, which may have large numbers of cores per node, including accelerator cores. The main goal of this project is to develop a library and an associated runtime system that provides the ability to manage data movement both for general-purpose central processing unit (CPU) cores and accelerator cores in an integrated, unified manner. The primary idea is to allow different message passing interface (MPI) processes to express data movement ability for shared accelerator cores and general-purpose CPU cores, thereby allowing the runtime system to manage the sharing and taking advantage of the architecture-specific flexibility in data movement and other aspects of resource management. We divided the work into five tasks with deliverables, as follows:

- **Task 1:** Develop a programming interface to provide a collective view of the shared resources to applications.
- **Task 2:** Provide runtime support to allow processes to access shared resources in a coordinated manner. This task includes three subtasks. (1) Allow multiple MPI processes to view and utilize accelerator resources either transparently or with minor modifications to the applications. (2) Dynamically migrate tasks on the available accelerators, which will allow for improved resource utilization and performance. (3) Create a high-level task management library to use this runtime support and provide an easier-to-use interface.
- **Task 3:** Improve runtime performance for data movement. This task includes three subtasks. (1) Provide the ability to pipeline data movement between the accelerator and host-accessible memory and between hosts. (2) Use accelerator-specific, memory-mapping techniques and coordinated direct memory access (DMA) techniques (such as those provided by NVIDIA accelerators and Mellanox InfiniBand adapters) to perform zero-copy communication. (3) Efficiently move noncontiguous data chunks for accelerators.
- **Task 4:** Make improvements to accommodate future architectures, including Intel's Knight's Ferry and AMD Fusion.
- **Task 5:** Integrate and evaluate with applications.

Mission Relevance

All of DOE's missions (in energy, the environment, and national security) and the science supporting them require advanced computer-based modeling and simulation on the fastest supercomputing systems. A goal of the Advanced Scientific Computing Research (ASCR) program in DOE's Office of Science is to reach a computing capability of 1 exaflop/second by the end of this decade, which is also known as exascale computing. This project is directly related to this goal, since accelerator-based architectures are one path to exascale computing.

FY 2012 Accomplishments and Results

In the past two years, significant progress has been made on Tasks 1 through 3. Some initial work on Tasks 4 and 5 was also started. This report describes the accomplishments that were achieved within two subprojects: VOCL and MPI-ACC.

VOCL: Graphics processing units (GPUs) have been widely used for general-purpose computation acceleration. However, current programming models (such as CUDA [Compute Unified Device Architecture] and OpenCL [Open Computing Language]) can support GPUs only on the local computing node, where the application execution is tightly coupled to the physical GPU hardware. We proposed a virtual OpenCL (VOCL) framework to support the transparent utilization of local or remote GPUs. This framework, based on the OpenCL programming model, exposes physical GPUs as decoupled virtual resources that can be transparently managed independent of the application execution. The proposed framework requires no source code modifications. In FY 2011, we did the design and initial implementation of VOCL. In FY 2012, we (1) further developed the implementation and proposed various strategies for reducing the overhead caused by data communication and kernel launching and (2) demonstrated about 85% of the data write bandwidth and 90% of the data read bandwidth compared to data write and read, respectively, in a native non-virtualized environment. We evaluated the performance of VOCL by using four real-world applications with various computation and memory access intensities and demonstrated that computing-intensive applications can be executed with negligible overhead in the VOCL environment.

We also extended the basic VOCL framework to support transparent, live migration of virtual GPU accelerators in a virtualized execution environment. Migration is a critical capability in such environments because it provides support for fault tolerance, on-demand system maintenance, resource management, and load balancing in the mapping of virtual to physical GPUs. Techniques to increase responsiveness and reduce migration overhead were explored. The system was evaluated by using four application kernels and shown to provide low migration overheads. Through transparent load balancing, our system provides a speedup of 1.7–1.9 for three of the four application kernels.

MPI-ACC: Moving data in high-performance computing systems accelerated by GPUs is still a challenging problem. Data communication in popular parallel programming models (such as MPI) is currently limited to the data stored in the CPU memory space. Auxiliary memory systems, such as GPU memory, are not integrated into such data movement frameworks, thus providing applications with no direct mechanism to perform end-to-end data movement. We introduced MPI-ACC, an integrated, extensible framework that allows end-to-end data movement in accelerator-based systems. MPI-ACC provides productivity and performance benefits by integrating support for auxiliary memory spaces into MPI. MPI-ACC's runtime system enables several key optimizations, including pipelining of data transfers and balancing of communication based on accelerator and node architecture. We demonstrated the extensible design of MPI-ACC by using the popular CUDA and OpenCL accelerator programming interfaces. We examined the impact of MPI-ACC on communication performance and evaluated application-level benefits on a large-scale epidemiology simulation. In FY 2011, we started to explore the integration of data movement in GPUs and MPI. In FY 2012, we extended this work and developed additional optimizations.

We also developed shared-memory communication techniques to significantly reduce the cost of intranode communication involving one or more GPUs. Results of experiments showed an increase of up to 2 times in bandwidth, resulting in an average improvement of 4.3% to the total execution time of a halo exchange benchmark. We also extended the shared-memory approach with techniques to perform efficient data movement between accelerators within the same node by using a direct memory access (DMA) -assisted, peer-to-peer intranode communication technique that was recently introduced for NVIDIA GPUs.

Finally, a particular challenge is the transfer of noncontiguous data to and from GPU memory. MPI implementations currently do not provide an efficient means of utilizing datatypes for noncontiguous communication of data in GPU memory. To address this gap, we developed an MPI datatype-processing system that can efficiently process arbitrary datatypes directly on the GPU. We developed a means for converting conventional datatype representations into a GPU-amenable format. Fine-grained, element-level parallelism is then utilized by a GPU kernel to perform in-device packing and unpacking of noncontiguous elements. We demonstrated a several-fold performance improvement for noncontiguous column vectors, three-dimensional array slices, and four-dimensional array subvolumes over CUDA-based alternatives. Compared with optimized, layout-specific implementations, our approach incurs low overhead while enabling the packing of datatypes that do not have a direct CUDA equivalent. These improvements can translate to significant improvements in end-to-end, GPU-to-GPU communication time. We also identified and evaluated communication patterns that may cause resource contention with packing operations, providing a baseline for adaptively selecting data-processing strategies.

Proposed Work for FY 2013

We plan to continue progress on all tasks. Most of the remaining work in these areas relates to using these raw capabilities in higher-level libraries and end applications. Apart from these two tasks, we started working on initial pieces for the remaining three tasks. Specifically, we began investigating unified data movement capabilities and Intel Knights Ferry architectures. We will evaluate the performance and capabilities of VOCL and MPI-ACC on real hybrid parallel applications and benchmarks that use GPUs within a node and MPI across nodes, such as the Scalable HeterOgeneous Computing (SHOC) Benchmark Suite from Oak Ridge.

Seminars

Balaji, P. (2011). "Transparent Virtualization of Graphics Processing Units." Institute of Software, Chinese Academy of Sciences (ISCAS), Beijing, China, August 22, 2011.

Balaji, P. (2011). "Are Graphics Processing Units Viable as Cloud Services?" Tsinghua University, Beijing, China, August 23, 2011.

Balaji, P. (2011). "Towards Virtualized Environments for Using Graphics Processing Units as a Cloud System Service." Shenzhen Institute of Advanced Technology (SIAT), Shenzhen, China, September 8, 2011.

Balaji, P. (2012). "Graphics Processing Units as a Cloud System Service." Shanghai Jiao Tong University (SJTU), Shanghai, China, May 23, 2012.

Balaji, P. (2012). "Fine-grained Resource Virtualization in Cloud Computing Systems." Shenzhen Institute of Advanced Technologies (SIAT), Shenzhen, China, January 4, 2012.

Balaji, P. (2013) "MPI-ACC: A Unified Data Movement Infrastructure for Heterogeneous Memory Architectures." INRIA-ANL-Illinois Petascale Computing Joint Lab workshop, Argonne, IL. November 19, 2012.

Balaji, P. (2012) "Early Experiences with MPICH over the Intel KNF Architecture." Intel Extreme MIC Workshop, Santa Fe, New Mexico. February 22, 2012.

Exascale Data Analysis for Multiphysics Computational Science

2011-106-R1

Michael Papka, Mark Hereld, Thomas Peterka,
Robert B. Ross, and Venkatram Vishwanath

Project Description

In this project, we are developing and implementing our acceleration techniques for data analysis to provide scientists with new capabilities and better performance. We are working in four technical areas to address challenges that are not being exploited, even for petascale computation:

1. The relatively inexpensive cycles on the simulation platform that could be applied to analysis,
2. The computational cycles and memory available on input/output (I/O) processors (e.g., Blue Gene I/O nodes [IONs] and file system server nodes),
3. The computational cycles and memory available on local analysis engines (i.e., fast network attached graphics clusters), and
4. The network bandwidth between simulation and analysis engines.

The outcome will be robust solutions to problems that scientists in many disciplines are struggling with now. As well, the outcome will enable powerful new capabilities and levels of performance for their future research.

Mission Relevance

This project is relevant to DOE's basic science mission — in supporting transformative science — in the areas of climate sciences, biosciences, astrophysics, computational chemistry, high-energy physics, materials science, and nuclear physics. Today's largest computational systems are providing unprecedented opportunities to advance science in these areas. Current DOE leadership-class machines, such as the IBM Blue Gene/P supercomputer at Argonne National Laboratory and the Cray XT system at Oak Ridge National Laboratory, consist of a few hundred thousand processing elements. In the case of FLASH, a multiphysics, multiscale simulation code with a wide international user base, the Intrepid Blue Gene/P supercomputer at the Argonne Leadership Computing Facility (ALCF) is enabling scientists to better model, validate, and verify phenomena in various fields, such as the study of thermonuclear-powered supernovae and high-energy density physics.

FY 2012 Accomplishments and Results

In FY 2011, we integrated efficient "data passing" with the I/O layer to enable full use of the network bandwidth out of IONs. We accomplished this task by modifying common I/O abstraction layers, such as HDF5 and pnetCDF, allowing users to apply new efficient approaches without changing their code. This enhancement was tested with FLASH simulation and several benchmark codes that mimic typical I/O behavior on the Intrepid system at Argonne. We designed and implemented an abstraction layer and application programming interface (GLEAN) for run-time analysis of simulations, and we tested it with both FLASH and Parallel Hierarchic Adaptive Stabilized Transient Analysis (PHASTA) codes on the Intrepid system at Argonne. The Do It Yourself (DIY) library was applied in three analysis applications: parallel particle tracing, parallel information theory, and parallel topological analysis The results indicated a 200% performance improvement in particle tracing, a 59% strong scaling efficiency in information theory, and a 35% end-to-end strong scaling efficiency in topological analysis. Additionally, we worked on analysis of the system logs of the supercomputing resources to better understand resources usage patterns.

We worked closely with Argonne computational teams in materials and cosmology on preparing codes for the ALCF Mira BG/Q supercomputer. We also continued to work with the Flash Center. In particular, we generalized the tools to work on not only the Blue Gene series of computing resources — both P and Q — but also on Cray supercomputers.

We updated our topology-aware mechanisms and reduced synchronization requirements of GLEAN to optimize the performance of MPI-IO implementations on various platforms. This update will greatly benefit the higher-level I/O libraries (including HDF5, pnetCDF, and ADIOS) built on top of the high-level file interface MPI-IO. We worked to continue to promote GLEAN as a new infrastructure for supporting co-processing.

We completed an initial means for transferring GLEAN to Cray systems and making the topology-aware mechanisms more generic. We developed GLEAN for the IBM Blue Gene/Q system. For this implementation, we had to scale our topology aware data movement to fully exploit the 5D Torus of the Blue Gene/Q system. We worked closely with the Argonne Hybrid/Hardware Accelerated Cosmology Code (HACC) cosmology team to incorporate GLEAN as part of their production simulation code base. GLEAN was key to HACC being able to accomplish their early science runs on the Mira Blue Gene/Q system. It achieved up to 160 GB/s I/O performance and successfully read and wrote ~5 PB of data, which is a remarkable achievement. For HACC, GLEAN achieved ~500% improvement over the traditional I/O mechanisms by exploiting the system topology and application semantics.

With collaborators at North Carolina State University, we investigated data compression techniques. We developed a new technique to compress data during I/O in GLEAN. We applied this technique toward compressing FLASH and HACC data.

Development of Software Infrastructure for the Simulation of Microbial Communities on HPC Architectures

2011-126-R1

Christopher Henry, Narayan Desai, Folker Meyer, and Rick Stevens

Project Description

Biological systems have tremendous potential with regard to their applications for biofuel production, carbon biosequestration, and waste cleanup. A significant investment has thus been made to develop high-throughput experimental techniques that could rapidly advance our knowledge of how these systems respond to environmental and genetic perturbations. Recently, the investment has yielded significant dividends: protein profiles from mass spectroscopic data; gene expression profiles from microarrays and sequencing; gene profiles from metagenomics sequencing; metabolite profiles from mass spectroscopy, nuclear magnetic resonance (NMR), and chromatographic data; phenotype profiles from Biolog arrays; and transcription factor and binding site profiles from chIP-chip (chromatin immunoprecipitation with microarray technology). At the same time, the investment in designing and fabricating high-performance-computing (HPC) platforms has led to the development of massively parallel architectures containing over 100,000 interlinked processors with petaflops of computing power. These HPC platforms can simulate systems at a scale and complexity not previously possible, but unfortunately, the conceptual paradigms and software infrastructures needed to apply the platforms to simulate and analyze biological systems are still not available.

We propose to build an integrative, extensible computational framework that will enable researchers in biology to assemble multicell models of complex biological communities and scalably simulate these communities on modern HPC architectures. Biologists will thereby gain new insights on community dynamics, emergent community behaviors, cell-to-cell interactions, and cell interactions with the environment. The framework will provide a generalized platform to predict how individual cell behavior affects the organization of a microbial community in its natural environment. The platform will facilitate the incremental building of biological models, since it will enable coarse-grained representations to be combined with more detailed biological modules. The system's modular architecture will be flexible enough that the framework will be able to address a variety of questions related to cellular communities. Most important, the framework will be parallel-ready, capable of efficiently using 100K+ processors and memory spaces on a wide variety of architectures to simulate biological communities at a massive scale.

Mission Relevance

This project is relevant to DOE's mission in science and through that, to its energy and environment missions as well. The framework will enable researchers in biology and computational biology to apply the HPC infrastructure to analyzing any biological phenomena that involve interactions within a complex community of cells. For example, simulations could focus on microbes in the human gut, cells organized into tissues, microbial communities in the soil and oceans, or microbe competition and evolution. Large-scale simulations are essential for gaining a complete understanding of the principal driving forces that control microbial communities. They will enable us to better predict how microbial communities will respond to changes in the environment, such as global warming or an oil spill. They will also enable us to control these communities and direct them toward a useful application, such as degrading biomass, sequestering CO_2, synthesizing biofuel, or storing energy in chemical form. The simulations will be invaluable to research in human health and will improve our understanding of how microbes interact with each other and with human tissue when living inside the human body. We will be able to simulate infections and microbial symbiosis with human tissue at a level of detail not previously possible.

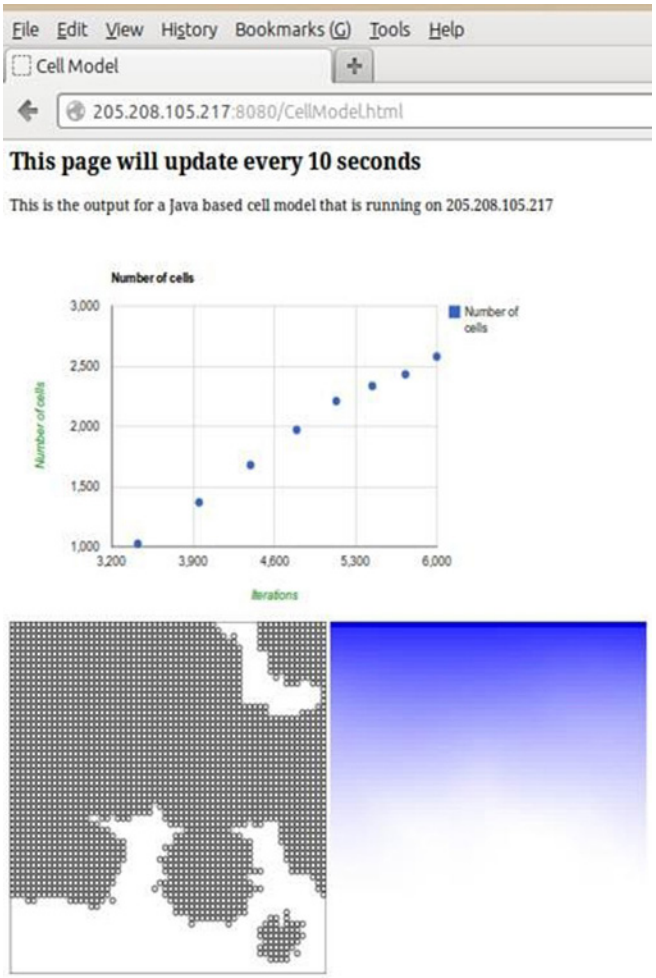
FY 2012 Results and Accomplishments

Significant progress made in FY 2011 can be summarized in the areas of software infrastructure, the development of new simulators, and successful testing. Specifically, we integrated an XML parser into the software (enabling users to specify complex models in terms of XML and negating the need to write code to formulate new models) and added software for printing simulation output in HDF5 (high-dimensional file) format. We created a finite difference method (FDM) simulator to capture the flow of nutrients through a three-dimensional (3D) environment over time. We also created an agent-based modeling (ABM) chemotaxis simulator to capture the movement of cells within the environment. The individual agents are at the prototype stage, but their movement was successfully demonstrated. The simulation framework was tested for scalability while running in parallel on the Blue Gene/P system.

In FY 2012, we made substantial progress in three areas: creating an ABM of cell growth, division, and death; developing elements of the user interface; and applying our simulation software to study the behavior of a real microbial community. We developed an ABM that incorporates the full range of microbial growth dynamics; it is a specific bacterial ABM that conforms to the standard protocol for biological ABMs. A central aim of the project is to produce an ABM toolkit that can be configured by nonprogrammers. General ABM toolkits are available, some of which can run on multiprocessor systems (e.g., Repast). These tool kits are designed to create an ABM of any system. We investigated using them in this project but found that their general design compromised their usability, integration, and performance. We then created our own microbe-specific ABM, which gives us more control of the model's execution on multiprocessor systems and will allow us to expose a bespoke interface specific to the creation of purely microbial models. The resultant user interface will be much easier for a biologist to use yet still be rich enough to capture all of the biological process the user wants to simulate. The ABM is written in a modular fashion so it can be easily combined with the flux balance analysis (FBA) solvers previously developed. The model can also work with any reaction diffusion model (RDM); currently, we are using the finite difference analysis model we developed, but we have investigated incorporating a general-use, open-source reaction diffusion system (RDS). Unlike the case for general-use ABM kits, we do not see any down side to using a general RDS, and we are now evaluating two systems: Nek5000 and Chombo. We successfully tested our ABM with a number of multispecies experimental communities and, on the basis of this experience, produced specifications for a user-programmable interface.

We developed a web page interface for a 2D version of our ABM (http://205.208.105.217/CellModel/CellModel.html) (see Figure 1). A web server is incorporated into the ABM's user interface. The page is updated in real time with data from executing the model. We developed the web interface to aid model development by allowing test communities to be run and evaluate in real time. The interface will also enable the progress of full experimental runs to be monitored. A full experiment can take many hours; monitoring allows errors in the model to be detected and the experiment to be aborted, saving computational time. This interface is a useful addition to the high-content output developed in FY 2011. We also developed a web page that will display the output from the full 3D ABM (Figure 2); it also displays data in real time.

We identified a suitable spatial microbial community to test in order to validate our ABM. This spatially structured microbial community is encapsulated in a "pill" to treat diseases associated with dysbiosis (microbial imbalance) of the human gut. The two-species microbial community has a simple biochemical system with three compounds: dextran, glucose, and butyrate. One species degrades dextran into glucose; the other species converts glucose to butyrate. Experiments are under way to measure the growth rates and short-chain fatty acid production levels of bacteria grown individually and in a community. We are developing a specific ABM to simulate the impact of spatial structure on the behaviors/interactions of these microbial communities. Complementary experiments are being done that will produce data to validate our model.



This page will update every 10 seconds

This is the output for a Java based cell model that is running on 205.208.105.217

Figure 1. Web page from the web server interface of the ABM. (The page is continuously updated as the model runs, showing a graph of the number of bacteria, a 2D map of the bacteria, and the metabolite concentration.)

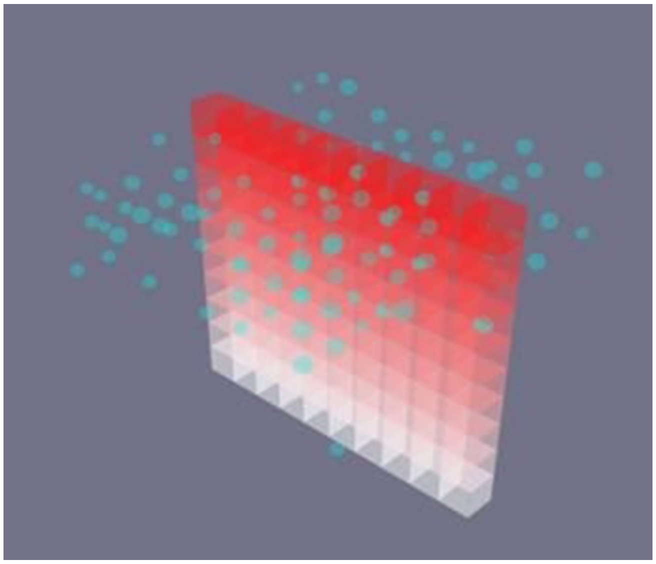


Figure 2. Output from bacterial ABM. (A 10 × 10 × 10 cube of a single species of bacteria is growing in a resource field. The resource concentration is indicated by red shading, and the biomass is indicated by blue points. The image was taken from a web page that acts as an interface to the model.)

Proposed Work for FY 2013

The focus of the final year will be integration and validation. All the project pieces have been developed; what remains is to integrate them into an easy-to-use web service that allows for community modeling. We propose that this integration occur in two parallel tracks. We will integrate the bacterial ABM, currently programmed in Java, with the multiprocessor agent model developed in the first year, programed in C++. We will also interface with our chosen RDM (Chombo or NEK5000). We will pay particular attention to load balancing. The modular design of the current ABM will be beneficial in this process. The continued use of the Java-based version of the bacterial ABM will allow further development of the user interface in parallel with the multiprocessor. The aim is to incorporate the model web service with the currently available genome selection and metabolic model generation found in the Model SEED. Using the output from Model SEED as the input for the community model should be seamless. The web service nature of the model should also make it possible to incorporate it into the workbench of KBase. A fully intuitive web-based workbench will make the model much more likely to be accepted as a useful, productive tool by microbial ecologists.

The model will stand or fall on its performance, however. Much effort will therefore go into producing an ABM of some real systems. Specifically, we will develop a 3D model of the spatially structured microbial community contained in a therapeutic pill — a system that can provide us with detailed experimental data on community interactions and productivity. We will also continue work on our large-scale soil model, integrating our newly sequenced and characterized microbes into a 3D representation of the soil environment to explore potential interactions. The goal of this study is to run a landmark simulation, studying soil microbes at a scale and level of detail that have never been attainable.

Beyond-Petascale Monte Carlo Methods for Practical Nuclear Reactor Analyses

2011-211-R1

Andrew Siegel

Project Description

This project is developing next-generation computational methods to enable a particle-based (Monte Carlo) neutron transport simulation of a realistic nuclear reactor core model. Monte Carlo (MC) methods have several potential advantages for performing such criticality calculations, when compared to traditional partial differential equation (pde) -based (deterministic) formulations. However, MC methods are limited in part by the very long integration times needed to get statistically meaningful results. Given the performance of current leadership-class machines (1–20 PFLOP/s), the raw computational power exists to enable robust MC reactor simulations, but significant algorithmic development is needed to bridge the gap between the software, the hardware, and the end application. This project aims to develop the underlying methods to enable efficient MC simulations on current leadership-class machines. While this project specifically focuses on the concrete goal of reactor physics calculations, many aspects of the underlying algorithmic innovations are relevant to a much broader class of neutral particle transport problems.

Mission Relevance

The project is broadly relevant to DOE's mission in science. Neutral particle transport algorithms (neutrons or photons) are common across a broad range of application fields — nuclear reactor design and analysis, weapons design, cloud physics, medical dosimetry, neutron shielding, source detection, and fusion reactors, for example. This work is highly relevant to the Nuclear Energy Enabling Technologies division of DOE-NE, where next-generation methods in neutron transport will be necessary for the design and analysis of innovative reactor concepts, especially those further from existing design points, such as the Small Modular Reactors currently gaining popularity. Advanced safety modeling (e.g., for accident-resistant fuels) and the study of reactor physics in other non-ideal scenarios all require fundamental algorithmic advances in accuracy of and time to solution.

This research is also relevant to the DOE ASCR (Advanced Scientific Computing Research) office. Innovative, extremely scalable (million+ way concurrency) algorithms for next-generation exascale machines need to be explored well ahead of the deployment of those machines. ASCR, as evidenced by the Co-Design Centers, has great interest in ensuring that key application areas are "ready" when exascale machines with non-traditional characteristics are deployed. This research fills this need perfectly, especially given that neutron transport is, in many ways, a broad and canonical area of computational physics. It is probably also the case that a general, robust, highly scalable MC code could also be used, in principle, to pursue work in a broad range of applied areas supported by such agencies as the National Science Foundation (NSF), National Institutes of Health (NIH), National Nuclear Security Administration (NNSA), and DOE-BES, where large particle simulations are necessary to explore a variety of issues in, for example, medical dosimetry and particle material interactions, among others.

FY 2012 Results and Accomplishments

Early work on this project focused on both developing the OpenMC code and exploring the feasibility of highly scalable strategies based on physical space domain decomposition. We have extended this early work to explore both extreme on-node scalability for shared memory architectures, as well as efficient data decomposition strategies (what we refer to as “memory servers” and “tally servers”) for distributed memory architectures. These approaches are described in detail below.

Accomplishments in FY 2012 include the following:

- Working with researchers at Massachusetts Institute of Technology, we developed and tested an innovative algorithm for decomposing the large quantity of tally data (approximately 1 terabyte) generated during a realistic reactor simulation. We refer to this as a “tally server” algorithm, where rather than replicating each processing node as done traditionally (not feasible for realistic working sets that go beyond traditional “toy” problems), a disjoint set of processing nodes dedicated to continuously receiving and storing tally data is run concurrently with a set of tracking processors. The new algorithms are part of the current distribution of the OpenMC code (now open source).
- We implemented on-node threading within OpenMC (added openMP on node to existing inter-node MPI) and carried out an exhaustive set of performance studies to identify key issues in attaining good on-node performance for multi-core architectures.
- We have started work and made significant progress in a few key areas:
    - *Memory server algorithms for partitioning cross-section data (we expect to finish this work in the next several months).* The approach involves using small disjoint processor clusters that serve only to store and fulfill remote read requests for cross-section data from disjoint sets of tracking processes. The algorithms are complex and involve energy banding to minimize communication latency, as well as topology aware clustering to minimize network traffic.
    - *Deeper analysis of multi-core programming bottlenecks and algorithms to circumvent them.* While the classic historical approach to MC is algorithmically perfectly scalable (modulo load balancing), in practice, on shared memory architectures, bottlenecks in the shared memory subsystem erode scalability. The extent of this erosion has been explored in depth, and a deeper analysis of what features cause it has been conducted.
- All of the algorithmic innovations discussed above are part of either the main or a forked branch of the OpenMC distribution.

Proposed Work for FY 2013

- Conduct deeper analysis of multi- and many-core architectures with strategies to mitigate memory bottlenecks and improve performance.
- Commence analysis of MC on modern heterogeneous single instruction, multiple data (SIMD) nodes (i.e., general-purpose graphics processing unit [GPGPU] architectures).
- Continue/complete work on the memory server model to enable much larger calculations.

Towards the Exascale Sky

2011-213-R1

Salman Habib, Sanghamitra Deb, Katrin Heitmann, Juliana Kwan, and Hendrik Weerts

Project Description

An intense global effort is under way to understand the deep mysteries posed by the existence of dark energy and dark matter. Extracting scientific knowledge from observations requires simulations of structure formation in the Universe at unprecedented scales. To meet this challenge, we are developing a petascale cosmology code suite, the Hardware/Hybrid-Accelerated Cosmology Code (HACC) framework, which is designed to exploit the full set of current and future high-performance computing architectures.

Combined with the arrival of the Mira supercomputer at Argonne, this theory and modeling capability will put us in a unique position to create breakthroughs in fundamental aspects of cosmology and to produce the best predictions for structure formation probes of the “Dark Universe.” As the first exascale computational cosmology capability for next-generation sky surveys targeted to future supercomputer architectures, HACC’s design encompasses all high-performance computing (HPC) architectures, including many-core and hardware-accelerated systems. In addition, we are co-developing the Cosmic Calibration Framework (CCF), an advanced statistical framework that melds HPC simulations with observational data, to provide rigorous error-controlled estimation of cosmological and modeling parameters.

Mission Relevance

This project is relevant to DOE’s basic science mission. The HPC advances underlying this project will have a broad impact over several fields, including accelerator and plasma physics, computational co-design, particle transport simulations, and management and analysis of very large datasets. The advent of the Great Surveys presents a significant and timely opportunity to play crucial frontline roles in DOE missions, covering both the discovery (cosmology, particle physics) and capability spheres (HPC, large datasets).

FY 2012 Results and Accomplishments

This project is aimed at developing a computational capability for large-scale cosmological simulations and their analysis. In FY 2011, the project work focused on porting the key codes to Argonne systems, including a new tree algorithm, and developing a new Fast Fourier Transform (FFT) method.

We made excellent progress in all project areas. The key advance is full implementation of the high-resolution HACC framework on the IBM Blue Gene/Q (BG/Q) platform. Using the new parallel Fast Fourier Transform implemented by our team in 2011, a new recursive coordinate bisection tree algorithm, and significant work with Argonne Leadership Computing Center staff on restructuring the code for performance on the BG/Q, HACC returned performance figures of 14 Petaflops on Sequoia (at Lawrence Livermore National Laboratory) based on a record-breaking benchmark run with 3.6 trillion particles. This is the largest cosmological simulation benchmark problem that has ever been run, and *the highest performance ever attained by a science code on any computer*.

We are currently running the largest fully instrumented cosmology simulation ever on Mira. Figure 1 shows zoom-in views from a trillion-particle test run on Mira. Figure 2 shows mass fluctuation power spectrum at a redshift, z = 2.65, from the fully instrumented 1.1-trillion particle run now under way on Mira.

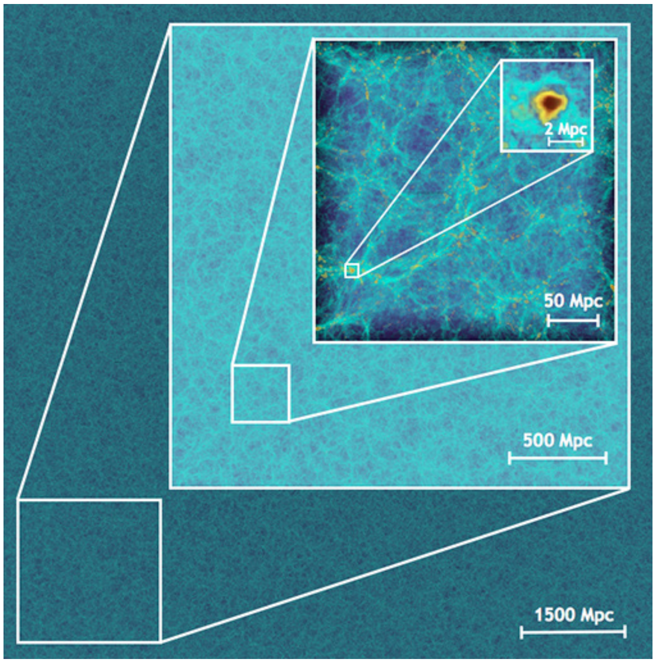


Figure 1. Zoom-in views from a trillion-particle test simulation on Mira. The large global dynamic range of the simulation is apparent from the figure. In the smallest box, the high resolution of the simulation is much finer than is shown; this is a limitation of the visualization process used, which could not follow the extreme details of the simulation.

There were several other notable achievements. The Graphics Processing Unit (GPU) version of the code was streamlined and tested on TitanDev at Oak Ridge National Laboratory (ORNL), and the performance results were very encouraging. We expect to run on the full Titan system in early FY 2013. HACC will also be one of the first codes run on the new Edison system at the National Energy Research Scientific Computing Center (NERSC). We are currently analyzing the results from a recent large run on the Hopper system at NERSC.

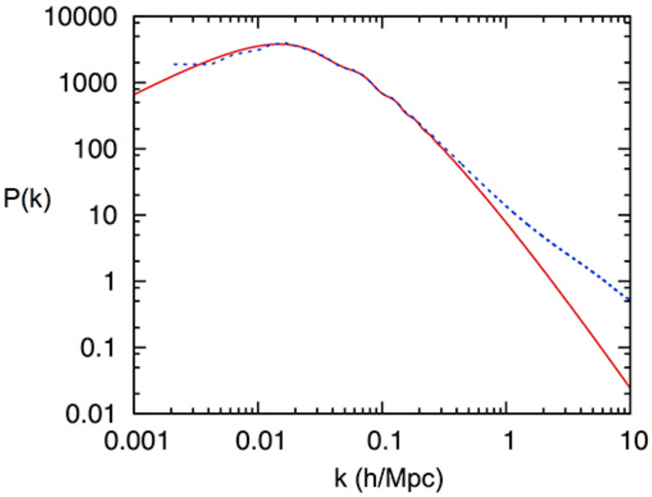


Figure 2. This figure shows the mass fluctuation power spectrum at redshift, z = 2.65, from a 1.1-trillion-particle simulation now being run on Mira. The red curve is the linear power spectrum, while the dashed blue curve is the evolved nonlinear power spectrum from the simulation. The large box size of the simulation (more than 4 Gpc) allows the subtle signature of the baryon acoustic oscillations (the wiggles in the power spectrum at around k = 0.1 h/Mpc) to be captured with high fidelity.

We developed a powerful *in situ* analysis framework for HACC that allows simultaneous analysis while the code is running on the supercomputer. The analysis framework includes a number of tools such as halo-finders, merger-tree constructors, implementations of methods for measuring correlation functions and power spectra, and a new tessellation method. Additionally, we completed a port of the semi-analytic structure formation code Galacticus to run within our framework. This enables us to generate synthetic sky catalogs and compare them against observations. Our work on large data analytics led to a significant project at NERSC, where we have access to large storage and analysis capabilities for post-simulation data processing.

We also extended the CCF in new directions, such as the dark matter halo concentration-mass relation. This allows researchers to predict the relation over a multi-parameter set of cosmologies with good accuracy, a significant improvement over previous analytic fits. The use of strong and weak lensing to characterize the mass distribution of galaxy clusters is becoming a powerful cosmological probe. Redshift space distortions (RSD) are an important cosmological probe, of primary interest to tests of modified gravity. Our large-volume simulations are particularly suited to this task.

Proposed Work for FY 2013

We will carry out large simulation runs by using our Early Science allocation on the BG/Q system. Using a set of proxy simulations (linear theory), we have a good plan for the sampling runs needed for the FY 2013 runs on Mira. Results from the Planck satellite will be made public in March 2013; these results will be very helpful in determining the appropriate parameter ranges.

In addition to running our GPU-enhanced code on Titan, we will begin the runs on Edison. After the Early Science allocation opens on Mira, we plan to run a number of large simulations to develop precision prediction capability for application to results from such surveys as the Baryon Oscillations Spectroscopic Survey (BOSS) and the Dark Energy Survey (DES). We will predict for a number of observational probes, including power spectra, weak lensing shear, halo occupation density models, and real-space and velocity-space two-point functions.

We will improve HACC's efficiency by using hyper-local trees implemented with chaining meshes instead of the current rank-local tree data structure. We expect this to improve load balancing when the code is running in a highly clustered regime. We will also implement extensions of the HACC algorithms beyond gravity (gas dynamics).

Mesoscale Elastic Problems

2012-015-N0

Olle Heinonen, Dmitry Karpeev, and Serge M. Nakhmanson

Project Description

The length and time scales of mesoscale systems are much larger than those of atomic systems but smaller than those of macroscopic systems. The key components in many mesoscale systems are strain fields and their interactions with charges and interfaces. The goal of this project is to develop scalable codes for inhomogeneous mesoscale systems in which the elastic strain fields are coupled to bound and free charges. Another important part of this project is to develop cross-cutting approaches for solving large computational materials science problems by integrating materials science, condensed matter physics, applied math, and computational science.

Mission Relevance

The project is tied to the DOE Basic Energy Sciences (BES) mission to support research in areas relevant to energy efficiency through use-inspired R&D on new materials for energy storage and the efficient use of energy. The project also addresses challenges articulated in the September 2012 BES Advisory Committee report, "From Quanta to the Continuum: Opportunities for Mesoscale Science," by studying how nanoscale building blocks can be combined into larger (macroscale) systems with new properties inherently derived from the interactions between the building blocks.

FY 2012 Results and Accomplishments

We focus on developing efficient, scalable solvers for heterogeneous elastic problems. We developed a scripting chain that can create an arbitrary geometry, endow the geometry with a grain structure according to some specifications (e.g., a certain distribution of grain sizes and Euler angles of the crystallographic axes), and then mesh the system in a way that respects grain boundaries and other geometrical constraints (Figure 1). A scalable, heterogeneous elastic solver was developed within the MOOSE framework, which is a C++ software project for coupled nonlinear problems developed primarily at Idaho National Laboratory. MOOSE leverages scalable algebraic solvers from PETSc (Portable Extensible Toolkit for Scientific Computing), which was developed and supported by Argonne's Mathematics and Computer Science Division. An important part of the work involved developing and optimizing new PETSc preconditioners for the algebraic problem that resulted from a so-called weak formulation of linear elasticity by using the finite-element method. In particular, the scalability of the heterogeneous elastic solver was substantially boosted by coupling PETSc's Geometric-Algebraic Multi-Grid (GAMG) preconditioner to MOOSE.

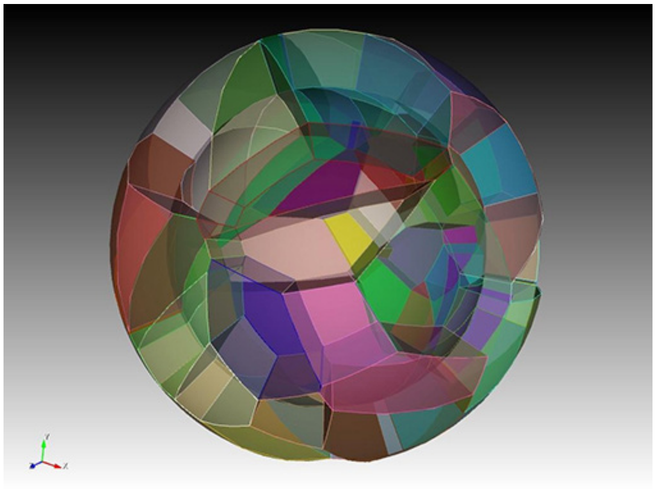


Figure 1. Spherical core-shell particle with grain structure. The particle is about 15 nm in diameter. The grains are generated using a Voronoi construction that seeds grains at random locations with a density set by an average grain size (in this case, a few nm). The crystallographic axes in each grain can be set explicitly or distributed according to some specified distribution scheme. Mismatch of the crystallographic axes at grain boundaries gives rise to irregular distributions of strain and stress.

We also studied a problem that involves coupling between strain field and ferroelectric polarization in a layered-oxide material, the polarization of which was predicted to rotate freely in the crystallographic *ab*-plane, which is a very unusual property. In collaboration with researchers at Texas State University, we investigated the strain-polarization phase diagram for patterned discs made from this material. In such discs, the polarization can form a vortex state, similar in many respects to that of magnetic discs. The dielectric response of the disc can be changed rather dramatically by applying an electric field or a strain field, leading to potentially interesting applications.

Finally, with researchers in Argonne's Nanoscience and Technology Division, we began using our code to study elastic response in silicon cantilevers that are used for probe microscopy, such as piezo-response force microscopy, as well as for novel energy-harvesting applications. Here, the ultimate goal is to design cantilever geometries with high piezoelectric response (for generating electrical current) and mechanical durability.

Proposed Work for FY 2013

We will demonstrate scaling of the heterogeneous elastic solver for up to 10,000 cores by using the Fusion computer cluster at Argonne and by applying for discretionary allocations on Argonne's Blue Gene platforms. The code development work will continue by integrating a Poisson solver for bound and free charges with the heterogeneous elastic solver. The best-known approach to this problem with bound charges involves discretization of singular boundary integral operators, the scalability and load balancing of which can be very challenging. We will also further develop a solver for strongly coupled systems, describing the nonlinear interaction of elasticity with polarization. Suitable preconditioners for scalable solution of the coupled system will be a focus of the code development.

With the Poisson solver in place, we will study the domain behavior in heterogeneous ferroelectric thin films. We are very interested in the interactions between the resulting inhomogeneous strain fields and the ferroelectric polarization in such systems. We will also study the strain distribution in nanoparticle core-shell systems. These have very inhomogeneous strain fields, which affect both the mechanical response of systems that are composed of such particles and the photoabsorption band gap.

A Novel Low-Level Software Architecture for Exascale Nodes

2012-082-N0

Kamil Iskra, Pete Beckman, Rinku Gupta,
and Kazutomo Yoshii

Project Description

With projections that computing hardware will feature hundreds or even thousands of central processing unit (CPU) cores per node by the time we reach exascale, we can expect to see a ripple effect across the software stack, from system software, through programming models, to applications, as the existing approaches will become prohibitively inefficient at such scales. New and highly dynamic execution models that use lightweight threading to respond rapidly to changing workloads (described by using directed acyclic graphs (DAGs)) are emerging as a possible replacement for the more static approaches. Because they have been developed on top of existing operating systems (OSs) and low-level runtimes, however, these execution models inherit some of their limitations. Determining the optimal division of labor and interfaces between the kernel and the runtime system is still an open research question. In this project, we are working on identifying new, low-level programming interfaces that will be needed to provide efficient support of these programming models on future hardware. Our objective is to develop a model of a low-level runtime system with native, high-performance support for lightweight threading, many-core systems, hierarchical memory-core mapping, and power usage awareness. As part of this effort, we intend to develop a practical many-core platform evaluation kit that combines hardware and software techniques in order to gain insights into the scalability of future many-core node designs.

Mission Relevance

This project is relevant to DOE's mission in science. Exascale computing has been identified as an important ingredient for continuing advances in key DOE mission areas. One of the key concerns for exascale is the availability of suitable, mature programming models. The work we are carrying out in this project is expected to benefit the emerging and dynamic graph-based programming models by providing a solid system-software foundation for optimal execution of such models on future hardware. A successful, high-performance programming model will benefit DOE by enabling a wider range of codes to run on future systems managed by DOE leadership computing facilities, ranging from optimized math libraries to complete applications engineered for graph-based execution.

FY 2012 Results and Accomplishments

Our early investigations during the initial year of this project have progressed along a number of lines.

An exhaustive literature study helped us identify several new DAG-related projects, including DAGuE from the University of Tennessee, Knoxville, and StarPU from INRIA. Both present ambitious visions for building unified DAG development environments. We initiated an informal exchange of information with the DAGuE team. We compiled their software on our system, along with its numerous dependencies, and successfully ran the test suite. Through the tests, we identified a few meaningful benchmarks, ran them through DAGuE, and are studying the interaction with the operating and low-level runtime system during execution using tracing and profiling techniques; this last activity is still ongoing.

In addition to the above top-down approach, we also started a bottom-up one, where we evaluated the performance of well-known OS primitives by using microbenchmarks in order to gain insight into what they are capable of on current and emerging hardware. For example, experiments with system-level thread creation routines performed on multiple platforms (IBM Blue Gene, Intel x86, Intel MIC) showed nontrivial differences in performance that cannot be explained merely by different clock speeds. A more complete evaluation is needed, including a projection to future highly parallel systems.

Proposed Work for FY 2013

Drawing on the top-down and bottom-up experiments on existing systems, we plan to summarize our characterization of the required OS primitives for emerging runtime systems. We then will design and develop a lightweight thread runtime that is better suited for future workloads and hardware. We also will evaluate various thread scheduling approaches, including different core specialization techniques, and will investigate incorporating hardware-driven optimizations into the scheduling decisions.

Although the platforms currently at our disposal have at most around 60 cores per node, we work on software intended for future many-core systems that may have up to 1,000 cores per node. Thus, we will need a practical simulation environment. We plan to evaluate and reuse the most promising existing software projects in this area, bringing them to a state where they can be built and run easily in our environment. We expect to end up with one working emulation/virtualization platform for accelerated single-node experiments, one probabilistic simulator, and one cycle-accurate simulator for timing-critical work, with simulation speed degrading from the first to the last. Our intention is to use this platform facility to conduct node-level performance and scalability studies of subsystems such as the memory management, scheduling, and communication in this and other system software projects.

Extreme-Scale Electromagnetic Modeling with Nanoscience Applications

2012-114-N0

Misun Min, Paul Fischer, and Stephen K. Gray

Project Description

This project seeks to provide an enhanced high-fidelity code that will enable future-generation electromagnetic device simulations for predictive modeling of nanosensors and photovoltaic devices, which will help researchers discover and explore innovative solutions for energy, medical diagnoses, and national security. To this end, we propose to dramatically increase the capabilities of the electromagnetic code NekCEM developed by Argonne staff, producing a single, comprehensive electromagnetic software package that will run in parallel at extreme scale.

Mission Relevance

Computational efforts will include leading-edge simulations in nanosensors and photovoltaic solar cells that are clearly related to DOE's science mission and will take full advantage of extreme-scale computer architectures in upcoming years. This project will enable scientists in the relevant communities to advance new scientific discoveries that will deliver real benefits to society, industry, and science, through highly efficient and accurate predictive modeling, with significant reduction of both the cost and the risk in the design process. The first users will likely be materials scientists and engineers, with possible extension to material synthesis and photovoltaic solar cell industries in the future.

FY 2012 Results and Accomplishments

Work on this project allowed us to significantly expand our efforts in the context of parallel algorithmic advances on DOE leadership-class computing systems, such as the IBM Blue Gene/P (BG/P) (Intrepid) at the Advanced Leadership Computing Facility and the Cray XK6 (Jaguar) at the Oak Ridge Leadership Computing Facility (OLCF). Key accomplishments during FY 2012 include:

- Development of a hybrid programming version (MPI + OpenMP/GPU) for computation, (to be further improved for the speedup performance),
- Development of threading I/O for total simulation time reduction,
- Performance analysis on IBM BG/P and Cray XK6,
- Development of Lorentz model describing the electron behaviors within thin metallic films (to be further tested for validation with experimental results),
- Development of time-dependent Schrodinger equation solver in NekCEM (2D/3D), and
- Development of a Dirichlet to Neumann (DtN) operator for non-reflecting boundary treatment in the frequency-domain for acoustic and electromagnetic waves.

Proposed Work for FY 2013

The essential aspects of our proposed effort for applications, algorithms, and parallel infrastructure for exascale include:

- Develop hydrodynamic model for surface enhanced Raman spectroscopy (SERS) simulations for detecting bacteria on a substrate and validation with experimental data,
- Study absorption characteristics of photovoltaic solar cells (e.g., nanoparticles on a Si substrate),
- Develop efficient time-stepping schemes for the time-dependent Schrödinger solver in NekCEM,
- Pursue scalability/performance tests/analysis/improvement for hybrid MPI/OpenMP/GPU models,on the IBM BG/Q at Argonne Leadership Computing Facility (ALCF) and Cray Titan at OLCF, and
- Add MOAB (a mesh-oriented database) interface into NekCEM for hexahedral/tetrahedral meshes.

A Future for Energy-Efficient General-Purpose Computing Based on Heterogeneity

2012-202-N0

Andrew A. Chien

Project Description

Changes in semiconductor technology scaling have created an inflection point (all integrated circuits are now increasingly energy/heat limited) for computer architecture, driving a shift to new approaches that improve energy efficiency. This shift has already resulted in radically changed mainstream designs, but changes will continue to accelerate for architectures and, as a consequence, programming tools. Multicore processors and graphics processing units (GPUs) are the first examples of this; however, the architecture changes will be profoundly greater. We are exploring new programming technologies and co-design with underlying architectures to exploit 10-fold or more heterogeneity in instruction set and implementation that deliver 10-fold or greater energy-efficiency and, thereby, much higher performance. The key is balancing the exploitation of architectural customization (which typically limits hardware to special-purpose) with the ability to cover a broad range of computations (general purpose computing). Integral to this approach is the programming and compilation challenge of flexibly exploiting heterogeneity with modest programming/porting effort.

Mission Relevance

This project is relevant to DOE's basic science mission. Potential implications of this project are broad across the full range of DOE high-performance computational science users of exascale (and petascale) high-performance systems. It is also likely to have an impact on emerging data-intensive computing (or "Big Data") systems. The research is expected enable understanding and provide perspective to make good strategic choices about DOE's Advanced Scientific Computing Research (ASCR) road map for high-performance computing and data-intensive computing, including hardware architecture (in partnership with vendors) and software tools.

FY 2012 Results and Accomplishments

In FY 2012, we accomplished the following:

1. We designed a 10 × 10 micro-benchmark program to map heterogeneous system performance, including computing capabilities, memory hierarchy, communication, and synchronization properties. This micro-benchmark enables the efficient mapping of heterogeneous capabilities and performance crossovers where use of a new heterogeneous computing element (e.g., a GPU) becomes profitable to use, thus enabling other software packages and applications to more efficiently exploit emerging heterogeneous systems.
2. On the basis of insights gained from using the 10 × 10 micro-benchmark to characterize NVIDIA, AMD/ATI, and Intel GPUs, as well as Intel and AMD central processing units (CPUs), we are now developing a set of portable benchmarks with challenging irregularly structured parallelism and a data reference structure. This set of portable benchmarks includes double-precision matrix-matrix multiplication (DGEMM), sparse matrix-vector multiplication (SPMV), and breadth-first search (BFS); for each of these kernels, we achieved top performance across all of the previously mentioned hardware platforms with only parametric changes. The detailed understanding and careful design required to achieve this portable performance enables the next step in studies of how to achieve portable performance across heterogeneous processors, such as CPUs and GPUs, and more aggressive exploitation of heterogeneity, such as the 10-fold approach contemplated in 10 × 10.
3. We also engaged in exploratory architecture design and evaluation with researchers in the Mathematics and Computer Science (MCS) division at Argonne. The results are surprising, because they show that a number of the mini-applications are extremely memory limited and may not be well-served by the projected exascale system balance (capacities). Further, the results show that for those mini-applications that are not well served, the potential benefits of increased memory bandwidth due to stacked DRAM are significant, but the benefits are much less substantial than the benefit of processing under memory.

Proposed Work for FY 2013

For FY 2013, we will continue to study portable benchmarks and evaluate heterogeneous architectures, with the goals of expanding the range of architectures covered and continuing to gain insights into key parameters and programmability challenges. On the basis of our experience with the portable benchmarks, we will take the first steps toward proposing a portable programming interface. This will be a relatively low-level interface, and we will seek to encapsulate the varied heterogeneous architectures features and achieve close to the best possible performance for each. Also based on our experience with architecture simulations and application studies, we will take the first steps toward a 10 × 10 strategic roadmap of accelerators.

Seminars

Chien, A. (2013). "Technology Scaling and the Future of Microprocessors: The 10x10 Approach." Purdue University, West Lafayette, IN, October 9, 2012.

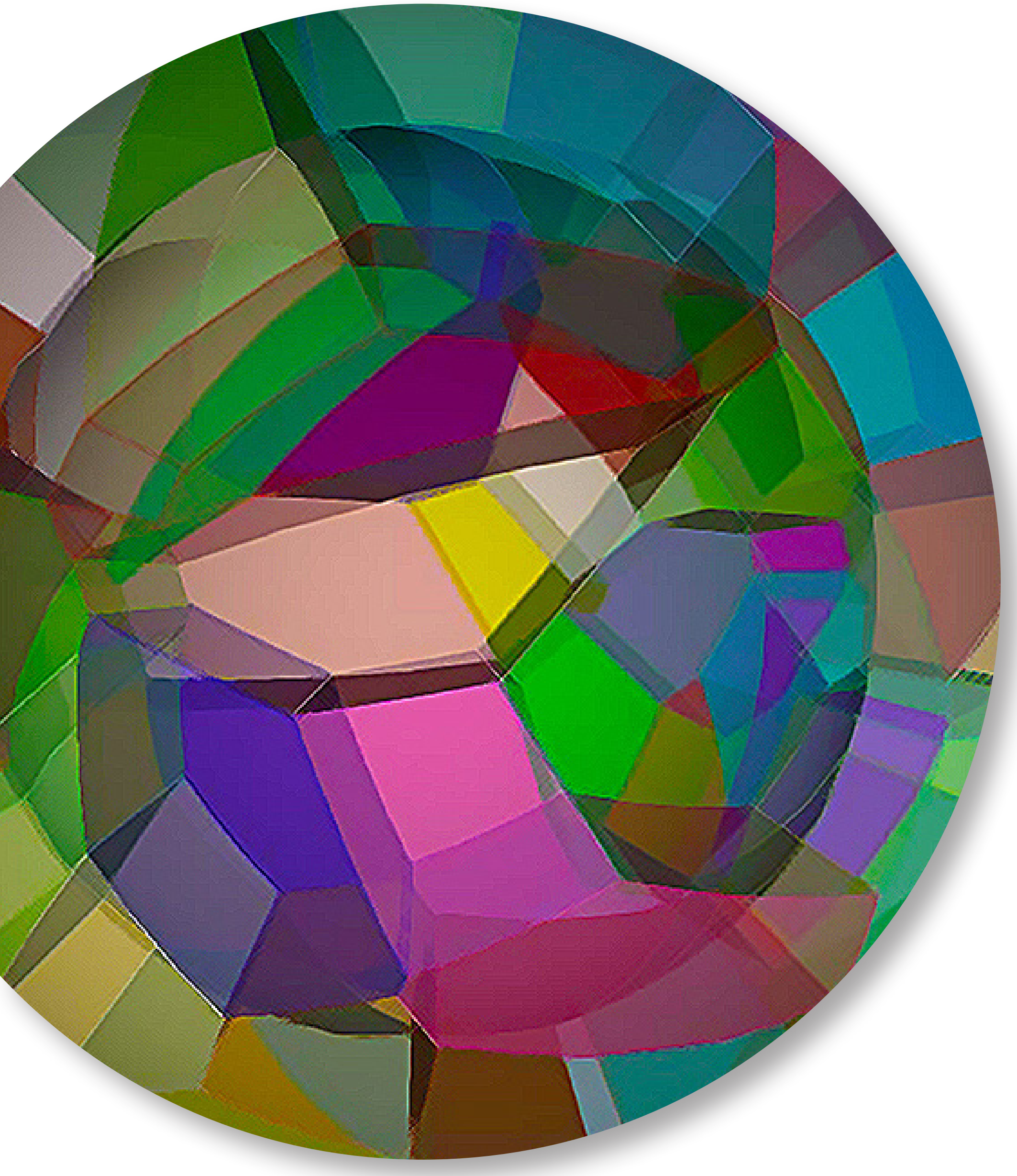
Chien, A. (2012). “Technology Scaling and the Future of Microprocessors: The 10x10 Approach.” University of Illinois, Urbana-Champaign, February 9, 2012.

Guha, A. and A. Chien (2012). “Systematic Evaluation of Workload Clustering for Designing Heterogeneous, General-Purpose Architectures.” Department of Computer Science, University of Chicago, Chicago, IL, June 19, 2012.

Guha, A., P. Cicotti, A. Snavely, and A. Chien (2012). “An Empirical Foundation for Heterogeneity: Clustering Applications by Computation and Memory Behavior.” Department of Computer Science, University of Chicago, Chicago, IL, February 16, 2012.

FY2012
annual report

HARD X-RAY SCIENCES



Combined Approaches toward a Hierarchical Understanding of Battery Materials

2010-074-R2

Karena W. Chapman, Jonathan D. Almer,
Mahalingam Balasubramanian, and Karoly Nemeth

Project Description

This project addresses the integrated application of a suite of emerging hard x-ray capabilities to the fundamental understanding of the factors that currently limit battery performance. Our unique approach applies unified experimental protocols to obtain directly comparable, complementary data covering multiple length and time scales. New *in situ* capabilities are being developed at the Advanced Photon Source (APS) to directly probe the material behavior within an operating electrochemical cell. Simultaneous analysis of all available data through multi-scale modeling will yield new fundamental insights into battery materials.

To understand the individual mechanisms within the different cell components that limit the performance of current-generation lithium-ion batteries (LIBs) and rationally enhance the performance of next-generation LIBs, an integrated program of state-of-the-art materials characterization and sophisticated data modeling is needed. Key x-ray methodologies, each capable of providing unique structural information and insights into battery materials, have been identified. While the individual analyses are primarily focused on particular aspects of the structure, by combining the complementary insights from the different selected methodologies, a complete understanding of the material structure can be built — from the atomic-scale structure (x-ray absorption fine structure [XAFS], pair distribution function [PDF]) through particle size and shape (e.g., small angle x-ray scattering [SAXS], imaging). Our uniquely concerted approach brings together the complementary information using multi-scale modeling of the multiple separate data sets, based largely on reverse Monte Carlo (RMC) methods.

In situ studies are a cornerstone of the work, in recognition of the importance of studying battery materials at other than ambient conditions — that is, actual conditions under which batteries operate — to explore the often complex structure-function relationships, including the structural changes, that occur during cycling. Electrochemical sample cells are being designed and optimized to allow high-quality and, importantly, comparable data to be collected *in situ* by using the different methodologies.

A local electrochemical laboratory has been equipped with specialized facilities to prepare electrode materials, as well as assemble and test electrochemical cells. This facility is pivotal to carrying out this project at the APS because our studies require the cycling of electrode materials (positive and negative) against metallic Li^0, which is subject to strict transport constraints.

Mission Relevance

Battery research is a key component of DOE's mission in energy. The integrated approach developed here will resolve complex structural problems that not only are relevant to batteries but can be readily extended to other material challenges. The facilities and capabilities developed as part of this project will be valuable to other DOE battery programs, including a number of new Energy Frontier Research Centers (such as the Center for Electrical Energy Storage) and the Northeastern Center for Chemical Energy Storage.

FY 2012 Results and Accomplishments

Before FY 2012, an *in situ* cell suitable for PDF, XAFS, diffraction, and SAXS was largely optimized and its performance benchmarked. We took preliminary *in situ* PDF and XAFS measurements for an initial test material (α-Fe_2O_3) and correlated the measurements with *ex situ* data obtained for the same system. A RMC code suitable for simultaneous fitting of PDF and XAS data was written. Efforts in FY 2012 built upon these accomplishments:

- Undertook *in situ* PDF, XAFS, diffraction and SAXS by using custom-designed *in situ* cells.
- Explored new opportunities for time-resolved studies using *in situ* cells to isolate reaction kinetics.
- Applied our multi-scale tools, combining *in situ* PDF/EXAFS (extended x-ray absorption fine-structure spectroscopy) with RMC, to understand the electrochemical reaction mechanism in selected Fe conversion systems, to identify the factors that contribute to improved cyclability and, subsequently, to target higher-performance systems.
- Developed more-efficient RMC algorithms, with suitable constraints, to permit faster convergence and the addition of SAXS to the PDF+EXAFS modeling.
- Packaged the RMC codes for broader use by our team.

In situ *electrochemical cell design:* The *in situ* cell, which enables reproducible and directly comparable experimental data to be collected, was optimized for PDF, EXAFS, SAXS, and diffraction measurements. The cell allows data to be collected for a single sample at fine reaction intervals (~0.1 Li reacted per formula unit is typical). The high consistency in the data allows subtle structural changes to be identified and complex reaction mechanisms to be distinguished. The mechanical and chemical stabilities of several alternative plastics were tested. PEEK (polyether ether ketone) seems to provide improved mechanical durability. A patent application on this cell design has been filed.

Multi-sample holders have improved experiment efficiency, allowing data to be collected on up to 10 cells in tandem. A modification of multi-sample holders, allowing simultaneous heating of the cells at moderate temperatures (~60°C), was tested. Heating the samples improves cycling kinetics and allows materials with slow kinetics at room temperature to be cycled within the typical time limits of a synchrotron experiment.

Electrochemistry Laboratory: A laboratory for preparing, assembling, and cycling Li-battery cells was established in Building 433-D-030 at Argonne. The laboratory was equipped with all necessary tools for *in situ* battery studies. A second cycler was acquired to allow more cells (>8) to be cycled simultaneously or to allow experiments at different beamlines.

Multi-Scale Modeling Tools: The RMC code is now capable of simultaneous various PDF (with SAXS particle distribution) and EXAFS fitting. Various analytical tools (coordination number calculation, angular distributions) were added to the code to describe the fit model. The implementation of the code was extended beyond the Linux/UNIX operating system used for development, to a Windows-based package. An initial draft of a user's manual was written, and the program is being tested by our team members.

New Insight and Understanding of Battery Materials: The conversion chemistry of nano α-Fe_2O_3 was selected as a case study to develop and evaluate our experimental approach. An initial PDF study of nano α-Fe_2O_3 electrodes recovered from various states of discharge was completed. This study revealed the structure of the intermediate in the conversion reaction and showed that the Fe nanoparticles formed near the end of discharge are defect-rich and restructure continuously with lithiation, without growing. This observation has important implications for the reversibility of the conversion process: if metal nanoparticles aggregate and grow significantly, reversibility can be reduced. We are studying other Fe-based conversion systems to understand the circumstances that contribute to nanoparticle growth. These include Fe_3O_4, FeO, FeF_2 and FeOF. Using the *in situ* cell, we are exploring how the nanoparticle size evolves when the cycling is paused or when switching from discharge to charge phase occurs. Continuing efforts in this area are funded by the Northeastern Center for Chemical Energy Storage Energy Frontier Research Center.

In situ studies of nano α-Fe_2O_3 using different methodologies show seemingly different results. The PDF indicates formation of a bcc (i.e., Fe nanoparticle) phase long before metallic iron is observed with EXAFS. Preliminary analysis of the SAXS data showed a broad distribution of particle sizes in the same regime where a bcc nanoparticle phase is initially observed in the PDF data, with an evolution to a narrower, consistent size distribution at the point where metallic iron is first observed with EXAFS.

Development of Picosecond X-ray Pulses at the APS Using MEMS-Based X-ray Optics

2010-117-R2

Jin Wang, Il Woong Jung, O. Daniel López,
Deep Mukhopadhyay, Craig Schwartz, Gopal Shenoy,
and Don Walko

Project Description

Rapid progress in micro- and nanoelectromechanical systems (MEMS and NEMS) provides a unique technical opportunity to design and fabricate x-ray modulating optics that can spatially disperse the current synchrotron-based x-ray pulses (of 100-ps width) so experimentalists can achieve picosecond temporal resolution for both scattering and spectroscopy experiments with close to 100% optical efficiency. The ultimate objective of this project is to develop MEMS-based x-ray optics that can demonstrate the feasibility of producing x-ray pulses with picosecond temporal resolution, broad energy tunability, and a high pulse-repetition rate by using the Advanced Photon Source (APS). The near-term goal of this development work, which can have an immediate scientific impact, is the ability to tailor and manipulate x-ray pulse trains by using MEMS-based optics, independently of the electron fill pattern of the storage ring.

Mission Relevance

This project is relevant to DOE's mission in science. The importance of developing fundamental understanding of far-from-equilibrium systems and processes has been epitomized by the DOE's "Five Grand Challenges" study. Ultrafast time resolution of x-ray interactions has been identified worldwide as the critical tool for investigating temporal development of far-from-equilibrium processes responsible for the control of complex materials and chemical processes, as well as real-time evolution of chemical reactions and dynamics of spins in the microsecond to femtosecond domains.

FY 2012 Results and Accomplishments

In FY 2011, we designed, fabricated, and tested several MEMS-based x-ray micromirror optics for x-ray modulation with resonant frequencies ranging from 2 to 75 kHz. We also improved the MEMS design to yield devices with resonant frequencies reaching 300 kHz. Dynamic x-ray reflectivity measurements at the APS showed that the current MEMS devices had great promise for use as x-ray choppers; these devices were able to produce an x-ray dynamic time window (DTW) with a width of ~ 2 μs, capable of separating the singlet pulses from the rest of the pulse trains in the APS Special Operation Mode 1. To further reduce the DTW width, in FY 2012 we focused our work on generating the window by using Bragg diffraction from the MEMS mirror crystal of Si(100), as shown in Figure 1.

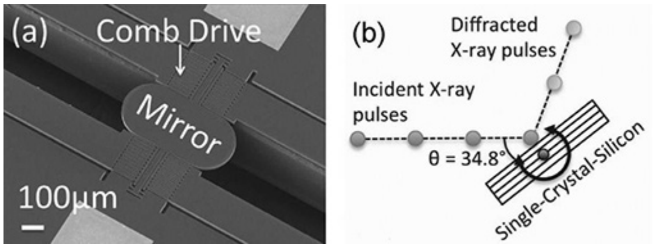


Figure 1. (a) Scanning Electron Microscopy image of the 75-kHz MEMS mirror device (b) used to generate nanosecond DTW under Bragg diffraction condition.

The major results and accomplishments in FY 2012 are summarized as follows:

1. Extensive static x-ray metrology was performed with the 75-kHz micromirrors under Bragg diffraction conditions. The rocking curve of the crystal was measured at Beamline 7-ID-C by using a synchrotron-based diffraction setup. The x-ray beam employed in the measurement was monochromatized to a bandwidth of 5 × 10^{-5}, and the x-ray photon energy was tuned from 5 to 20 keV. The rocking curve at 8 keV indicates that the diffraction peak width from Si(400), 56 µrad, is close to the theoretical value of 47 µrad. The rocking curve also revealed that there is a doped layer at the mirror surface, resulting from the foundry fabrication process. The existence of such a layer was confirmed by cross-sectional scanning electron microscopy.
2. The x-ray measurement was extended to a dynamics regime where the MEMS element oscillated at 74.670 kHz, its resonant frequency. Through the Si(400) Bragg diffraction, this window was significantly reduced, by three orders of magnitude, to about 2.7 ns (as shown in Figure 2), from 2 µs during the external reflection. This DTW width indicates that the MEMS mirror can be used as a high-repetition-rate beam chopper for any APS storage-ring time pattern.

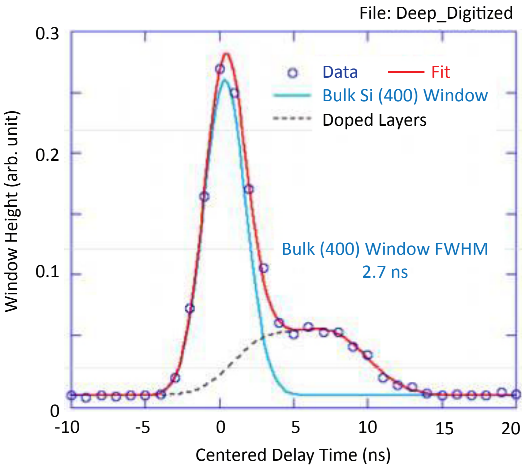


Figure 2. Dynamic "rocking curve" measurement from the same MEMS crystal during oscillation. The DTW width (FWHM) from the (400) diffraction is 2.7 ns.

3. A new MEMS device with a resonant frequency of 68 kHz was fabricated. The device was tuned by focused ion beam machining to a sub-multiple of 67.9 kHz, which is one-quarter of the APS storage ring frequency. With this device, the synchronization of the MEMS element and the APS ring was demonstrated. The DTW of this device is shown in Figure 3.

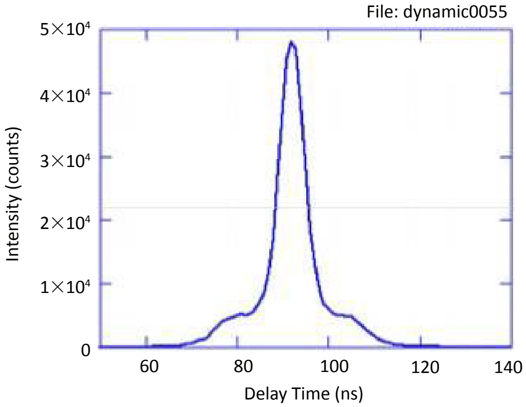


Figure 3. Dynamic time window of a tuned MEMS mirror synchronized with the APS storage ring at 67.9 kHz, one-quarter of the APS storage ring frequency.

X-ray Nanoimaging for Life Sciences

2010-183-R2

Barry Lai, Si Chen, Lydia Finney, Chris Jacobsen, Mark Jensen, Ken Kemner, Jörg Maser, Lynda Soderholm, and Stefan Vogt

Project Description

In recent years, it has become increasingly clear that metals bound to proteins and enzymes play vital roles in the control and signaling of many cellular or pathologic processes. It is estimated that one-third of all known proteins contain metal cofactors, often with important regulatory or enzymatic functions. At the same time, metals also may act as environmental contaminants (e.g., Hg, Pb) or carcinogens (e.g., As, Cr), which could present significant health hazards. This project aims to develop high-resolution x-ray nanoimaging methods that will allow elements of interest to be studied in their natural form without any chemical labeling. In particular, it will enable for the first time not only the visualization and analysis of trace elemental content at a spatial resolution of 30 nm — an order of magnitude better resolution than current x-ray fluorescence microscopes — but also the visualization of frozen-hydrated samples, which are as close as possible to the native state.

Mission Relevance

X-ray nanoimaging will impact areas that are crucial to DOE missions, including basic science, environmental stewardship, and national security. For instance, bacteria can drastically influence the fate of environmental contaminants, and a better understanding of the local chemistry and metal reduction process near a bacterium may lead to more effective bioremediation schemes. Among all actinides, plutonium is the most poisonous and has a long residence time in the body, although its cellular uptake and retention pathway are almost unknown. X-ray nanoimaging will reveal the subcellular location and oxidation state of intracellular plutonium and possibly provide targets for interruption.

X-ray nanoimaging also will afford insights into the growth of diatoms, which play a major role in carbon fixation in vast regions of the global ocean. However, the growth is often limited by the availability of the micronutrient iron. In general, the fundamental capability to study metalloproteins, metalloenzymes, and nanoparticles at the level of the individual organelle within cells and tissues preserved in a native state will enable novel research in diverse areas of interest to DOE and other federal agencies, such as the National Science Foundation, National Institutes of Health, and U.S. Environmental Protection Agency.

FY 2012 Results and Accomplishments

To reduce radiation damage and to preserve the sample in its native frozen-hydrated state, the sample must be maintained at a cryogenic temperature both before and during the measurement within the x-ray micro/nanoprobe. To this end, we investigated two sample-cooling schemes: conduction and convection. We concluded that the conductive approach would offer higher resolution, whereas the convective approach would offer greater flexibility in the sample environment and temperature range. Together with an external vendor, we designed (in FY 2010) and completed development (in FY 2011) of an in-vacuum, conductively cooled bionanoprobe, which was installed at Beamline 21-ID-D. In FY 2012, the bionanoprobe was commissioned with x-rays, and it demonstrated excellent performance. High spatial resolution was achieved at both ambient and cryogenic temperatures. The robotic cryo sample transfer, the fast scans, and the control system were shown to meet or exceed specifications. For the first time, frozen hydrated eukaryotic cells labeled with nanoparticles were imaged in 3D, thereby demonstrating the unique capabilities of x-ray fluorescence nanotomography. With increasing beamtime devoted for new users and applications, the bionanoprobe is expected to impact the study of metals in life sciences for many years.

At the same time, we also conducted testing of a convectively cooled cryojet with an existing x-ray microprobe at Beamline 2-ID-D. We confirmed that the cryojet did not adversely affect the spatial resolution down to 200 nm. In FY 2012, after demonstrating that cells may be imaged repeatedly in the cryojet without visible damage, the cryojet microprobe was initially opened to the external general user for the study of trace metals in dopaminergic neurons with x-ray micro-fluorescence and spectroscopy. It is anticipated that this new development will significantly enhance the scientific capability of Beamline 2-ID, not only in life sciences, but also in soft materials (e.g., new applications involving organic photovoltaics, polymer batteries, and fuel cells).

Award received: Microscopy Society of America Presidential Post Doctoral Awardees for 2012 included Si Chen for her submission on "2D/3D Trace Elemental Mapping of Frozen-hydrated Biomaterials using the Bionanoprobe."

Seminars

Chen, S. (2012). "Biological Applications of Synchrotron-based X-ray Fluorescence Micro/nano Probe." Dartmouth College, Hanover, NH, September 14, 2012.

Lai, B., S. Vogt, L. Finney, J. Maser and C. Jacobsen. (2010). "Status and Plans for XRF Nanoprobes at the Advanced Photon Source." Biological Applications of X-ray Fluorescence Microscopy Workshop, Chicago, IL, August 14, 2010.

Vogt, S. (2011). "X-ray Fluorescence Microscopy: Imaging Trace Metals." Xradia, Inc., Pleasanton, CA, May 27, 2011.

Vogt, S. (2011). "X-Ray Fluorescence Microscopy Capabilities at ANL." QBIC-ANL Collaborative Meeting, Northwestern University, Evanston, IL, April 12, 2011.

Vogt, S. (2012). "Imaging Trace Metals in Life and Disease with X-Ray Fluorescence Microscopy." Purdue University, Purdue, IN, September 18, 2012.

Vogt, S. (2012). "X-ray Fluorescence Microscopy: A Tool for Biology, Life Science and Nanomedicine." James Madison University, Harrisonburg VA, May 16, 2012.

Real-Life Imaging: Before and After the Microscope

2010-193-R2

Chris Jacobsen, Lydia Finney, Qiaoling Jin, Rachel Mak, and Stefan Vogt

Project Description

This project is aimed toward the development of new capabilities in x-ray microscopy and imaging. One goal is to develop capabilities for the preparation of frozen hydrated specimens for biological and materials science research. A second goal is to develop methods for multivariate statistical analysis of spectrum image data acquired by using x-ray microscopes and imaging systems at the Advanced Photon Source (APS) and to apply those methods to electron microscope studies. Electron microscopes are able to acquire spectrum image data with different physical mechanisms and over smaller length scales than x-ray microscopes, yet mathematically the treatment of the data can be identical; this allows one to find image regions with common compositional characteristics automatically.

Mission Relevance

This project is relevant to DOE missions in Basic Energy Science (BES) and in Biological and Environmental Research (BER). The BES mission includes the development of high-end instrumentation for synchrotron radiation research on materials, and the BER mission includes improved methods to elucidate the structure of biological materials. This project supports the BES mission by developing ways to make better use of the data acquired with x-ray microscopes at the APS. The DOE Workshop on Data and Communications in Basic Energy Sciences held in October 2011 highlighted the need to add sophisticated analysis approaches, such as those we are developing (non-negative matrix factorization), to process the flood of data emerging from DOE's light source facilities. The cryo sample handling capabilities we are developing are relevant to both BES studies of soft materials and BER studies of biological materials, since cryogenic sample conditions provide a way to study organic films, cells, plant tissues, and the like with a thousandfold reduction in radiation damage.

FY 2012 Results and Accomplishments

In the area of cryo sample preparation, in FY 2010 we identified and procured the key equipment items for a cryo preparation lab. Following initial demonstration experiments in FY 2011, the FY 2012 accomplishments include the following:

1. *Preparation of frozen hydrated and freeze-dried specimens for x-ray microprobe experiments.* As part of evaluating various preparation protocols for different applications, hawse worked with collaborators on x-ray microscopy studies. Their samples were either (i) prepared for direct examination in the Bionanoprobe at APS Beamline 21-ID at cryogenic temperatures or (ii) freeze-dried and examined at APS Beamline 2-ID-E at ambient temperature.
2. *Studies on some fundamental factors related to cryo sample preparation.* We studied the effect of different wash buffers and chemical fixation methods on cryogenically preserved specimens. We also carried out a systematic study of the behavior of various substrates, such as silicon nitride windows, sapphire discs, TEM (transmission electron microscope) slot grids, and aclar films for cryogenic specimen preparation. Finally, we carried out studies on methods for safe handling of Biosafety Level 2 specimens under cryogenic conditions, where we demonstrated that UV sterilization can be used even for a sample at ~1 centimeter depth in liquid nitrogen, and that it has minimal effect on the distribution of diffusible ions in cells.
3. *Improvements in cryosectioning techniques for frozen hydrated specimens.* Our high-pressure freezer was used to prepare thick samples, from which ultrathin samples were produced by cryo cutting of sequential section "ribbons" in the ultramicrotome.

These sample preparation activities were essential for developing the protocols that are now being used at the Bionanoprobe, a new cryogenic x-ray microscope being operated at APS Beamline 21-ID. This microscope is now delivering high-quality images of beautifully preserved cells for studies of the action of potential cancer therapeutic agents and for studies of the uptake of metal contaminants by plant cells. The successes in this area have led to this research being continued with support from a National Institutes of Health grant.

In multivariate statistical analysis of spectrum imaging data, in FY 2010 we procured and installed our computer systems, and in FY 2011 we began to develop test code using non-negative matrix factorization to find the spectroscopic "themes" in complex spectromicroscopy data. In FY 2012, we included key optimization factors, such as sparsity, to best separate the spectral components and have written the algorithm into a so-far-"hidden" mode of the program *Mantis*, the development of which we have supported. *Mantis* experts have taken our methods and made them available on the web as an open-source software project (code.google.com/p/spectromicroscopy) via a contract we arranged with 2nd Look Consulting, a scientific software development firm. This program is now being used in tests of spectromicroscopy capabilities at the APS Beamline 32-ID transmission x-ray microscope, and it is also planned for adoption at the I08 scanning transmission x-ray microscopy beamline at the Diamond Light Source in the United Kingdom. The code is being validated by testing it on data involving the speciation of arsenic in mine tailings, as well as on spectromicroscopy data for visualization of lignin and cellulose in biofuel materials (relevant to DOE's mission in energy research).

The results of this work have contributed to efforts to apply non-negative matrix factorization to x-ray fluorescence data, which are being pursued in a parallel LDRD project (2011-149, "Next Generation Data Exploration: Intelligence in Data Analysis, Visualization and Mining").

Seminars

Jacobsen, C. (2012). "X-ray Scattering and Imaging in Biology: Radiation Damage Limitations and Solutions." DESY Research Course: New X-ray Sources for Life Science Applications, Hamburg, Germany, March 23, 2012.

Jacobsen, C. (2012). "X-ray Microscopy: Cold, Hard Truths for Soft Studies." Paul Scherrer Institut, Switzerland, April 25, 2012.

Jacobsen, C. (2011). "X-ray Imaging for Environmental Science." Colloquium, Pacific Northwest National Lab, Richland, WA, February 6–8, 2011.

Jacobsen, C. (2011). “X-ray Imaging.” National School on Neutron and X-ray Scattering, Argonne National Laboratory, IL, June 2011.

Jacobsen, C. (2011). “4th Generation Light Source Applications in Microscopy.” Higher European Research Course for Users of Large Experimental Systems (HERCULES), Orsay, France, March 20–23, 2011.

Jacobsen, C. (2011). “Soft x-ray spectromicroscopy and 4th generation light source applications in microscopy.” Higher European Research Course for Users of Large Experimental Systems (HERCULES), Orsay, France, March 20–23, 2011.

Jacobsen, C. (2011). “Cryo: Samples, Damage, and Instruments.” Biomedical Applications of X-ray Microprobes, Northwestern University, Evanston, IL, August 11, 2010.

Tuning Electronic Structure at High Pressures: Toward Novel Materials Discovery from X-ray Science under Extreme Conditions

2011-023-R1

Daniel Haskel

Project Description

We seek to develop a state-of-the-art x-ray spectroscopy capability for transformational studies of electronic and energy materials under simultaneous extreme conditions of high pressure (P = 1–2 Mbar), high field (H = 6.5 Tesla), and low temperatures (T = 2 K). The new capability will allow changes in electronic structure and electronic ordering to be explored in a much larger (P, H, T) range than currently available at any synchrotron radiation facility.

Mission Relevance

This x-ray science project is relevant to DOE missions in basic science and will thrive from its synergy with other research focused on the design and discovery of novel superconducting materials, complex oxides, multiferroics, and molecular magnets, as well as actinide research. As stated in the DOE-Basic Energy Sciences report on Materials under Extreme Conditions (2007), the Grand Challenges for energy research on materials under extreme conditions include “*Can the movement of electrons be predicted and controlled to form bonds under pressure? Will the materials formed under these conditions have unique chemical (reactivity) and physical (electronic, magnetic, superconducting) properties?*” We intend to address some of these challenges within this project.

FY 2012 Results and Accomplishments

The effort during FY 2011 was devoted to the initial design work on a superconducting magnet/cryostat interface that would be compatible with x-ray spectroscopic probes of electronic structure and magnetism at high pressures. Key parameters included a vibration-free sample environment, ability to cool a diamond anvil cell to 2.2 K, high magnetic fields, and optical access for *in situ* pressure calibration and fluorescence detection. These efforts culminated in near-final design of the instrument and procurement of its cryostat section.

During FY 2012 we worked on final specifications and procurement of a 6.5-Tesla split-coil superconducting magnet and on implementation (at Beamline 4-ID-D of the Advanced Photon Source) of an x-ray micro-focusing system for high-pressure magnetic spectroscopy, to be used in conjunction with the procured magnet. Completed tasks include the following:

- Designed re-entrant radial bores along the magnet split to accommodate a Ruby fluorescence system for *in situ* pressure calibration (Figure 1) and an x-ray fluorescence detector.

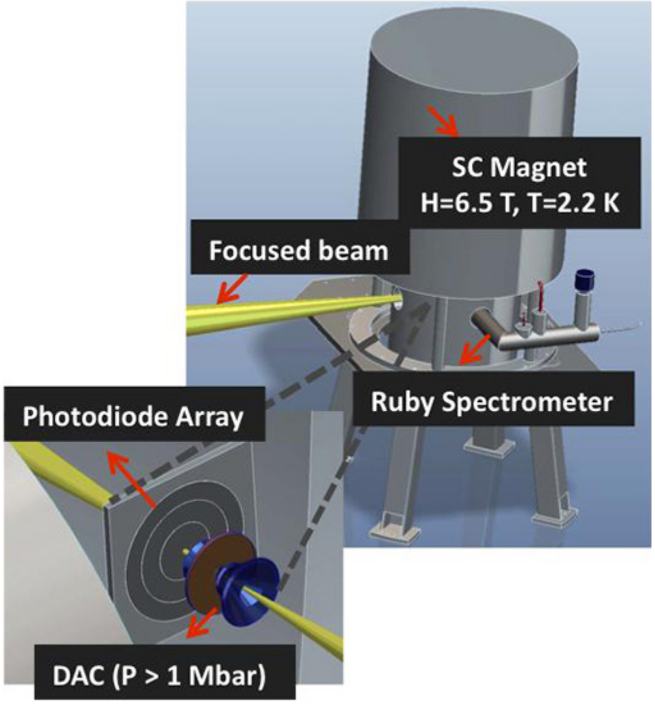


Figure 1. Sample environment for x-ray absorption/dichroism experiments under extreme pressure conditions.

- Installed re-entrant bores, window ports, and superconducting magnet in existing cryostat that was procured in FY 2011.
- Designed and procured magnet support for installation at Beamline 4-ID-D.
- Implemented x-ray micro-focusing system compatible with magnet environment. A toroidal mirror, in conjunction with a pair of Kirkpatrick-Baez (K-B) mirrors, focuses 85%

of the undulator x-ray beam into a 12 × 15-mm^2 spot. Alternatively, the K-B mirrors alone accept 22% of the x-ray beam for focusing into a 5 × 9-mm^2 spot (working distance = 0.6 m to center of magnet in both focusing schemes). This system increases the flux available for high-pressure experiments by a factor of 50 and enables transmission experiments through a beryllium (Be) gasket instead of through diamond anvils, avoiding contamination of absorption spectra by diamond Bragg peaks.

- Tested focusing capability with high-pressure, Ru K-edge x-ray absorption measurements of $SrRuO_3$ by using a transmission geometry through a Be gasket (Figure 2).

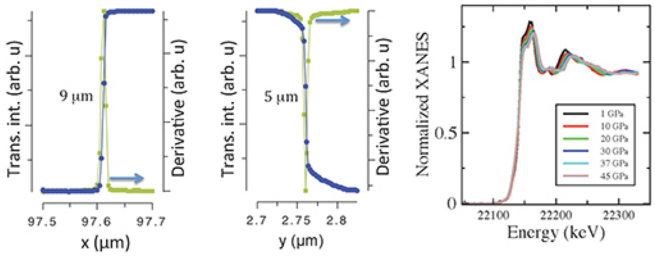


Figure 2. Left and center panels: Transmitted x-ray intensities (and their derivatives) obtained in knife-edge scans of a tungsten wire (100 µm in diameter) across the focused x-ray beam. Right panel: absorption data collected using a transmission geometry through a Be gasket thus avoiding Bragg peaks from diamond anvils.

Proposed Work for FY 2013

- Procure optical components and spectrometer for Ruby fluorescence system; build and install in magnet's re-entrant bore (Figure 1).
- Demonstrate cooling of membrane-driven diamond anvil cell to T = 2.2 K; test membrane operation at low T to pressures > 1 Mbar (100 GPa).
- Procure concentric photodiode array for fluorescence measurements in backscattering geometry; install in sample environment (Figure 1).
- Demonstrate instrument capability with high-pressure x-ray absorption and x-ray magnetic circular dichroism experiments to 1 Mbar (100 GPa) at T = 2.2 K and H = 6.5 Tesla, by using transmission (concentrated samples) and fluorescence (dilute systems, single crystals) geometries.

Development of *in situ* Radioactive Materials Probes Using High-Energy X-rays

2011-063-R1

Meimei Li, Jonathan D. Almer, Erika Benda, Yiren Chen, Ali Mashayekhi, Ken Natesan, Dileep Singh, Leyun Wang, and Frank Westferro

Project Description

Hard x-ray technology propels materials science research by providing *in situ* characterization capability for engineering materials under various conditions (e.g., loading, temperature change, and pressure). A challenging application, though, is materials used in nuclear energy systems. These materials are often activated, which makes them difficult to handle at an open x-ray beamline. A viable approach to overcome this challenge is to develop a specialized containment that can shield the irradiated specimen while allowing x-ray measurements under *in situ* thermal-mechanical loading at a beamline. Such an experimental capability would allow us to gain critical knowledge on the microstructural evolution of irradiated materials under various temperature and loading conditions that are relevant to real environments in nuclear power plants. The knowledge gained will enable scientists, engineers and nuclear regulators to accurately evaluate and predict the performance of nuclear components over an extended service life and to develop new materials more resistant to damage in nuclear environments, both of which will have a significant economic and environmental impact on energy usage.

In this project, our goal is to develop and demonstrate an innovative *in situ* high-energy x-ray scattering and imaging capability for characterization of irradiated materials subjected to elevated temperature and stress. We are taking full advantage of the *in situ* high-energy x-ray scattering and imaging capability at Beamline 1-ID at the Advanced Photon Source (APS) and developing an experimental module that will enable us to make synchrotron-based x-ray measurements on irradiated samples. The experimental module will be connected to a mechanical testing frame at the beamline, permitting the enclosed irradiated sample to be characterized *in situ* by concurrent small- and wide-angle x-ray scattering (SAXS/WAXS) and imaging under relevant thermal and mechanical loading conditions (e.g., tension, creep, and fatigue). An internal rotation mechanism will enable three-dimensional (3D) tomography of the irradiated specimen under load. With this capability, the evolution of lattice strain, texture, and crystallographic defects in irradiated materials can be followed in real time during annealing and deformation.

Mission Relevance

This project is directly relevant to DOE's energy mission, as exemplified by programs of the Office of Nuclear Energy, the Office of Science (Basic Energy Sciences and Fusion Energy Sciences), and the National Nuclear Security Administration. It will also benefit other agencies, such as the U.S. Nuclear Regulatory Commission, and the nuclear industry. First, the experimental capability being developed for irradiated materials is essential to fundamental studies of the structure-property relationship of materials under various extreme conditions, particularly high irradiation. Second, the results obtained from these pioneering experiments will help us better understand the behavior of different types of reactor materials in nuclear environments, which will allow us to improve the material design of different structural components in nuclear reactors. In addition, these experimental results can be used to assess existing computational models for predicting materials performance in nuclear reactors.

FY 2012 Results and Accomplishments

Before FY 2012, we completed the initial design, feasibility study, and technical and safety evaluation of the experimental module. Initially, the module was designed for performing *in situ* characterization in an existing experiment station. The APS upgrade, including sector 1 beamlines, requires that the engineering design of the experimental module be compatible with a newly built experiment station. In addition, we broadened the project scope to include an internal rotation mechanism for performing 3D x-ray tomography of an irradiated specimen under load to allow concurrent SAXS/WAXS/tomography measurements.

The major component of the experimental module is a high-temperature vacuum chamber with heating capability to 1,200°C and a mechanism for direct loading of a miniature specimen inside a mechanical test frame. Integrated interior radiation shielding and shield shutters for the x-ray windows provide comprehensive protection from radiation exposure. This interior shielding is sufficient for handling low-activity specimens with minimal radiological control at the APS beamlines. Secondary external radiation shielding can be added for handling high-activity specimens, when needed. A dedicated transport cart is designed to safely transport the vacuum chamber containing the activated specimen between an on-site radiological facility and the APS. The transport cart is sufficiently robust and adaptable to allow smooth connection of the chamber to the test frame at APS beamlines.

To take advantage of the recently developed x-ray tomography capability at APS Sector 1, the design of the vacuum chamber was modified to allow the internal rotation of the specimen grips under tensile loads of up to 2.5 kN at high temperature. The internal rotation capability is achieved by installing a dynamic O-ring housing and a Huber high-precision rotation stage mounted to the bottom pull rod outside the chamber, as well as a thrust-bearing assembly inside the chamber that connects the upper pull rod and the specimen grip (shown in Figure 1). To ensure rotation with high precision, the thrust bearing must have a low friction coefficient (< 0.04) to minimize the rotational friction and maintain its functionality at high temperature. Dicronite™-coated steel thrust bearings and ceramic bearings were considered for high-temperature vacuum operations. Initial assessments of friction torque measurements and surface characterization of heat-treated Dicronite™-coated bearings showed promise for elevated-temperature applications, while ceramic bearings may be needed at higher temperatures than appropriate for Dicronite™. The specimen grips were modified to meet the strict requirements imposed by the tensile rotation device. If the rotation mechanism is realized, absorption and phase contrast tomography can be used to study microstructural features (> 1 μm) such as cracks and pores, as well as to complement the nanoscale SAXS/WAXS probes for characterization of structural features at a broad range of length scales.

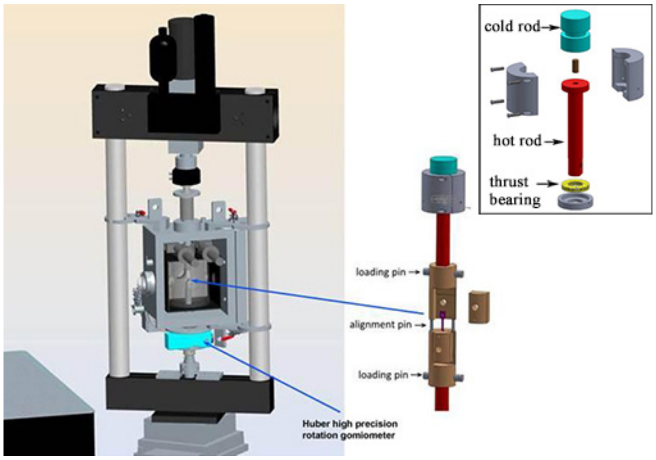


Figure 1. An internal rotation stage incorporated into the high-temperature vacuum chamber.

Another major challenge in the design of the experimental module is x-ray windows. The high-temperature vacuum chamber is equipped with four view ports, two of which will directly interact with x-ray beams. X-ray windows must meet multiple requirements, including low x-ray scattering and absorption, thermal stability, radiation stability, optical transparency, and mechanical integrity. The design of the two x-ray windows was further improved: the inner layer consists of a 2-mm-thick single-crystal sapphire lens coated with a thin gold film and an intermediate layer of 5-nm-thick Cr, and the outer layer consists of a 1-mm dome-shaped Lexan lens. The choice of gold and the choice of thickness are driven by the need to maximize the infrared reflectivity while maintaining optical transparency. Significant R&D was conducted to develop the optimum coating strategy for the gold film. Gold films of various thicknesses were deposited on quartz micro-slides. Reflection-wavelength profiles were measured for these films by using a spectrophotometer. The results indicated that a 30-nm gold film can effectively reflect most infrared waves (wavelength >1,000 nm) while providing high transmission of visible light (wavelength ~ 400–700 nm). Chromium is used for optimum adhesion of the gold thin film to the sapphire substrate.

To optimize the design of the *in situ* irradiated material probes, a number of experiments on non-irradiated nuclear materials (e.g., steels) were conducted by using the established WAXS and SAXS techniques at APS Beamline 1-ID. *In situ* tensile and creep tests of non-irradiated steel specimens were conducted at a wide range of temperatures of up to 650°C. WAXS and SAXS data were collected simultaneously *in situ* during straining until specimen failure. The dimensional change of the specimen was monitored via changes in the specimen transmission of x-rays. As shown in Figure 2, the WAXS measurements revealed the development of lattice strain and dislocation activities in the ferrite/martensite matrix and different types of precipitates, whereas the SAXS data revealed void formation and growth that leads to the final failure in a ferritic-martensitic steel. The combination of multiple probes in a single experiment allows the mechanical behavior of the material to be directly linked with microstructural information about the material. The measured Von Mises stresses of second-phase precipitates, $M_{23}C_6$ (M: primarily Cr) and MX (M: V, Nb, X: C, N), can be compared with the strengthening theories, leading to a quantitative understanding of the strengthening mechanisms. Likewise, strain- and temperature-dependent void formation and evolution revealed by SAXS data shed light on the damage initiation and progression inside the specimen. These concurrent, real-time measurements provide valuable insight into the design of a new alloy with improved mechanical performance. The same WAXS/SAXS technique (combined with x-ray imaging) will be used with the experiment module that is being developed for characterization of irradiated specimens, to study the correlation between irradiation-induced microstructural changes and a material's degradation mechanisms.

Proposed Work for FY 2013

In FY 2013, the module will be inspected and tested; radiation safety procedures will be reviewed, and the control of temperature and mechanical loading will be evaluated. Significant efforts are still needed to verify the internal rotation concept. Confirmatory experiments will be conducted on non-irradiated specimens, followed by experiments on irradiated specimens.

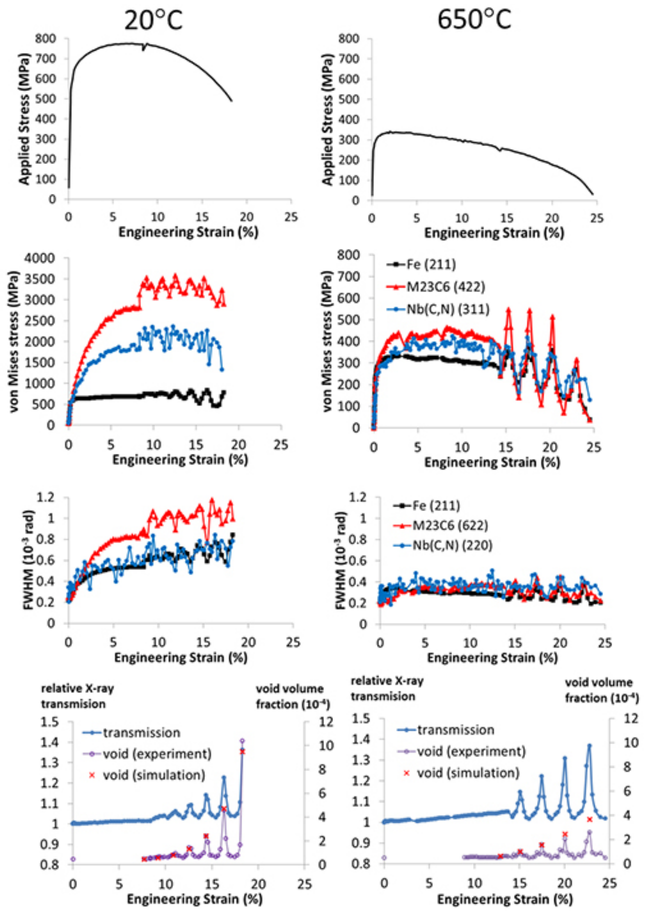


Figure 2. Simultaneous measurements by WAXS and SAXS during in situ *tensile tests at 20°C and 650°C allow a quantitative understanding of the temperature-dependent structure-property relationship in a material (here, ferritic-martensitic steel). Top row: macroscopic stress-strain curves showed significant strength reduction from 20°C to 650°C. Second row: Load partitioning among different phases was quantified by their respective von Mises stress (σ_v) measured by WAXS. At 20°C, $M_{23}C_6$ (red) and MX (blue) developed much higher σ_v than the Fe matrix (black); at 650°C, σ_v in the precipitates and the matrix are similar. The observation can be attributed to different dislocation/precipitate interaction mechanisms at low temperature versus high temperature. Third row: peak broadening (quantified by the full width at half maximum, FWHM) was more significant in the specimen tested at 20°C than the one tested at 650°C. The difference can be understood by the dislocation theory. Bottom row: volume fraction of voids as a function of the strain was estimated on the basis of SAXS profiles. A strong correlation between void and necking (high x-ray transmission) was observed. Increase of void volume with strain can be simulated by using a mathematical model.*

Fast X-ray Detectors Based on Multichannel Plates

2011-067-R1

Bernhard W. Adams, Jeffrey W. Elam, Henry J. Frisch,
Harold E. Gibson, and Zinetula Z. Insepov

Project Description

The goal of this project is to develop a novel type of x-ray photon detector with a 2-dimensional spatial resolution of the order of 0.1 mm, a time resolution of better than 1 nanosecond, and the capability of acquiring 10^8–10^9 photons per second. The project runs concurrently with, but is distinct from, the large-area, picosecond photon detector (LAPPD) programmatic project that is centered at Argonne and it leverages Argonne's atomic-layer-deposition technology for x-ray-specific adaptations. In such a detector, x-rays incident on a microchannel plate (MCP) optimized for x-ray photoabsorption generate photoelectrons, which are then amplified to current pulses in a stack of two more MCPs. An array of microwave striplines directs these pulses to fast waveform-sampling electronics for time and location determination.

In the cathode MCP, the x-rays hit the inside walls of the pores at a grazing-incidence angle to match the x-ray to the electron path lengths, while the large number of pores presents a sensitive area that is useful for imaging applications. Emission from the cathode MCP can be gated by application of voltages of several hundred volts in the reverse direction. Fast gating on the 100-ps time scale is achieved with a pair of microwave power amplifiers in conjunction with microwave tapers to increase the voltage. This capability is aimed at nuclear-resonance time-domain spectroscopy, where the prompt 100-ps pulse from a synchrotron radiation source blinds detectors to the first few nanoseconds of the evolution of nuclear-resonant emission.

Unlike other time-resolving imaging detectors, this one can supply a continuous data stream of time- and location-tagged events. This stream is useful for applications in time-resolved imaging and photon-correlation spectroscopy, where large ranges of time scales and large dynamic ranges of photon flux are encountered.

Mission Relevance

This project is relevant to the DOE mission in basic science because it introduces a powerful new x-ray detection technique with numerous applications in imaging and spectroscopy. Beyond the immediate application in synchrotron environments, spin-off applications are to be expected in fields as diverse as medicine and homeland security.

FY 2012 Results and Accomplishments

In FY 2011, a vacuum chamber was designed with fixtures to hold the MCP stack, high-voltage supplies, and signal extraction, and a first x-ray-based test was performed with conventional MCPs.

In FY 2012, this fixture was improved (see Figure 1). A photocathode MCP was fabricated by coating an MCP with tungsten oxide. Gating of emission from this MCP with static voltages of 300–500 V was demonstrated in a test assembly with two conventional LAPPD-style amplifier MCPs.

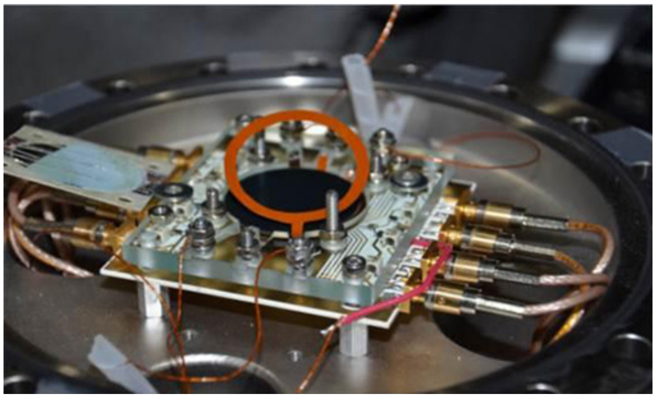


Figure 1. Test fixture for the MCP stack on a vacuum flange with a glass plate holding the MCP stack atop a printed circuit board, which houses the readout striplines and microwave amplifiers. The signals are sent to the outside through 50-Ohm cables (SMA connectors visible). Of the MCP stack, the two amplifier MCPs are in place (black disc), and the cathode MCP with WO3 coating is flipped over to the left. It would normally be placed atop the brown-colored ring (flex-circuit board used as spacer and electric contact).

When operating at the typical gain of 10^6, a pore in an MCP stack takes about 1 millisecond to fully recover from a discharge generating a pulse. This is a severe limitation in high-data-rate applications, such as imaging in a synchrotron-radiation environment. To address this problem, a readout stripline assembly with integrated microwave amplifiers was designed to permit reduction of MCP gain and thus improve recovery in high-rate applications by discharging pores only by a few percent for each photon hit.

It was demonstrated that a 100-micrometer spot (corresponding to about 10 pores, each 40 micrometers in diameter) over a single stripline illuminated with x-rays from the Advanced Photon Source (APS) could detect x-rays at the full 6.5-MHz rate of the APS 24-bunch mode (Figure 2). Extrapolating to 16 striplines, this amounts to a rate of 10^8 photons per second.

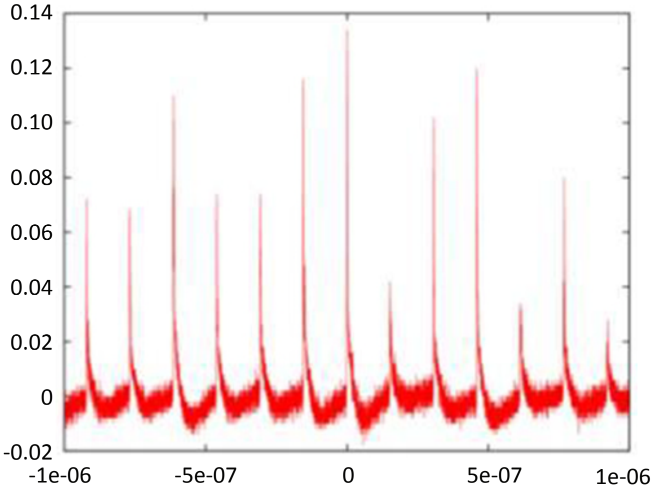


Figure 2. Signal (volt amplitude over time in seconds) from the fabricated detector, showing x-ray bunches at a 6.5-MHz rate. This demonstrates a very fast recovery of the microchannel plates as a result of operation at low MCP gain, which is enabled by integration of microwave amplifiers.

To generate a gating pulse of several hundred volts and 100 ps duration, a combination of high-power, broadband microwave amplifiers and broadband microwave impedance tapers is needed. The amplifiers were procured and tested to provide pulse amplitudes of about 40 V into 50 Ohms. This is increased to 120–150 V by sending the pulses through a 1:3 broadband impedance matcher, a so-called Klopfenstein taper. By generating bipolar pulses, the total gating voltage amplitude is increased to about 250 V. In a first test, four 1:4 Klopfenstein tapers were put in a bipolar up-down (50 to 200 to 50 Ohms) configuration. On the basis of these tests, the design was changed to be longer (reaching to lower frequencies of about 50 MHz) and tapering was only 1:3, and a set of these tapers was procured from a printed-circuit manufacturer.

Monte Carlo simulations of the processes of x-ray photoelectron generation in a cathode MCP and subsequent gain in the MCP stack were performed. The simulations show that there is some amount of gain of the order of 100–1,000 in the cathode MCP and the pulse shapes that can be expected from it.

The PSEC-4 waveform sampling electronics were tested with an LAPPD-style detector assembly. The tests show that the data acquisition system is working as designed with 10 gigasample/s, 30-channel parallel acquisition at each end of a stripline array. The electronics can be triggered externally or by the signals themselves. For each event, the high sample rates are sustained for 25 ns. The data are then digitized, and the array is ready for the next event after 20 microseconds.

Proposed Work for FY 2013

The microwave tapers will be included in the detector test assembly, and 100-ps gating of x-ray photoemission will be tested. A readout stripline array will be produced on a GaAs substrate to improve the spatial resolution by making use of the high dielectric constant to increase stripline density and reduce the signal propagation velocity. Waveform acquisition will be done by using the PSEC-4 electronics instead of an oscilloscope.

X-ray Optics Fabrication with Self-Assembled Nanostructures

2011-104-R1

Yuxin Wang, Jeffrey W. Elam, and Hsien-Hau Wang

Project Description

In this project, our goal is to develop techniques to fabricate a new generation of high-performance x-ray optics optimized for high efficiency and reliability, particularly at high energies well above 20 keV. Our technique uses a self-assembled nanostructure, anodic aluminum oxide, as the basis to fabricate Fresnel zone plate lenses with 20–30% efficiency and extremely high structural stability. With the combined gains in efficiency, operating x-ray energy range, and stability, these optics will become a critical core technology for operating the Advanced Photon Source (APS).

Mission Relevance

This project is relevant to the DOE mission in basic science. Its success will supply a critical technology for APS operations and R&D. In APS imaging programs, for example, it will enable routine x-ray studies in five dimensions — that is, three spatial dimensions, x-ray energy (hence material composition), and time progression — to achieve the goal of completely characterizing samples' 3D structure, their 3D material composition, and their dynamic evolution in time — even under extreme operating conditions. In addition to microscopy and imaging applications at the APS, this development will bring significant benefit to other facilities at both the APS and other DOE user facilities, enhancing a wide range of other x-ray techniques, such as grating-based phase contrast imaging, protein crystallography, and micro-diffraction. For example, a 100-micrometer (μm) -diameter zone plate with 40-nm resolution could generate over 1,000,000-fold flux concentration at its focal point. Such a lens would dramatically transform researchers' ability to study sub-micrometer features with high-speed dynamics and would further enhance the capabilities of advanced methods, such as multi-wavelength anomalous diffraction.

FY 2012 Results and Accomplishments

The key challenge of this project is the development of a complex process (shown in Figure 1) for fabricating high-aspect-ratio nanostructures. In FY 2011, we focused on the substrate preparation and lithography approaches. These two steps contain the most uncertainty and potentially require the most development effort, while the remaining steps are relatively well understood. We successfully developed a mechanical polishing technique that consistently produces surface roughness of less than 0.15 nm per 1-μm × 1-μm area and a basic e-beam lithography workflow. In FY 2012, we developed a custom code for writing curvilinear lines with the JOEL system at the Center for Nanoscale Materials (CNM) and refined metal coating processes to produce consistent pattern transfer from the photoresist layer to the AAO (anodic aluminum oxide) layer. We fabricated AAO-based zone plates with outer zones 5 μm thick and as little as 100 nm wide and performed efficiency tests at APS.

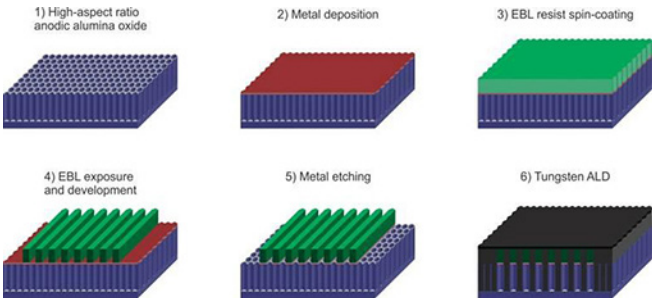


Figure 1. Illustration of the fabrication process.

Custom JOEL E-beam Pattern Generation Code: Since e-beam machines are designed primarily for process development in semiconductor applications, their pattern-generation algorithms are tailored for writing rectilinear patterns. A consequence is that when a line feature width is below 100 nm, the diagonal portion of the circular pattern receives a different dose from the vertical and horizontal portions. We developed a custom code that will work with a range of substrates, including commonly used silicon nitrite windows and AAO substrates, different photoresist types, and various buttress patterns, as well as different types of zone plates, including spiral zone plates and a multi-focus zone plate designed to generate interference contrast images. This code successfully generated 20-nm zone plate patterns. Figure 2 shows several patterns generated by this code.

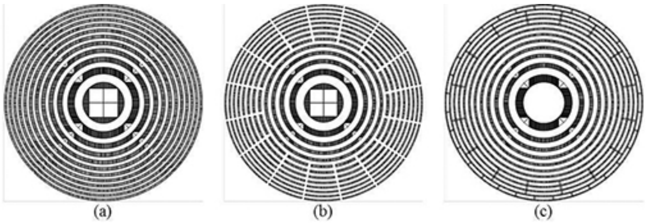

(a) (b) (c)

Figure 2. Examples of e-beam patterns generated by our custom code: (a) a regular zone plate, (b) positive resist with buttressing, and (c) negative resist with buttressing.

Pattern Transfer Process Refinement: In our first attempts, we used an aluminum coating to block AAO pores prior to the lithography process (Figure 1, step 2). The process largely worked, but the resist developer attacked the aluminum coating in certain locations, leading to some random pore opening. We developed an alternative chromium coating process that produces very consistent patterns after the lithography process, as shown in Figure 3.

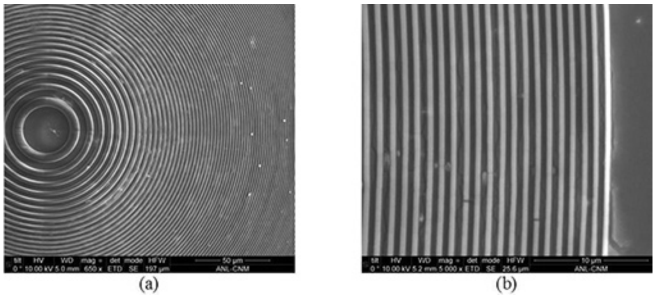

(a) (b)

Figure 3. Zone plate pattern made on AAO substrate with Cr coating after lithography process. Two magnifications are shown. The finest zone width is 100 nm.

Zone Plate Fabrication: Using the patterning techniques described above and the process described in Figure 1, we completed fabrication of zone plates. Figure 4(a) shows the pattern after the Cr layer is etched away. Figure 4(b) shows the zone plate after the ALD process step.

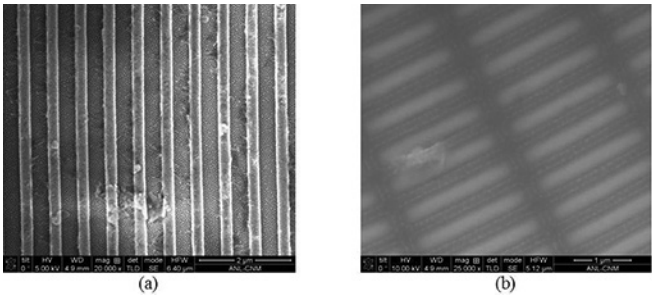
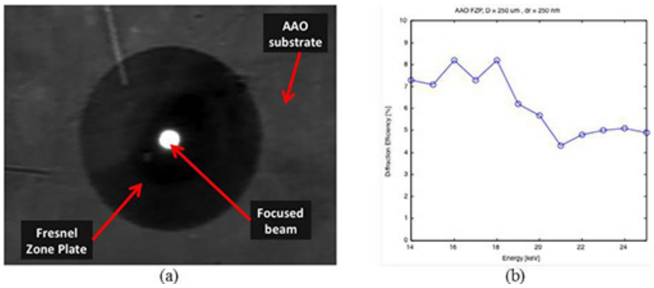

(a) (b)

Figure 4. (a) Zone plate pattern made on AAO substrate after removing the Cr coating and (b) after filling pores with Tungsten.

Performance Test: The initial batch of AAO zone plates was tested using the transmission x-ray microscope at Beamline 32-ID-C. The focus beam spot is shown in Figure 5(a), and the diffraction efficiency is shown in Figure 5(b). This is the first time a zone plate has been used for energies above 20 keV.



(a) (b)

Figure 5. (a) Typical zone plate focus image and (b) measured focusing efficiency. (See Figure 3 for scale.)

Proposed Work for FY 2013

In 2013, we propose to proceed according to the originally proposed milestones, as follows:

1. Refine AAO fabrication techniques to optimize the process for smaller pore sizes, allowing finer feature patterning.
2. Refine the e-beam fabrication process to reduce line width to less than 100 nm while maintaining 5-µm thickness, achieving an aspect ratio of at least 50.

Next-Generation Data Exploration: Intelligence in Data Analysis, Visualization, and Mining

2011-149-R1

Stefan Vogt, Lydia Finney, Mark Hereld, Chris Jacobsen, Sven Leyffer, Claude Saunders, Siwei Wang, Jesse Ward, and Stefan Wild

Project Description

In this project, we are developing a new generation of data analysis and visualization tools for multidimensional microscopy. The focus is on three capabilities: (1) software that can interpret data, identify and classify object types within datasets, and enable researchers to ask complex questions of a single but complex dataset; (2) software that has the ability to analyze datasets that represent the combined results of several instruments (e.g., to classify objects on the basis of all the available input data); and (3) software that has data-mining capabilities, through the integration of the developed software with database organization of datasets. The goal is to probe and correlate very large datasets acquired over several years and that span multiple instruments and researchers.

Mission Relevance

The scientific applications of the analytical methods developed in this project will impact areas crucial to DOE's missions, including basic science, environmental stewardship, and national security. These areas range from addressing issues related to bioremediation of heavy metal or radionucleotide contamination, to investigating novel approaches toward efficient biofuels and to understanding nutrient cycling in the ocean and its impact on climate change. This project will also create a fundamental change in the scientific impact of imaging capabilities at the Advanced Photon Source (APS). We expect that these capabilities will directly enable new science in metallomics, cell biology, pathogenesis, novel therapeutic agents, bioremediation, biofuels, and nanoengineering, and it will be uniquely leveraged by Argonne's high-performance computing capabilities. In addition, this work will establish a model and a framework that can be used for future projects targeting different areas of data analysis.

FY 2012 Results and Accomplishments

Before FY 2012, working with other x-ray imaging groups, we developed a standard for a common HDF5-based file format that will be used for data storage and analysis and implemented the new file format. We evaluated different approaches to object classification, in particular unsupervised neural networks (Self-Organizing Maps) and k-means cluster analysis, as well as multi-phased approaches (c.f.: "Efficient and Effective Clustering Methods for Spatial Data Mining" by Raymond Ng and Jiawei Han, 1994) for identifying and distinguishing different cells.

In FY 2012, we developed an approach to automatically identify and classify single cells of different types in complex images. Our approach is based on two basic computer vision ideas: (1) the formulation of energy functionals that have global optimum solutions (e.g., graph-cut and Potts-model based Markovian random fields) and (2) the family of level set/active contour methods. Both methods cannot be used "as is" when it comes to processing the x-ray fluorescence images. First, these methods are developed on the basis of bright-field images and visible light fluorescent images, which only have a very small number of possible intensity channels as opposed to more than 1,000 raw intensity channels for the case of x-ray fluorescence datasets, or 20+ analyzed elemental channels. The significant increase in the number of necessary intensity channels makes it impossible for straightforward applications of these methods to provide sensible results (i.e., the affinity between graph nodes would be completely different). Second, they are not able to handle object overlapping, which is a common scenario in x-ray fluorescence images of various cell types.

We developed a two-step approach: we first locate cell position markers by using image segmentation on candidate elements, and then we determine the number of cells present in the dataset and their respective exact locations on the basis of a statistical model of element content distributions. In the first step, our goal is to distinguish the subset of pixels that are inside of cells from background areas. In the second step, we process all cell regions, especially those with possible overlapping cells, and determine their occurrences by a tree-structured hypothesis test. The novelties of our approach include developing a framework on how to combine multiple intensity channels, performing image segmentation on different intensity channels according to cells types, and modeling multiple dimensional element distributions to grow deformable curves and evaluate cell occurrences at a scale that manual annotation cannot provide. In addition, our algorithm can model cellular regions of arbitrary shapes, which means that our segmentation and curve growing can be easily extended to model objects with major deformations (like concave shapes) as opposed to ellipsoid-based cellular/nuclei regions (and thus is extendable to completely different applications). The proposed hypothesis test successfully employs expert knowledge to output the most likely occurrences of cells and their rough positions, without knowledge of "ground truth," which match the need of high-dimensional x-ray fluorescence imaging processing where extensive labeling is impossible.

We also conceived of test experiments in which we created an "artificial" mixture of different cell types to be able to test algorithm performance with a somewhat known outcome. Interestingly, we observed deviations from the expected outcome (which we later verified manually), where elemental content distributions implied a much wider variance in elemental content between different cells than we previously thought realistic.

We also started recasting our analysis software into a framework that is easier to use in software pipelines. Specifically, we ported the main analysis routines to an APS-supported python distribution and carried out verification of performance. We changed the file format we are using to HDF5, which improved analysis speed in some cases by an order of magnitude (built-in compression reduces file size vastly and minimizes the time to read in large datasets). We also made progress on the routine use of multivariate analysis to speed up analysis of large datasets and implemented analysis methods based on matrices for near-realtime initial data analysis.

Proposed Work for FY 2013

In FY 2013, we will:

- Finish porting the core analysis code we have used in the past ("MAPS") into a more open programming platform (python), so as to be better able to support it and make use of data analysis pipelines.
- Develop a toolbox of analysis methods routinely available for pipeline analysis and implement the analysis pipeline.
- Make use of high-performance computational mathematics tools, such as parallel nonnegative matrix factorization techniques, and build parallel tools for support-vector machines.
- Build our data analysis tools on top of the Toolkit for Advanced Optimization, which has been developed by the Mathematics and Computer Science (MCS) division and has demonstrated parallel scalability on clusters, such as Argonne's Fusion cluster.
- Develop a portal to a data and analysis repository, including web-based technologies that enable integrated collection, creation, management, annotation, analysis, and browsing of data from disparate sources (e.g., data from several APS beamlines, electron microscopy, and visible-light microscopy).

Seminars

Vogt, S. (2012). "Hyperspectral Imaging: Visualizing Trace Elements and Chemical State." University of Chicago, Chicago, IL, November 11, 2011.

Vogt, S. (2011). "Data Acquisition for Fluorescence Imaging and Spectroscopy." NSLS User Meeting, Brookhaven National Laboratory, Upton, NY, May 25, 2011.

Vogt, S. (2011). "X-ray Microscopy for the Life Sciences and Bio-Nanotechnology." Northwestern University, Chicago, IL, January 15, 2011.

Development of Grating Interferometers for Quantitative High-Energy X-ray Imaging and for Real-Time Wavefront Monitoring

2011-170-R1

Lahsen Assoufid, Francesco De Carlo, Ralu Divan,
Kamel Fezzaa, Chian Liu, Albert Macrander,
Derrick C. Mancini, Shashidhara Marathe, Alec Sandy,
Michael Wojcik, and Xianghui Xiao

Project Description

The aim of this project is to develop high-energy, x-ray, grating-based Talbot interferometry for quantitative, high-speed, two-dimensional (2-D) and three-dimensional (3-D) phase contrast imaging and tomography; wavefront sensing; and at-wavelength characterization of optics. Fast phase imaging relies on in-line holography techniques, which suffer from qualitative phase contrast artifacts. Quantitative phase imaging based on grating interferometry will greatly reduce such artifacts and is uniquely suited for imaging dynamical systems under real conditions and real time.

Mission Relevance

This project supports DOE's mission in energy sciences and in national user facilities. It will advance synchrotron science and imaging capabilities, as well as optics development. Quantitative phase imaging is essential for the study of specimen morphology and component distribution. Fast quantitative phase imaging could have profound implications in many applications requiring time-dependent imaging. Preserving incident wavefront shape and coherency is critical to advancing key experimental techniques at synchrotrons, like the Advanced Photon Source (APS). The proposed interferometer would fit well in the agenda of the Optics Testing Beamline currently being implemented at the APS.

FY 2012 Results and Accomplishments

In FY 2011, in collaboration with the Center for Nanoscale Materials (CNM), we designed an interferometer and developed fabrication procedures for one-dimensional (1-D) and 2-D gratings with high aspect ratios. We also used Talbot imaging to evaluate the coherence properties of multilayer optics.

In FY 2012, we successfully completed an extensive test of the interferometer setup. During the test, we obtained transmission, differential phase, and dark-field images from measured interferograms for the vane of a tail feather from a Hispaniolan Amazon Parrot and a sea shell sample. 3-D tomography measurements were also completed on a sea shell sample provided by Prof. Les Butler of Louisiana State University (Figure 1). We developed an improved algorithm for processing interferograms obtained using our x-ray grating interferometer which efficiently transforms the data fitting operation into a matrix manipulation. During initial trials of x-ray optics and beam wavefront characterization, we obtained phase images from a reflected wavefront of an Rh-coated x-ray mirror at an APS beamline (1-BM) (Figure 2). Differential phase contrast images of the beam wavefront profile obtained at another beamline (32-ID-C) revealed the condensation of water on the beamline front-end Be window. We improved the data processing algorithm by reducing the artifacts in differential phase and dark field images.

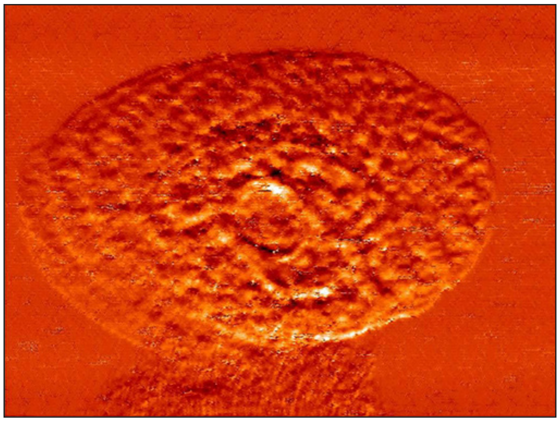


Figure 1: One of the differential phase projection images from a tomography image set of a seashell sample acquired at 25-keV x-rays.

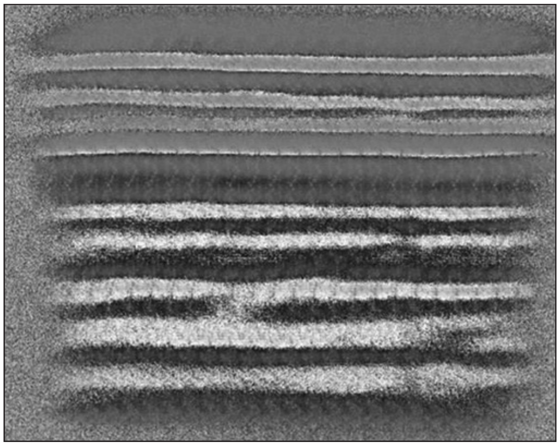


Figure 2: Phase map derived from the grating interferometer data in the stepping mode. The stripe features seen in the phase map are typically observed in beam reflected from mirror or a multilayer.

At present, we are developing codes to process the Moiré fringe measurements performed at the 1-BM beamline. Using previously developed processes, we fabricated 2-D checkerboard gratings of various pitches from as small as 2.4 µm to 9.6 µm. We also developed a new kind of x-ray grating based on multilayer technology. With this technique, gratings with sub-micrometer pitch and high aspect ratio can be fabricated. This capability is essential for high-energy x-ray applications. Tests carried out by using this type of grating have shown promising results.

Proposed Work for FY 2013:

We will continue to:

1. Implement grating interferometry as a testing tool for optics and beam wavefront characterization;
2. Develop grating interferometry for static and fast tomography with high energy x-rays;
3. Fabricate checkerboard gratings appropriate for 25 keV and beyond;
4. Further develop and test sub-micrometer pitch gratings with high aspect ratio by using multilayer coatings; and
5. Improve data acquisition, processing, and analysis.

Development of Revolver Undulator for APS

2011-204-R1

Efim Gluskin and John Grimmer

Project Description

Undulators are magnetic arrays designed to produce a vertical magnetic field that alternates in direction with position along the undulator axis. This magnetic field causes the electron beam in the 7-GeV Advanced Photon Source (APS) at Argonne to wiggle horizontally, producing high-brilliance, hard x-ray beams. The x-ray energy can be tuned very precisely by adjusting the gap between the upper and lower magnet arrays. The minimum and maximum x-ray energies that can be produced by an undulator are a function of the period of the alternating field. The period is chosen either to provide maximal brilliance over a narrow (and possibly discontinuous) spectral range or somewhat lower brilliance over a broader (and possibly continuous) range. This project seeks to develop a revolver undulator to provide the benefits of two undulators of different periods in the space currently required for one undulator. This revolver undulator will have two upper and two lower magnet arrays of different periods; either period can be selected for use by rotating the revolver mechanisms.

Undulators operate remotely for months at a time, and must do so reliably, safely, and precisely, while countering magnetic attractive forces exceeding 5000 lb (22,241 N). The challenge in developing a revolver undulator is to maintain performance with an inherently more complex system. To that end, this project will develop two revolver undulators, both based on the existing gap separation mechanism.

Mission Relevance

Revolver undulators are a key component in the APS, as they will meet demands for the greater flexibility of two different-period undulators while occupying the footprint of only one undulator. This will be accomplished without the schedule delays that would be required for swapping undulators of different periods. Successful completion of this project will advance DOE's science mission to enable world-class science and technology by making Advanced Photon Source insertion devices more versatile and accessible to a broad spectrum of researchers.

FY 2012 Results and Accomplishments

In the first year of this project (FY 2011), the needs to be met with revolver undulators were defined, an early proof-of-principle undulator was built, and design of two conceptually different developmental undulators (the main difference being use of non-revolving and revolving strong-back jaws began. A path was established for building and developing both types of undulator, including their control systems, and then testing them in functionally representative ways.

In FY 2012, the proof-of-principle undulator was further tested with a novel drive scheme using "Geneva mechanisms," which allow very precise indexing between two orthogonal positions. The test results showed promise, but a drawback was identified in the need for synchronization of the drive motors at both ends of the revolver undulator.

Magnets and magnet structure parts for both of the single-revolver-jaw developmental undulators and for a final two-revolver-jaw undulator were designed and procured. The developmental undulators use a revolving top jaw with two magnet structures of the same period (3.3-cm) opposing a non-revolving lower jaw with a single 3.3-cm period structure. The final undulator will use 2.7-cm period and 3.3-cm period magnetic structures. Sufficient magnet structure parts were purchased to allow both developmental undulators to have their own magnet structures. As a result, the parallel evaluation and development of both designs became possible.

Two gap separation mechanisms and control systems were built for the developmental undulators. The non-revolving strong-back jaw parts for one of the developmental undulators were fabricated and then precision assembled by an outside firm. This jaw was assembled directly to the gap separation mechanism (Figure 1). Parts for the revolving strong-back jaw to be used in the other developmental undulator were precision assembled by APS technicians, before the jaw was installed on a gap separation mechanism (Figure 2). Both undulators are in the final stages of wiring and debugging of controls.

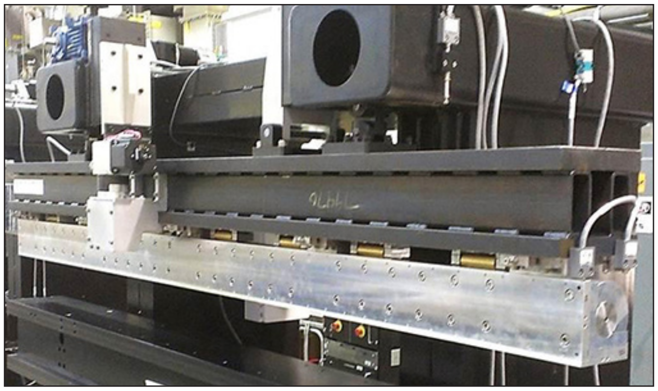


Figure 1. Non-revolving strong-back design. Only the magnet arrays (not shown) and their mounting structures revolve. The revolver drive is located at the mid-point of the arrays to minimize differential torsional deflection of the arrays.

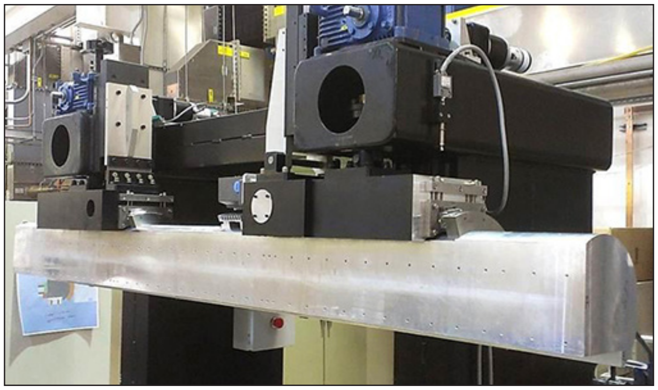


Figure 2. Revolving strong-back design. The entire strong-back revolves with the magnet arrays (not shown). Two support trays (non-revolving) and four guide rails per strong-back jaw minimize differential bending deflection of the arrays.

The key finding from the work in FY 2012 is that there are no "show-stoppers" in either design. Further, both designs are proving capable of using the existing APS-designed gap separation mechanism, with no modifications, only additions, namely, switches, wiring, and personnel guarding. Thus, the APS has two viable platforms for this vital technology, and is in the enviable position of being particular about choosing between the two.

Proposed Work for Fiscal Year 2013

During FY 2013, the following tasks are planned:

- Testing of both designs will be completed without magnets, and any necessary modifications will be made to ensure safe and reliable operation.
- A new tooling will be designed and built to address the challenge of installing magnets on the revolver undulator's dual magnet structures without risk to the technicians. This tooling then will be used to install the magnet structures and magnets.
- The two developmental undulators will be measured magnetically in both magnet structure positions. Some magnetic tuning will be done to baseline the magnetic performance in the two positions, which will, of necessity, be a compromise because two different upper magnet structures are being used with a single lower magnetic structure.
- The performance of each developmental undulator will be evaluated in absolute terms, relative to non-revolver undulators and relative to one another. Automated operation of each revolver through hundreds of open-gap/revolve/close-gap/repeat cycles will be performed. One of the two developmental designs will be selected for the final design, based primarily on long-term mechanical reliability and on the reproducibility of magnetic performance.

High-Power Radio-Frequency (RF) Dampers for Superconducting Radio-Frequency (SRF) Deflecting Cavities

2011-206-R1

Alireza Nassiri, Branislaov Brajuskovic, Geoff Waldschmidt, and Genfa Wu

Project Description

A key challenge for future superconducting radio-frequency (SRF) technology to be used in linear particle accelerator (linac) cavities is to mitigate the effect of the non-fundamental resonance frequency (mode) that will be present at higher-order modes (HOMs). These modes are typically broadband in nature, which requires suitable radio-frequency (RF) damping materials to absorb the HOM-generated power without any negative effect on the fundamental mode. In addition to the RF properties, the chosen material needs to have excellent mechanical and thermal properties, be compatible with operation in vacuum, and be particulate-free as not to impact SRF cavity operation.

The purpose of this project is to design HOM and lower-order-mode (LOM) waveguide dampers for SRF deflecting cavities, such as those that might be used in the Advanced Photon Source (APS) storage ring at Argonne. A dual-wedge design using a lossy dielectric material (e.g., silicon carbide) has been proposed for both modes. These high-power dampers for the SRF deflecting cavities will be required to operate in a vacuum environment. It is critical that the dampers efficiently absorb and dissipate unwanted power in all non-deflecting mode frequencies during operation, without generating particulates that will contaminate the cavity and degrade or destroy its performance. It is also important to understand the quantity and nature of damper material particulate generation when ultimate strength limits are exceeded and the materials are stressed to the point of failure.

Mission Relevance

This project is relevant to DOE's basic sciences mission in accelerator science and technology. There is a strong synergy between this work and next-generation accelerators, such as x-ray free electron lasers and energy recovery linacs. Both will likely be constructed by using SRF technology operated in a continuous mode to take full advantage of high average x-ray beam brightness. Extensive modeling, analysis, prototyping, and testing conducted on silicon carbide materials in this project will provide valuable insight supported by experimental test data that can be applied to other accelerators based on SRF technology.

FY 2012 Results and Accomplishments

In FY 2011, we optimized the designs to the SiC dampers to distribute this RF loading over the damper volume to (1) reduce the temperature gradient and stresses in the damper and (2) symmetrize the deformation. HOM damper designs were also analyzed to optimize the dampers for broadband damping up to 8 GHz.

Low-power and high-power testing of the dampers started in FY 2011 by using a 5-kW klystron-based RF amplifier. In addition, sample SiC damper material was received and machined, and several brazing tests of the SiC damper material to various copper substrates were done with encouraging initial results. A copper cavity was designed and fabricated. This cavity was used to evaluate the effectiveness of the dampers on reducing the cavity impedance.

The work during FY 2012 focused on the production of five developmental dampers. The fabrication methodology of the metal components of the dampers, silicon carbide (SiC) bonding, and surface preparation/cleaning procedures were strictly enforced as a trial run for the production of dampers for actual installation into a superconducting environment. High-power testing of the dampers was then performed to validate and characterize the design. The damper manufacturing steps are depicted in Figure 1.

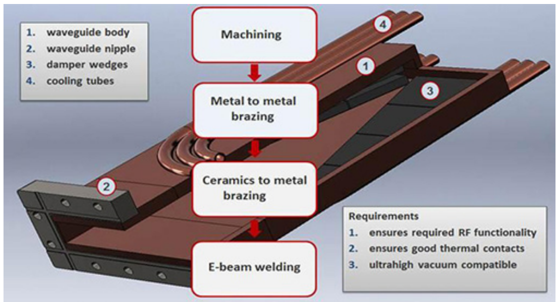


Figure 1. Manufacturing steps for fabrication of high-power dampers.

In preparation for determining an optimal damper geometry and fabrication process, we developed a reliable method for bonding the SiC material to a copper substrate and explored its dependence on surface preparation, brazing/soldering alloys, intermediate buffer layers, and copper substrate geometry. RF and mechanical engineering (ME) analysis was completed on the damper design to improve its RF performance and reduce the temperature gradient and resultant stresses.

Preliminary high-power testing was performed on SiC samples brazed/soldered to a cooling flange, as shown by the inset in Figure 2, including vacuum compatibility tests, conditioning tests, lifetime tests, and particulate tests. Preliminary testing was done before the fabrication of the developmental dampers to validate the various surface preparation techniques, bonding options, and material choices for compatibility/reliability in ultrahigh vacuum environments and/or near superconducting components. Figure 2 shows the test setup for the particulate tests where the SiC tile and bonding alloys were tested for particulate generation — a critical issue for superconducting cavities.

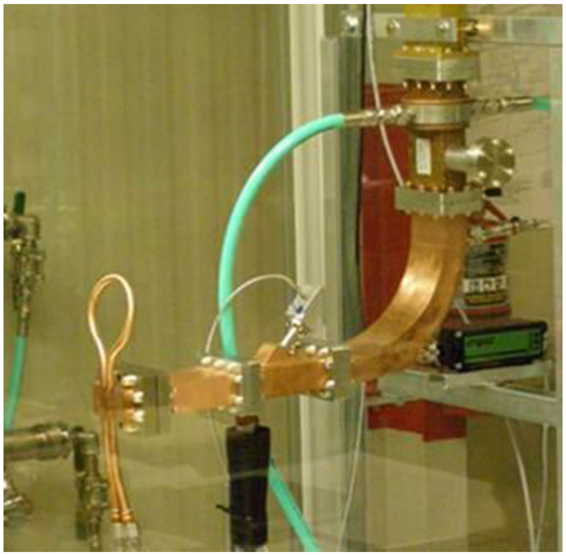


Figure 2. High-power test setup for evaluating particulate generation. Inset shows the SiC sample soldered to cooling flange.

After discussions with vendors, five high-power developmental dampers were procured: three brazed and two soldered dampers. We completed the copper waveguide/pinbed machining, flange interface machining, cooling channel brazing, SiC tile brazing/soldering, electron beam (e-beam) welding, and cleaning (Figure 3). Interaction with vendors resulted in improvements in the underbead of the e-beam weld (for RF performance) and in cleanliness standards, especially with regard to fixturing during SiC bonding (graphite residue) and e-beam welding (copper contamination). Figure 4 shows a fully assembled developmental waveguide damper with soldered SiC.

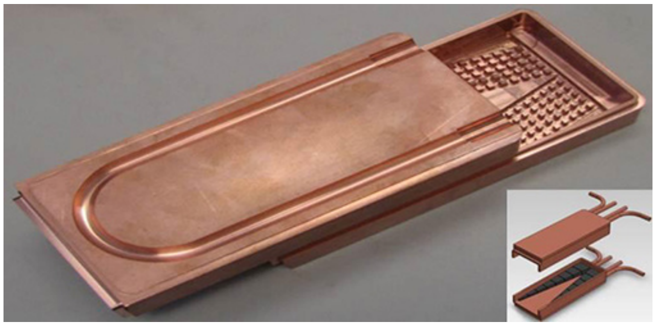


Figure 3. Developmental HOM damper with copper pinbed substrate. Inset shows LOM damper with SiC tiles.

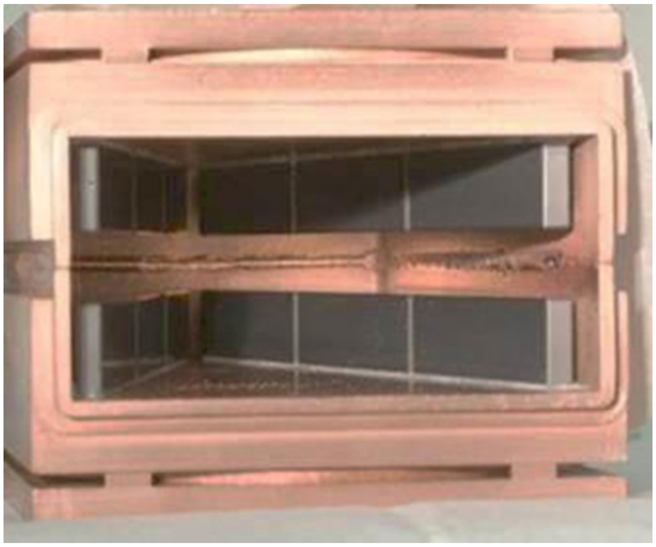


Figure 4. A fully assembled developmental damper with soldered SiC tiles.

We performed high-power tests to evaluate RF performance, high-power conditioning, mechanical integrity, and particulate generation. The soldered dampers were successfully tested in an ultrahigh vacuum and conditioned up to their design specification without any mechanical or RF issues.

Device Engineering for High-Performance Photocathodes

2011-207-R1

Marcel Demarteau, Henry J. Frisch, and Junqi Xie

Project Description

Multi-alkali photocathodes are widely produced in industry. They are grown by using a cost-effective thin-film technology that permits the use of a wide range of amorphous and polycrystalline substrates. In industry, however, photocathodes are grown in a glass phototube and sealed in vacuum. The details of the growth mechanisms of photocathodes (such as structural formation, chemical composition, cathode thickness, and surface roughness) and their relationship to overall quantum efficiency are poorly understood. The goal of this project is to understand how growth parameters affect overall quantum efficiency to enable the development of an optimized reproducible formula for high-quantum-efficiency photocathode production. We focus on understanding the correlations between the factors determining the cathode efficiency and the fundamental development of novel device structures of semiconductor cathodes, which should enable producing devices with enhanced quantum efficiency, tunable cathode wavelength, and fast response.

Mission Relevance

Photodetectors are key devices in DOE's portfolio of detectors to accomplish its science mission. They are used in a wide spectrum of applications, ranging from night-vision devices to monitoring of fuel cores of nuclear reactors, to large-area neutrino detectors. A common feature of these devices is that they have relatively low quantum efficiency. A better understanding of the growth process will be key to providing the tools to develop detectors with substantially higher quantum efficiency and wavelength tunability. Such detectors will enable new science programs in support of DOE's mission to understand how our universe works at its most fundamental level at a significantly lower cost. Immediate beneficiaries would be large-scale neutrino and collider detector experiments.

FY 2012 Results and Accomplishments

In previous years of the project, an in-house photocathode growth facility and an optical-electrical characterization station were constructed and commissioned. Bi-alkali, small form-factor photomultiplier tubes with a peak quantum efficiency of 24% were produced and characterized. In FY 2012, most of the effort was aimed at understanding the fundamentals of the growth of bi-alkali and multi-alkali photocathodes. From the study of the small PMT photocathodes growth and *in situ* x-ray scattering measurements with collaborators from Brookhaven National Laboratory, two major factors affecting the cathode performance were identified: antimony (Sb) film thickness and potassium (K) and cesium (Cs) activation.

A large glass vacuum vessel was designed to scale up from the small PMT photocathode to grow 8-in. × 8-in. photocathodes. This system gave us the ability to systematically investigate and characterize the parameters, conditions, and procedures of formulas for photocathode growth in a large volume. A series of photocathodes with different Sb thicknesses were deposited to study the relation of Sb thickness and the overall cathode quantum efficiency, and the growth process parameters were carefully monitored. The experiments established the relationship between the Sb film thickness and the quantum efficiency, as shown in Figure 1. When the Sb thickness is thinner than the optimal thickness (penetration depth), only a portion of the light is absorbed by the cathode, resulting in poor quantum efficiency; when the Sb film is thicker than the optimal thickness, fewer photoelectrons escape to the vacuum. For our experiment, the optimized Sb film thickness is around 9 nm (78% transmission).

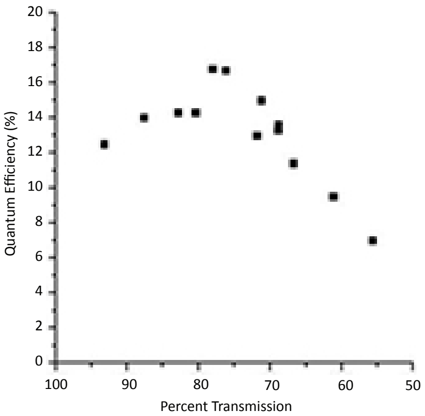


Figure 1. The dependence of the overall quantum efficiency as a function of the transmission of the base Sb film, indicating an optimal Sb thickness of ~9 nm (78%).

In FY 2012, in collaboration with Brookhaven National Laboratory, we studied three different bi-alkali and multi-alkali photocathode (KCs-Sb, K-Sb, and Cs-Sb) growth processes through *in situ* x-ray scattering measurements, including x-ray diffractometry (XRD) and x-ray reflectometry (XRR). The Sb phase transitions during film growth and the selective growth of K and Cs along Sb crystalline faces were established. Figure 2 shows the real-time x-ray reflectivity measurement during K_3Sb photocathode growth on top of an *ex situ* grown Sb layer. The figure shows the details of the K diffusion into the Sb layer and the formation of K_3Sb islands. More experiments, in the framework of the DOE supported Large-Area Picosecond Photodetector project, are planned to reveal more details of the cathode growth process.

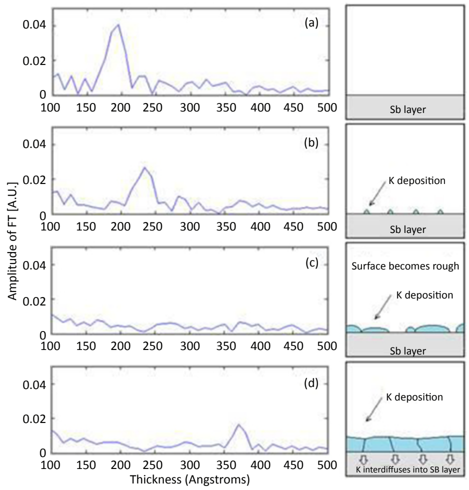


Figure 2. Real-time x-ray reflectivity measurement during K_3Sb photocathode growth on top of an ex situ *grown Sb layer. (a) Sb layer was grown* ex situ *before K deposition. (b) Peak reduces as K is deposited and forms islands. (c) Peak disappears when surface becomes very rough by forming K cluster. (d) During further deposition, islands of deposited K grow bigger and meet adjacent islands, K starts to form a thin film, and fringes start to appear again.*

Studies of Thermomechanically Induced Fatigue in GlidCop® for Use in Photon Absorbers for High Power Density X-ray Beam Applications

2011-215-R1

Jeffrey Collins, Patric Den Hartog, Ali Khounsary, Gary Navrotski, and Jeremy Nudell

Project Description

GlidCop, a dispersion-strengthened copper alloy, is the material most commonly used to fabricate x-ray absorbers for third-generation synchrotron facilities. The available thermomechanical and fatigue data for GlidCop are very limited. Although the design criteria for stress and temperature limits of x-ray absorbers fabricated from GlidCop at the Advanced Photon Source (APS) have been successful in preventing component failures over the 18-year life of the facility, several research studies suggest that these criteria, similar to those used at all third-generation synchrotron facilities, may be too conservative. Operators of synchrotron facilities throughout the world, including the APS, are contemplating upgrades that will result in higher total power and higher peak heat flux levels. As such upgrades are implemented, the thermal load on x-ray absorbers will increase significantly, exceeding the existing design limits for these devices in many cases. To define new design criteria for GlidCop, we conducted an engineering research project based on experimental determination of the thermomechanical conditions that lead to crack formation and propagation. Using x-ray power from the APS, we subjected numerous GlidCop samples to 10,000 thermal loading cycles under various beam load conditions and examined the samples metallurgically to determine their morphology and identify the presence of cracks. Data from these studies were correlated with strain levels computed by finite element analysis (FEA) simulation to predict the expected fatigue life of x-ray absorbers.

Mission Relevance

This project supports DOE's missions in basic science and in national user facilities. The ability to accurately predict the thermal fatigue life of GlidCop x-ray absorbers could justify the extended use of existing designs, leading to a significant cost savings for the APS and other synchrotron facilities. Such predictions will also help support the development of operational procedures to prevent absorber failure from impacting facility reliability. In addition to the APS, other existing and proposed third- and fourth-generation x-ray synchrotron facilities will benefit from a better understanding of the failure mechanism governing the fatigue life of GlidCop.

FY 2012 Results and Accomplishments

The Sector 29-ID-A beamline at the APS was used to test numerous GlidCop Al-15 (UNC-C15715) samples. The samples were exposed to severe cyclic thermal loading at normal incidence by using two in-line Undulator A devices. Several different power levels were chosen, and each sample was subjected to 10,000 thermal cycles with 1-second heating and 9-second cooling times. We performed *in situ* charge-coupled device (CCD) imaging and collected data from an acoustic emission system. Sample testing started in FY 2011 and continued through FY 2012. A total of 45 samples were tested, and all of the samples were metallurgically examined for surface roughness and crack presence/geometry. Several failure mechanisms were noted, including ablation, deep cracking, fine cracking, exfoliation, and surface roughening.

We also performed tests to determine the true stress versus strain behavior of GlidCop Al-15 plate material at various temperatures under both tensile and compressive stress conditions in accordance with American Society for Testing and Materials (ASTM) E21-09 and ASTM E209-89a (2000), respectively. The data were used to complete elastic-plastic FEA simulations on the test samples to determine the equivalent total strain range and peak surface temperatures at each load condition. Figure 1 provides a typical hysteresis loop generated from this analysis for sample number 29; for this analysis, the undulator gaps were set at 22.07 mm, generating a nearly 950-W thermal load at greater than 45 W/mm^2 average power density.

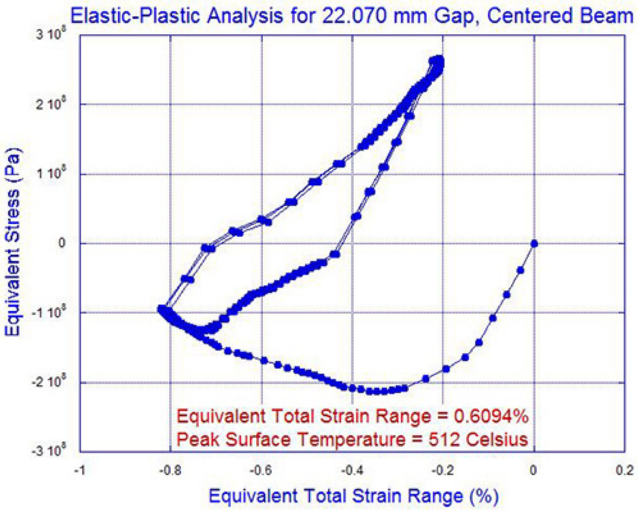


Figure 1. Equivalent stress versus equivalent total strain range from elastic-plastic FEA simulations for test sample number 29.

In addition, we performed strain-controlled uniaxial mechanical fatigue tests on GlidCop Al-15 plate material at various temperatures in accordance with ASTM E606-04. The data were used to develop a temperature-dependent mechanical fatigue model based on the Manson-Coffin strain amplitude-endurance relationship, as shown in Figure 2. Data generated from the elastic-plastic FEA simulations were then used in the mechanical fatigue model to predict the number of cycles to failure for each test sample. These predictions were compared with the actual number of cycles to failure for each test sample using regression from the *in situ* CCD imaging when possible. The results of the project will be used to establish new design limit criteria for GlidCop on the basis of the experimental determination of the thermo-mechanical conditions leading to crack formation and propagation.

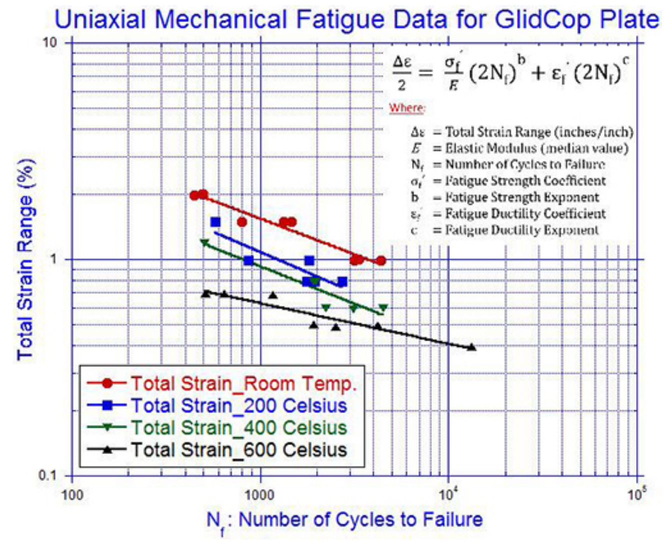


Figure 2. Uniaxial mechanical fatigue data for GlidCop Al-15 plate material used to formulate the Manson-Coffin strain amplitude-endurance relationship.

Development of Wavefront-Preserving Mirrors for Extreme Heat Load X-ray Beamlines

2012-197-N0

Ali Khounsary and Lahsen Assoufid

Project Description

The Advanced Photon Source (APS) at Argonne is the nation's largest synchrotron facility. It provides extremely powerful high-energy x-ray beams for academic, industrial, and government users working on scientific, technical, medical, and industrial applications. The high-quality x-ray beams are conditioned and delivered to users by using a number of slits and optical elements. These optical elements (e.g., x-ray mirrors) are not perfect; surface imperfections from inevitable manufacturing limitations degrade the quality of the beam they deflect to some degree. Such degradations are very undesirable for some high-end x-ray applications. There is thus a need to measure the magnitudes, extents, and distribution of these surface imperfections, analyze their impacts on beam quality, determine which features are most detrimental, and work with mirror manufacturers on improving fabrication and measurement techniques. In addition to fabrication-induced imperfections, mirror surfaces can become distorted from the increasing thermal load that the incident high-power x-ray beams deposits. This thermal distortion further degrades the reflected x-ray beam, and novel cooling techniques are needed to remove the heat in such a way as to minimize the undesirable thermal distortions.

The focus of this work is to help advance x-ray science areas that require a clean beam that takes full advantage of the APS beam quality and increasing power (expected during a planned upgrade) by addressing two challenges: (1) thermal management of the optical substrates to minimized undesirable thermal distortions and (2) development of manufacturing techniques to improve the quality of the mirror surface and better preserve the quality of the x-ray beam (i.e., the beam wave front).

Mission Relevance

This project supports DOE's scientific mission. Delivering high-quality x-ray beams would allow users to take full advantage of the x-ray beams' properties. For example, minimizing thermal deformation and manufacturing imperfections would allow users to focus an x-ray beam to the smallest size possible. This would make it possible to examine and interrogate simple and complex materials (including biological samples) with higher resolution and in greater detail than currently possible. The improvements would also let users obtain higher-quality x-ray images of complex structures. Therefore, improving the optics used on synchrotron beamlines results in fuller utilization of the x-ray beams with qualitative and quantitative improvements in the scientific results. Technical collaborations with the U.S. mirror manufacturers, including sharing mirror performance data, greatly assist them in improved polishing techniques and optical surfaces. Currently, synchrotron mirrors with the best optical surfaces are not produced in the United States.

Results and Accomplishments

We worked with two U.S. manufacturers on fabricating the finest mirror surfaces that they could produce with their tools and metrology system. Extensive in-house metrology was carried out at the APS, and the results were provided to the manufacturers on an ongoing basis for additional polishing. To understand how size, material, orientation, and subsurface preparation can affect the polishing quality, we established an ongoing dialog with the manufacturing partners while examining several high-end silicon and silicon carbide mirrors of various sizes and with various surface profiles (flat and spherical).

Concurrently we also studied the issue of thermally induced deformations in optics; which also adversely affect the x-ray beam quality. Our goal was to optimally cool x-ray mirrors. We first developed a comprehensive database on the thermo-mechanical properties of several important substrate materials (Si, SiC, Ge, Be, and diamond), with an emphasis on their anisotropic properties. We carried out thermal and structural analyses of mirrors for the highest expected incident x-ray beam power (from two co-linear undulator sources at the expected 150-mA ring energy); the objective was to find the best solutions in which the mirror geometry and the cooling scheme were optimized to minimize undesirable thermal distortions. We found that in many instances, the optimal cooling geometry with water as the coolant was satisfactory; in others (e.g., for x-ray beams with strongly nonuniform power profiles), it was advantageous to cool silicon mirrors at liquid nitrogen temperatures taking full advantage of the low thermal expansion of silicon in the vicinity of 120 K.

Figure 1 shows the temperature profile for a 1,200-mm long, horizontally deflecting water-cooled silicon mirror subjected to one of the highest expected incident x-ray beam heat fluxes at the APS. A 2 × 3-mm x-ray beam incident at 0.15° with a total power of 3,100 W and a peak heat flux of 560 W/mm^2 was assumed. The wave fronts of the x-ray beams reflected from such a mirror were somewhat distorted. Various cooling schemes geometric optimization to further improve the performance of the optics are planned.

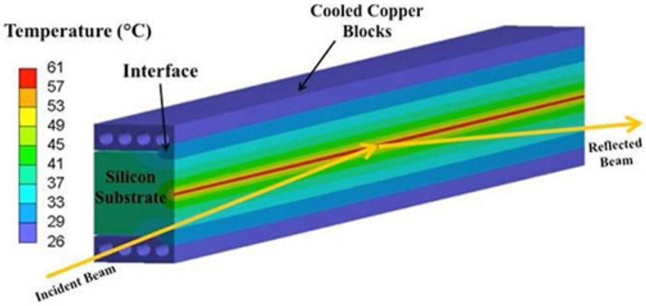


Figure 1. Temperature profile for a side-cooled mirror with a 2 × 3-mm high-heat-load incident beam with a total beam power of 3,100 W and a peak heat flux of 560 W/mm^2. The beam strikes the mirror at an angle of 0.15°. The moderate temperature gradients seen produce a moderate amount of surface distortion.

High-Heat-Load Hard-X-ray Monochromators

2012-199-N0

Albert Macrander, Lahsen Assoufid, Eric Dufresne,
XianRong Huang, Gary Navrotski, and Mohan Ramanathan

Project Description

In conjunction with upgrade plans for the Advanced Photon Source (APS), the storage ring current of 100 mA will be increased to 150 mA. As a result, the heat load on a monochromator will be increased, and previously engineered designs for cooled crystals may not be adequate. To address these problems, we are evaluating the limits of extant monochromators and working toward new designs that will mitigate the increased heat load while preserving beam brilliance. An effort was initiated that would be conducted in parallel to simulate measured data using finite-element analyses (FEA). In addition, measurements were completed to assess the usefulness of grating interferometry for measuring heat-load-induced crystal distortions.

Mission Relevance

The project is tied to DOE's mission in science through the upgrade of one of the Department's premier user facilities where much mission-related science is done. Further R&D is needed to devise methods for mitigating the high heat load on monochromator crystals and thereby to achieve science objectives at existing APS beamlines, as well as at the new beamlines planned for the APS-Upgrade. For the APS-U, tandem undulators will be placed in long straight sections for the Wide Field Imaging, Resonant Inelastic X-ray Scattering, and High-Flux Pump-Probe beamlines. There may also be distortions in the wavefront after the monochromator, which will require new design solutions. Anticipating and mitigating the effects of heat load from a more intense x-ray beam is a prerequisite for achieving maximum benefit from the upgraded capabilities of the APS.

FY 2012 Results and Accomplishments

Experiments were conducted at beamline 29-ID, to measure the (111) and (333) rocking curves of a silicon (Si) double crystal monochromator (DCM) by using two in-line, APS type-A undulators as a combined source. Measurements were for a 102-mA ring current and were taken for a variety of heat-load conditions. The heat load was adjusted by varying the undulator gaps and the size of white beam slits. For slit sizes corresponding approximately to the central cone of the undulator radiation, the rocking curve distortion was found to be small (see Figure 1). The crystal that was studied had a so-called "thin-web" region adjacent to bulk crystal. The crystal was thinned in this region in order to allow an undiffracted x-ray to pass through and thereby minimize the absorbed heat load. However, rocking curves with the beam footprint located over the bulk crystal were consistently narrower than those over the thin web.

We concluded that the thin-web region thermally distorts too readily to be optimally effective in designs for the APS-U. We further conclude that thin-web designs will not be as effective as bulk crystal designs. A crystal design that will mitigate the higher heat load arising from 150-mA operation may be feasible by optimizing the dimensions of presently applied crystals in the case where only the central cone of the undulator radiation is needed.

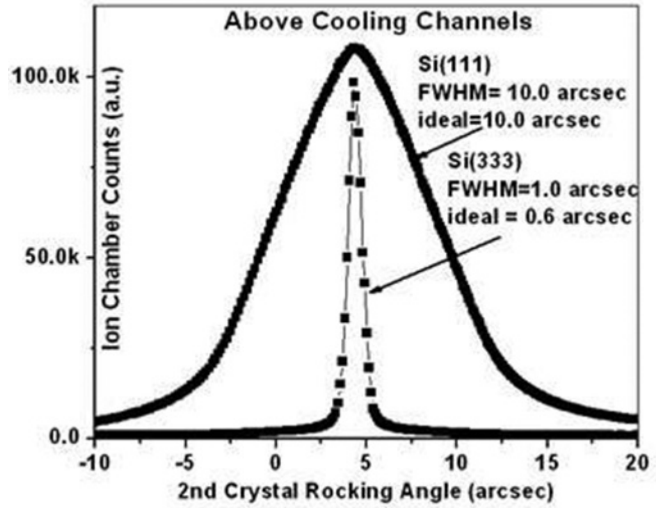
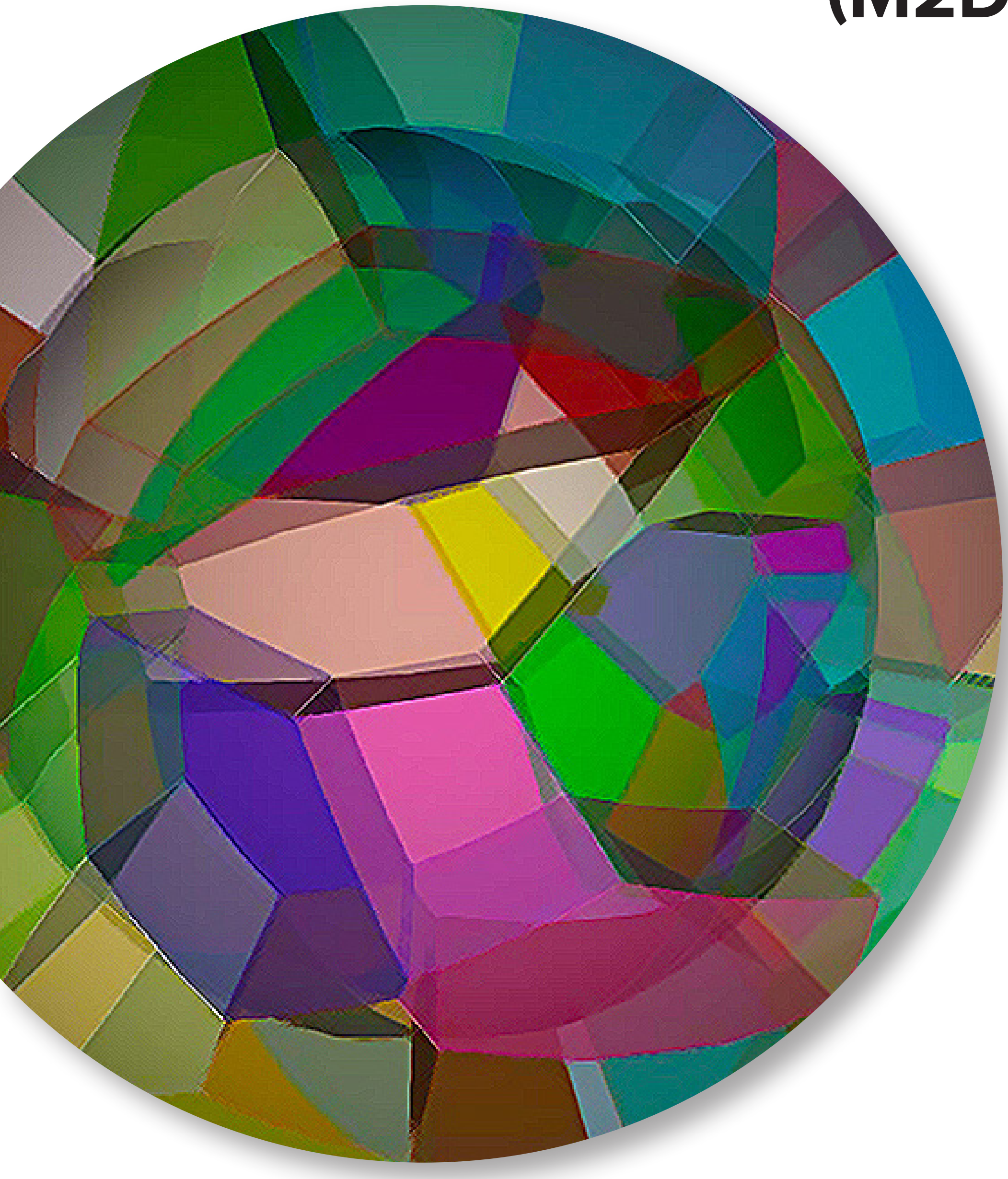


Figure 1. Rocking curves for a monochromator Bragg angle set to diffract at 8 keV with two in-line undulators (type A), both gapped so that the first undulator harmonic is at 8 keV. In this arrangement, the (333) reflection was for radiation in the third harmonic of the undulators at 24 keV. The white beam slits were set to 1 mm × 1 mm, which corresponds to radiation limited to the central cone of the undulators. The current in the storage ring was 102 mA. The observed broadening of the (333) reflection was only 0.4 arcsec.

FY2012
annual report

MATERIALS AND MOLECULAR DESIGN AND DISCOVERY (M2D2)



Investigation of Novel Relativistic Quantum States in Iridates

2010-190-R2

Bum Joon Kim and John F. Mitchell

Project Description

Transition-metal oxides are renowned for a diverse spectrum of tunable physical properties that range from superconductivity to colossal magneto-resistance, which results from competing interactions among charge, orbital, and spin degrees of freedom. Recent findings indicate that the delicate balance between spin and orbital degrees of freedom can be greatly altered by relativistic spin-orbit coupling to result in microscopic hopping processes and magnetic interactions that are quite different from the established picture of transition-metal oxides, thereby opening a novel route to Mott phenomena and realizing novel quantum phases of matter (such as a topological Mott insulator and quantum spin liquid).

Our project focuses on the systematic investigation of the role of spin-orbit coupling in the electronic and magnetic structures of 5d transition-metal oxides. The goal is to identify material realizations of this novel physics. In the course of our research, we produced high-quality single crystals for a number of candidate materials. We then studied their magnetic order and excitations by using resonant x-ray scattering and examined their electronic structures by using angle-resolved photoemission. We discovered distinct magnetic excitations arising from spin-orbit coupling and assessed their role in stabilizing certain magnetic orders, which clarified the nature of magnetic interactions strongly modified by spin-orbit coupling. We will continue our investigation to determine how the magnetic order affects the electronic band structure. Specifically, we will analyze how the magnetic order correlates with the structure of the Mott gap and topological properties of the electrons.

Mission Relevance

Our research is squarely in the area of discovery science. This project addresses the DOE Grand Challenge to understand electron correlation and novel states of matter by controlling the structure of materials. The DOE Basic Energy Sciences program emphasizes the design and discovery of new materials to understand such new states of matter. The work proposed here is well aligned with this new area of emphasis.

FY 2012 Results and Accomplishments

In FY 2010–2011, we established that resonant x-ray scattering (RXS) is a very powerful tool to study magnetism in 5d transition-metal oxides with strong spin-orbit coupling, as a result of the extremely favorable matrix elements and thus the resonant enhancement of the RXS signal at the 5d absorption edges. Using this property of 5d oxides, we made a first successful mapping of the spin waves in Sr_2IrO_4, a representative 5d oxide, to reveal the spin-orbit coupled nature of the valence electron and characterized the magnetic couplings among them.

In FY 2012, we have extended our studies of the nature of magnetic couplings in strongly spin-orbit coupled oxides to other members of Ruddelsden-Popper (RP) series iridates $Sr_{n+1}Ir_nO_{3n+1}$, which are unconventional magnetic insulators that approach a metallic state with increasing *n* (number of IrO_2 layers). Because of the strongly spin-orbit-coupled nature of the electronic ground states in this series of compounds, it was predicted that they may host unconventional types of magnetic Hamiltonian and ground states. Particularly interesting among them is the Kitaev model with a quantum spin-liquid ground state, which has attracted much interest because of its relevance for quantum computing. The Kitaev model is built on the pseudodipolar couplings between neighboring spins, which strongly deviate from the conventional magnetic coupling of the Heisenberg type.

Through our RXS studies, we proved the existence of strong pseudodipolar coupling in the RP series iridates by showing that the RP series undergoes a spin-flop transition as a function of *n*. The spin-flop transition is a direct manifestation of the strong pseudodipolar coupling acting between two neighboring IrO_2 planes in a bilayer slab, thus causing the spin to flop when two IrO_2 layers are stacked together. To characterize the magnitude of the pseudodipolar coupling, we used inelastic RXS to measure the spin-wave dispersion from which the magnetic coupling constants could be extracted. We found that while the n=1 member of the RP series is characterized as a Heisenberg antiferromagnet, the n=2 member, $Sr_3Ir_2O_7$, has a strong Ising character because of the strong pseudodipolar coupling, as manifested by the anomalously large spin-wave gap shown in Figure 1. Further, by fitting the spectra to a microscopic model, we established that the pseudodipolar coupling is greatly enhanced when the system is brought close to a Mott critical point. Our results show that strong pseudodipolar coupling does exist in nature. These findings further suggest a materials strategy to enhance pseudodipolar coupling for the possible realization of novel types of magnets.

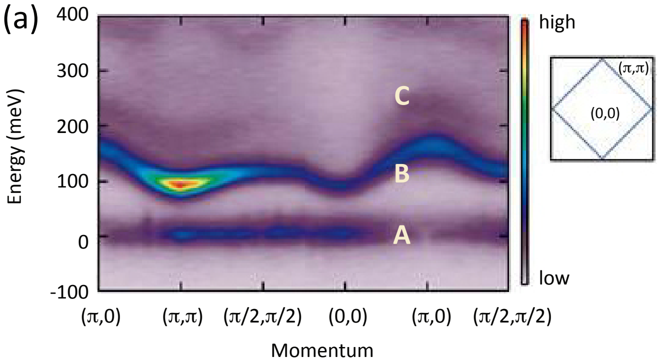


Figure 1. The image plot shows the raw experimental spin-wave spectrum measured along high-symmetry directions, thus revealing an anomalously large energy gap in the spin-wave excitations. The magnitude of the gap is about 90 meV — much larger than the total bandwdith of the spin-wave band, which is about 70 meV. The letters A, B, and C indicate elastic line, single magnon, and bimagnon modes, respectively.The black and blue square show the Brillouin zones of the undistorted square lattice and the magnetic unit cell, respectively.

Seminars

Kim, B. J. (2011). "Entangled Spin-orbital Waves in Sr_2IrO_4." Telluride Science Research Center Workshop, Telluride, CO, July 18–22, 2011.

Kim, B. J. (2011). "Isospin Dynamics in Sr_2IrO_4 – Forging Links to High-T_c Superconductivity." Swiss Light Source User Meeting, Paul Scherrer Institute, Villigen, Switzerland, September 16–17, 2011.

Kim, B. J. (2010). "Zooming Into Electronic Fine Structure Using Resonant X-ray Scattering." Seoul National Institute, Seoul, Korea, June 25, 2010.

Kim, B. J. (2010). "Mott Transition in 2D Square Lattice: In-gap Kondo-like Quasiparticles, Negative Compressibility and Phase Separation." Seoul National University, Seoul, Korea, March 5, 2010.

Molecular and Fluidic Transport in Nanostructured Soft Materials and Composites

2010-198-R2

Derrick C. Mancini

Project Description

The study of nanostructured soft materials is a burgeoning field of research with wide application. Many soft material systems consist of polymers, macromolecules, clusters, and/or nanoparticles that are in fluid or aqueous environments or that are permeated with solvents. The behavior, properties, and structure of the materials are governed by their interaction with the fluid or with chemical species or moeties transported within or through the nanoscale fluidic environments and complexes. Also, many of the systems self-assemble or organize, driven thermodynamically but still controlled by the same nanoscale transport phenomena in solution.

This project uses a multiscale approach to simulation, from molecular dynamics (MD) through finite element methods (FEMs). The results from the simulations are compared with experimentally observed behavior and related to the physical and chemical structure. We synthesize or obtain soft material systems, including hydrogels, hydrogel-nanoparticle composites, and nanoparticles with organic chain functionalization. Other molecules, macromolecules, ions, and clusters are used to incorporate into or to interact with these systems in an aqueous phase. We structurally characterize the systems by using optical microscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM), dynamic light scattering (DLS), x-ray diffraction (XRD), small-angle x-ray scattering (SAXS), small-angle neutron scattering (SANS), and ultra-small-angle x-ray scattering (USAXS). We chemically characterize the systems by using Fourier transform infrared (FTIR), Raman, and ultraviolet visible (UV-vis) spectroscopies. Modification of these materials and transport phenomena will be measured by using some of the same techniques in real time and *in situ*.

Mission Relevance

The development of modeling and simulations of nanoscale transport of fluids and ions in nanostructured polymeric and membrane systems will contribute to DOE's science, environment, and energy missions. These systems are ubiquitous and have applications in energy storage and conversion, environmental systems and mitigation, sensor technology, and drug delivery.

FY 2012 Results and Accomplishments

Our laboratory has capabilities for synthesizing hydrogel polymers, inorganic nanoparticles, and their composites. We also have DLS capabilities and conducted initial studies of collapse and agglomeration behavior of thermally responsive poly(N-isopropylacrylamide) (PNIPAM), co-polymers, and nanogels by using DLS, USAXS, SAXS, and atomic force microscopy (AFM) under varying temperature and pH conditions. We demonstrated that PNIPAM can be patterned by using soft x-ray contact lithography and extreme ultraviolet interference lithography. We established and significantly advanced modeling by using MD calculations of hydrogel oligomers, focusing on solvation dynamics and the role of water at the atomistic level in defining the lower critical solution temperature (LCST) of thermo-sensitive polymers. We investigated the collapse behavior of oligomers containing 30 monomers or less and examined changes in conformation, size, and vibrational behavior that can be measured by using DLS, SAXS, SANS, ultra small-angle neutron scattering (USANS), and FTIR.

In FY 2012, we significantly expanded our MD computational efforts to model and understand the oligomer-solvent interaction and the conformational change and agglomeration behavior for an ionic polymer in aqueous solution. We specifically examined the hysteresis behavior of PNIPAM at varying temperatures. We also investigated the effect of solvent mixture on the LCST of PNIPAM for methanol and water. We compared various force field and charge distributions to determine an optimal set for MD simulations of PNIPAM. Finally, we initiated the scaling up of our models to include larger individual molecules (100 to 1,000 mer), ensembles (2–5 oligomers), and brush structures on nanoparticles. Specific investigations included:

1. The role of solvation dynamics and local ordering of water in inducing conformational transitions in PNIPAM oligomers through the LCST by using MD simulations both below and above the LCST for different chain lengths of PNIPAM. This study provides atomic-scale insights into the role of solvation dynamics in inducing coil-to-globule phase transitions through the LCST for thermo-sensitive polymers, like PNIPAM.
2. Vibrational spectra of proximal water in a thermo-sensitive polymer undergoing conformational transition across LCST.
3. Agglomeration dynamics in thermo-sensitive polymers across the LCST by carrying out MD simulations of 5 chains of 5 mer and 2 chains of 30 mer at 278 K and 310 K.
4. The effect of heating rate on the hysteresis in coil-to-globule transition in 30 mer of PNIPAM solvated in water when heated from 285 to 315 K (from below to above the LCST) and cooled down from 315 to 285 K at various rates.

The case for an arbitrary 3D geometry of a pH-sensitive hydrogel was solved by using a FEM in COMSOL software, as an extension of our previous 2D approach. This allowed modeling of 3D shapes with reduced symmetry for comparison to experimental results from more realistic micro- and nanogel structures.

In order to study fluidic transport and diffusion dynamics during micromixing of micro- and nanogels, a micromixer was designed and simulated by using computational fluid dynamics (CFD). Fabrication of various initial microfluidic mixtures is under way, with the first test devices completed. The final working device will be used on Advanced Photon Source (APS) beamlines to perform *in situ*, real-time SAXS studies of the mixing behavior.

Six PNIPAM oligomers were synthesized from reversible addition-fragmentation chain transfer polymerization, group transfer polymerization, or free radical polymerization, chosen for studies to cover a wide range of molecular weights, poly-dispersity, and end group charge conditions. Compared with PNIPAM, poly(acrylamide) and poly(ethylene glycol) of similar repeat units synthesized from reversible addition-fragmentation chain transfer polymerization and living anionic polymerization, respectively, were studied to investigate the effect of monomer structure on their phase transition behavior. Protocols for producing PNIPAM brush structures on Fe_3O_4 magnetic nanoparticles and gold nanoparticles were successfully implemented and tested. These brush structures will be used for studies of brush structure collapse at the LCST by using SAXS and SANS and will be compared with the results of MD simulations.

Scattering techniques, including static light scattering, DLS, SAXS, and USAXS, were employed to study collapse and swelling behavior of PNIPAM oligomers and nanogels. Molecular weights were obtained from static light scattering experiments of PNIPAM solutions. The weight-average molecular weight, M_w, and average radius of gyration, R_g, were determined via Zimm plot and Guinier plot. DLS was carried out in two instruments; most PNIPAM polymer chains aggregate to form mesoglobules of narrow size distribution above the phase transition. The mesoglobules sizes increased with decreasing heating rate. Hydrodynamic radii were determined from autocorrelation functions by using CONTIN software. Equilibrium SAXS was conducted with flow cell at Sector 18 BioCAT of the APS. Radii of gyration, R_g, of polymers below the phase transition temperature were successfully calculated from SAXS curves, which was not possible for static light scattering because of different scattering vector range. Time-resolved SAXS was used to study the kinetics of the collapse of individual polymer chains, by coupling fast SAXS data acquisition with ultrafast-pulse, infrared-laser heating to obtain a time-resolved scattering curve. Under such conditions, the molecules have no time to diffuse and aggregate and allow the separation of collapse from agglomeration behavior. Initial data were obtained and are being analyzed.

Proposed Work for FY 2013

We will continue studying the kinetics of swelling/collapse of PNIPAM nanogels by employing USAXS integrated with microfluidic devices. SANS of nanogels may be used to probe the phase separation of backbone and side groups of PNIPAM in water. SANS of PNIPAM in water/ethanol mixtures may help explain the origin of co-non-solvency. SANS and SAXS of PNIPAM brush structures on gold nanoparticles will be used to understand brush behavior in such composites. Time-resolved SAXS using laser heating will reveal the thermodynamics and kinetics of the conformational change between the random coil and fully collapsed globule for PNIPAM. Experimental results will be compared with the combined results of FEM and MD calculations to relate phenomena to molecular mechanisms. Many of these studies will require controlled mixing or confined transport of polymer solutions to study the kinetics and dynamics of oligomers and nanoparticles by using all of these techniques. We will use our capillary and microfluidic systems to conduct these experiments.

We will extend our MD calculations to include more complex transport phenomena that include specific effects, including:

1. The collapse of PNIPAM brush structures on inorganic nanoparticles at the LCST.
2. The effect of salt ions on the ordering/cage of proximal water near the polymer surface and on the LCST of PNIPAM.
3. The effect of charged end groups on collapse and agglomeration behavior.
4. Simulations of hydrogels of PNIPAM at various pH levels with different cross-linkers in the presence of different ions.

We will continue to integrate our modeling results with experimental measurements to relate the molecular mechanisms to the observed behavior of these systems.

Soft Catalysts for Green Chemistry and Energy Applications

2011-060-R1

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Project Description

Given the rising world demand for energy and growing concerns about the long-term availability of crude oil and natural gas and the environmental impact associated with their use, there is an urgent need to use resources more efficiently. Energy research must include investigation of catalysts for efficient transformations that better use existing resources, as well as alternative chemical feedstocks in combination with renewable energy sources. To address this need, we have designed and developed a new class of solid catalysts that integrates highly selective organometallic active sites into permanently porous organic polymers (POPs). This modular and tailorable class of catalysts is designed to combine the best aspects of homogeneous catalysts (high selectivity at low temperature, tunability) and heterogeneous catalysts (stability, ease of separation). The new catalysts will lead to more efficient use of raw materials and energy supplies and, thus, significantly reduce both the demand for them and the negative environmental impacts of their use. By incorporating metal-binding groups that differ greatly from those found in traditional oxide supports (including zeolites), the new catalysts will lead to new chemistries that are not feasible with traditional catalyst technologies. The design principles developed here will have applications beyond the specific systems that we target. We have developed and validated methods for (1) reproducibly and reliably synthesizing the needed POPs and (2) incorporating the desired catalytic metal sites into the POPs. The current focus is on defining and tuning the catalytic activity of the metallated POPs.

Mission Relevance

This project is tied to DOE’s energy mission. Catalysis has an extraordinary impact on the U.S. economy, as evidenced by U.S. Department of Commerce statistics. The statistics indicate that nearly 90% of all processes in the chemical and petroleum industries and nearly 30% of all goods manufactured in the United States involve one or more catalytic processes to maximize the rate and conversion of feedstocks to the desired product(s), as well as to lower process energy requirements. New catalysts are urgently needed both to enable more efficient use of existing, traditional resources and to permit the exploitation of alternative, renewable feedstocks and carbon dioxide. The proposed catalysts are designed to complement traditional molecular and solid catalysts, enabling the discovery and development of new chemical transformations.

FY 2012 Results and Accomplishments

In FY 2011, three initial POPs were synthesized from pairs of molecular building blocks (tetrahedral “node” building blocks with linear “strut” building blocks that connect the nodes). The POPs were synthesized by using two different types of metal-catalyzed bond-forming reactions to link the node molecules with the strut molecules. Two different transition metals were then incorporated into these POPs in amounts exceeding 5% by weight.

In FY 2012, seven new POPs were synthesized from pairs of molecular building blocks (Figure 1). Two additional metal-catalyzed bond-forming reactions were used in constructing the new POPs, thus validating four catalytic methods for synthesizing the POP network polymers. One of these POP-forming reactions was identified as generally producing POPs with larger surface areas and pores, both of which are desirable for the planned catalysis applications. The POPs each contain one of three different types of metal-binding sites. In addition, a fourth metal-binding site was identified, through density functional theory (DFT) calculations, as being desirable; a strut that contains this site was synthesized. This strut will bind metals through nitrogen atoms and thus will provide an electronic environment that is very different from those found in the existing POPs.

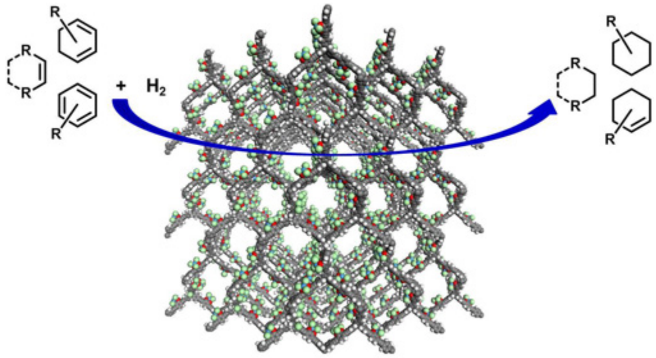


Figure 1. Schematic Representation of Hydrogenation Catalysis by a Porous Organic Polymer (POP) that Contains Tantalum-Alkyl Units. The gray, white, and red spheres represent the atoms (carbon, hydrogen, and oxygen, respectively) that make up the POP. Pale blue and green spheres represent the tantalum-alkyl fragments, held in place within the POP by coordination to oxygen atoms (red spheres). R represents organic fragments attached to the substrate (left-hand side) and product (right-hand side) molecules in the hydrogenation reaction (blue arrow).

Several "control" POPs that lack explicit metal-binding sites were synthesized analogously for comparison and were shown to take up only trace quantities of metals, demonstrating that very few metal-binding sites are formed unintentionally during the POP synthesis reactions. For the POPs that deliberately incorporate metal-binding sites, we identified and validated two different chemical methods for introducing a transition metal fragment (that will serve as the catalytic site) and incorporated three different transition metal fragments in amounts exceeding 10% by weight (wt%) (~20 wt% metal in two cases). A suite of analytical techniques confirmed that metallation of the ligand sites is essentially quantitative but self-limiting (i.e., excess metal fragments do not react with the POPs and are not retained by them). The surface areas of the metal-free and metal-containing POPs fell into the 300–1,300-m^2/g range. We also measured pore size distributions. The POPs that are most thermally robust (stable to greater than 350°C under nitrogen) are amorphous. A tantalum-containing POP was found to catalyze the hydrogenation of arenes and olefins at temperatures of 60°C or less.

We validated two key hypotheses in FY 2012. First, building the metal-binding sites into the POP struts leads to metal coordination environments that are more predictable and controllable than those obtained when these same sites are added as small-molecule ligands (metal-binding molecules) for transition metal complexes in solution. Thus, a single ligand of a particular type binds to the target metal ion in the POP because these ligands are widely dispersed in the POP and fixed in place so they cannot diffuse. In contrast, in a homogeneous solution, addition of a second (or even a third) such ligand occurs, yielding metal coordination environments that differ from the desired composition and can be hard to predict *a priori*. Second, metal coordination sites that would not be stable in fluid solution (or that would be prohibitively difficult to stabilize) can be prepared within POPs. In this case, attempts to prepare similar coordination environments in solution led to rapid aggregation of the metal centers, which did not occur within the POPs because the POP-bound metal centers are fixed in place and cannot diffuse.

Proposed Work for FY 2013

The new metal-binding site identified by DFT calculations (see above) will be incorporated into POPs. High-throughput experimentation (HTE) techniques will be used to prepare diverse metal complexes of the best available POPs. Particular emphasis will be placed on POPs with metal-binding groups that rely on metal-phosphorus and metal-nitrogen bonds to hold the desired metal center in place and to control its electronic properties. Screening of these new metallated POPs for catalytic transformations of small molecules (e.g., nitrogen, hydrogen, olefins, alkynes, arenes, alcohols, carbon monoxide, carbon dioxide) will also employ HTE. Solid-state infrared, nuclear magnetic resonance, electron paramagnetic resonance, and x-ray absorption spectroscopies, as well as other spectroscopic methods, will be used as appropriate to characterize the structures of the most interesting catalytic POPs on a molecular level, both before and after metallation. The structures of the catalytic sites will be characterized under catalytic conditions, by using one or more beamlines at the Advanced Photon Source. We will develop needed potentials for molecular dynamics simulation studies of the processes involved in the synthesis and the thermal stability of metal-free and metal-containing POPs. We will also perform computational studies of reaction pathways leading to observed and desired product molecules for explicative and predictive purposes. These activities in theory, simulation, and modeling will be performed to guide the synthesis of next-generation catalytic POPs.

Guided Discovery of Crystalline Molecular Materials for Advanced Energy, Information, and Communication Technologies

2011-083-R1

John Schlueter, Karena W. Chapman, Gregory Halder, Dean Miller, and Peter Zapol

Project Description

The goals of this project are the design and crystallization of functional electronic molecular materials for applications in energy, information, and communication technologies. We are developing synthetic methods to selectively control phase formation; stabilize new metastable phases; and perfect the crystallization methodology for the growth of large single crystals that will be used to perform detailed studies of electronic and magnetic properties. Our approach involves combining the same set of chemical reagents under a variety of distinct reaction conditions, including solution, electrochemical, solvothermal, solid-state, and high pressure, to bias the competition for intermolecular interactions that drives phase selectivity. Metastable and kinetic phases often possess improved properties, such as higher superconducting transition temperatures than their thermodynamic analogs, or fluxional electronic coupling.

Mission Relevance

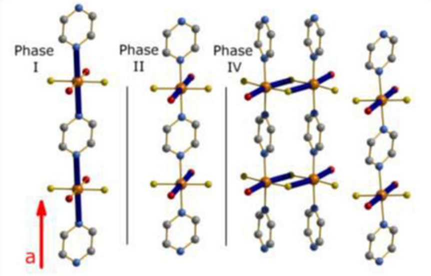
This project is tied to DOE's energy mission. Several key reports have been issued that recognize the importance of crystal growth capabilities for the continued development of basic energy sciences; this project contributes to this goal. The electronic and magnetic molecular materials developed during this project will have applications in various energy, communications, and information technologies (including superconductivity, solid-state lighting, and spintronics) and will address outstanding issues in these fields that have been outlined in DOE's Basic Research Needs series. A fundamental approach to understanding aggregation and crystallization in molecular materials under both ambient and extreme conditions is needed to allow development of these materials to their full potential.

FY 2012 Results and Accomplishments

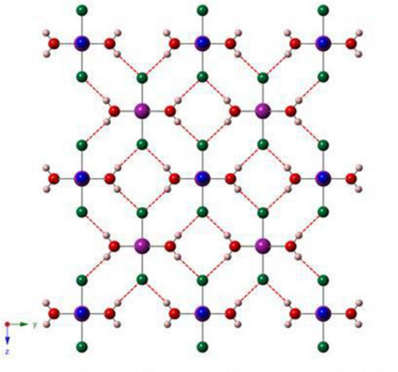
A fundamental energy-related research challenge involves the control of polymorphism (the various ways that molecules arrange themselves in a solid); slight differences in molecular arrangements can have dramatic effects on the collective magnetic and/or electronic behavior of solids. In response to this challenge, we designed a new class of magnetic coordination polymers that contain strong directional hydrogen bonds. Biasing the competition for these interactions allows us to stabilize polymorphic structures. A dramatic illustration of this phenomenon is the $CuF_2(H_2O)_2$ (pyrazine) coordination polymer, which contains structure-directing hydrogen F···H-O bonds. During FY 2011, we developed a basic understanding of the response of this material to external pressure. Under ambient conditions, this system is characterized by two-dimensional $CuF_2(H_2O)_2$ sheets within which the antiferromagnetic exchange is mediated through hydrogen bonds. At pressures up to ~1 gigapascal (GPa), the Jahn-Teller axis lies along the copper-pyrazine chains. As the pressure is increased above ~1 GPa, a structural phase transition results from the reorientation of the Jahn-Teller axis along the copper-water direction. This transition effectively eliminates magnetic superexchange through the $F\cdots OH_2$ network, resulting in a one-dimensional magnetic structure with coupling through the copper-pyrazine chain.

During FY 2012, we performed electron paramagnetic resonance (EPR) studies on single crystals of $CuF_2(H_2O)_2$(pyrazine) as a function of pressure. The goal of these studies was to provide direct, local information on the symmetry of the wave functions associated with the unpaired magnetic electrons through their spin-orbit mixing with excited ligand field states. These experiments clearly demonstrate the reorientation of the Jahn-Teller axis.

To more thoroughly understand the pressure-induced transitions in this material, we performed single crystal x-ray diffraction studies as a function of pressure in a diamond anvil cell. The results clearly indicated that the Jahn-Teller axis had reoriented from the N-Cu-N to the O-Cu-O vector, relieving the tension in the F···H-O bonds. A perhaps even more dramatic solid-state structural transformation occurs as the pressure is further increased. As revealed by single crystal x-ray diffraction at 3.3 GPa, this phase transition results in the ejection of one water molecule per copper unit from two thirds of the chains, forcing them to dimerize through the F-atoms to fill the vacant coordination sites (Figure 1, top).



Pressure has a dramatic effect on structural and magnetic properties of $CuF_2(H_2O)_2$(pyrazine). Disposition of the Jahn-Teller axes (dark blue rods) in the three phases of $CuF_2(H_2O)_2$(pyrazine).



Similar to $CuF_2(H_2O)_2$(pyrazine), the $CuF_2(H_2O)_2$(3-chloropyridine) structure contains a 2D $CuF_2(H_2O)_2$ sheet that propagates long range magnetic order.

Figure 1. (Top) Pressure has a dramatic effect on the structural and magnetic properties of $CuF_2(H_2O)_2$(pyrazine). Disposition of the Jahn-Teller axes (dark blue rods) in the three phases of $CuF_2(H_2O)_2$(pyrazine). (Bottom) Similar to $CuF_2(H_2O)_2$(pyrazine), the $CuF_2(H_2O)_2$(3-chloropyridine) structure contains a 2D $CuF_2(H_2O)_2$ sheet that propagates long-range magnetic order.

To more thoroughly understand the importance of the geometry of this $CuF_2(H_2O)_2$ network and its relevance for magnetic super-exchange, we constructed an analogous material in which the rigid coordination polymer was replaced by non-bridging molecular units with flexible intermolecular interactions. As expected, this material possesses a similar 2D $CuF_2(H_2O)_2$ layer through which magnetic coupling occurs (Figure 1, bottom). However, instead of the more common square bipyramidal geometry of the copper(II) center, this complex is five-coordinate and possesses a trigonal bipyramidal geometry. The highest occupied molecular orbital of $CuF_2(H_2O)_2$(3-chloropyridine) contains the water and fluoride ligands. In addition to the unusual coordination geometry, this is a rare example of a molecular solid (not a coordination polymer) that possesses long-range magnetic order at a modest temperature (2.2 K).

Proposed Work for FY 2013

Research will be aimed at discovering new crystalline phases of magnetic coordination polymers by using high-pressure synthetic methods. The same set of precursors will be combined under various conditions including solution, solvothermal, solid-state annealing, high-pressure solvothermal, and high-pressure solid-state, and the products will be analyzed in search of new polymorphs. The high-pressure solid-state reactions will occur at pressures as high as 5 GPa. Of particular interest are materials that crystallize with open coordination sites or porous structures at ambient pressure because these are expected to produce materials with greater density.

Seminars

Schlueter, J.A. (2013). "Assembly of Molecular Units for the Crystallization of Electronic and Magnetic Materials." Johns Hopkins University, Baltimore, MD, November 5, 2012.

Schlueter, J.A. (2012). "Controlling Electron Spin and Its Transport in Molecule-based Materials." Institute for Solid State Physics, Tokyo, Japan, January 18, 2012.

Schlueter, J.A. (2012). "Controlling Electron Spin and Its Transport in Molecule-based Materials." International Training Program, Tokyo, Japan, January 17, 2012.

Schlueter, J.A. (2012). "Controlling Electron Spin and Its Transport in Molecule-based Materials." Spring 8, Hamira, Japan, January 19, 2012.

Schlueter, J.A. (2013). "Assembly of Molecular Units for the Crystallization of Electronic and Magnetic Materials." University of Oxford, Oxford, United Kingdom, October 1, 2012.

Schlueter, J.A. (2013). "Synthetic Challenges of Molecule-based Frustrated Magnets." Kavli-Institute of Theoretical Physics – Exotic Phases of Frustrated Magnets, Santa Barbara, CA, October 8, 2012.

Reactive Synthesis of Metastable Materials

2011-101-R1

Peter Zapol, Paul Fuoss, Matthew Highland, and Peter Stair

Project Description

While the prediction and characterization of new materials structures with outstanding properties is a key component of materials research and development, in many cases, the primary challenge is to discover methods that can be used to synthesize these desired structures. Often, the structure is metastable and must be grown through a non-equilibrium, kinetically controlled path. This project aims to address the fundamental science underlying the synthesis of such metastable materials as InN — in particular, the mechanisms by which non-equilibrium chemical activities can be created and controlled during film growth from chemically reactive vapors. By using hard x-rays from the Advanced Photon Source (APS) at Argonne to penetrate the reactive vapor phase and chamber walls, we are performing *in situ* scattering and fluorescence studies to observe the structure and composition during growth. We are simultaneously performing *in situ* infrared spectroscopy to characterize the molecular species on the surface that determines the nitrogen activity. Multiscale theory and simulation — from first-principles calculations of the molecular reaction pathways and barriers to continuum modeling of the crystal nucleation and growth processes — will provide a fundamental understanding of and guidance for the experiments. Experiments and simulations in which we vary surface properties (e.g., composition, crystal orientation, step density, and orientation) are expected to elucidate the mechanisms by which the high-nitrogen activity is produced in this system, resulting in strategies to control the growth of metastable InN and its alloys. By these methods, we will show how atomistic understanding of the reaction pathway *and* the role that different reaction intermediates play in the formation of metastable materials — can enable the synthesis of new materials with previously unattainable properties.

Mission Relevance

The project is tied to DOE's missions in energy security and environment. The development and application of pioneering *in situ* experimental techniques and multiscale modeling to the science of materials synthesis will pave the way for new approaches to far-from-equilibrium materials synthesis and new fundamental programs impacting energy security and environmental quality. Our results will have broad applicability in the growth of metastable materials by chemical routes. The development of combined *in situ* x-ray techniques and infrared spectroscopy will benefit multiple DOE programs that are focused on surface reactivity, in both synthesis and catalysis focus areas. Advances in synthesis of high-quality $In_xGa_{1-x}N$ alloy films with band gaps spanning the visible and solar spectra will impact applied programs in photocatalysis, solid-state lighting, photovoltaics, and optoelectronics.

FY 2012 Results and Accomplishments

As an initial step in predicting the mechanisms of metastable InN formation, first-principles calculations were used before FY 2012 to calculate surface phase diagrams and reaction barriers in GaN and InN exposed to NH_3. We identified a new lowest-energy surface structure on InN. We also simulated x-ray crystal truncation rod profiles for all the calculated structures to help identify those in *in situ* x-ray experiments. The coverage and structure of adsorbed chemical species on the GaN and InN surfaces under different environmental conditions were predicted from a surface phase diagram calculated by using first-principles methods.

In FY 2012, first-principles calculations were used to calculate surface reaction energies for surfaces exposed to NH_3 and metal precursors and reaction barriers on GaN and InN, relevant to the mechanisms of metastable InN formation (Figure 1). Calculated barriers identified NH decomposition as a rate-limiting step. We proposed that NH species subsequently undergo hydrogen exchange with other species to produce N on the surfaces. Our results for calculations on metal adsorption suggest that when In (Ga) adatoms are present, NH_3 does not have to undergo a complete dissociation to N and H prior to interactions with metal atoms. Instead, In(Ga)-NH_2 and In(Ga)-NH complexes are likely to form and the growth will proceed from these complexes.

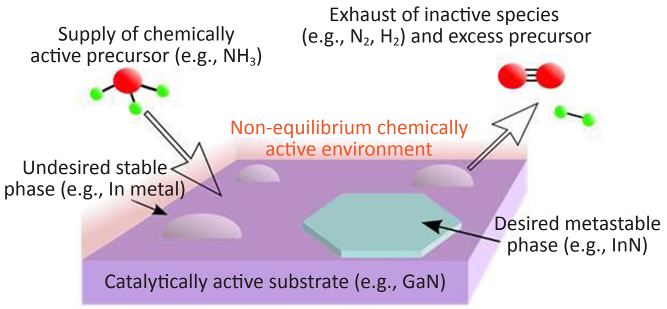


Figure 1. Schematic of reactive synthesis of metastable materials.

In situ x-ray scattering of GaN in N_2/NH_3 and N_2/H_2 gas mixtures measured off-specular crystal truncation rods, which were shown to reproducibly depend on the temperature at 500–700°C and a chemical environment that switched back and forth from N_2 or H_2 to NH_3.

To help identify surface species, a reflection absorption infrared spectroscopy (RAIRS) setup was designed to be compatible with the *in situ* metal-organic chemical vapor deposition system (MOCVD) at sector 12 of the APS. The setup has been completed with the integration of an infrared spectroscopy (IR) spectrometer into the existing MOCVD growth system and tested; the IR spectrometer shows changes in signal upon gas mixture exposure.

We studied the dissociation of H_2 on the ZrB_2(0001) surface, which is a possible metallic substrate for GaN growth, using density functional theory and reflection absorption infrared spectroscopy. Our results show that H_2 readily dissociates on the Zr-terminated (0001) surface, up to an H coverage of one-half monolayer. Furthermore, H is very mobile on the surface and it desorbs between 545 and 625 K. The calculated vibrational frequencies for the adsorbed H are in excellent agreement with our RAIRS measurements.

Proposed Work for FY 2013

To determine substrate properties responsible for high-nitrogen activities and high-quality InN films, we will rely on theoretical predictions, as well as *in situ* experimental observations. We have made arrangements to obtain an array of growth substrates of experimental interest, including semi-polar GaN on m-plane sapphire, AlN, and SiC. We will vary substrate properties (such as-Miller-index crystal orientations) and include other nitrides and nitrided surfaces of oxides and carbides. Real-time IR spectroscopy measurements will track the decomposition of NH_3 and the formation of intermediate surface species, such as NH_2 and NH. Surface x-ray scattering will be used to measure surface structure and dynamics of reconstructions, step morphology, and faceting as a function of vapor composition and temperature. These data will be compared with first principles calculations. By combining *in situ* x-ray and IR spectroscopy measurements, we will determine the substrate orientation and composition dependence of the effective nitrogen activity for comparison with reaction models based on parameters determined from calculations. Exploration of the surface chemistry of both the nitrogen and metal-containing precursors will lead to establishing the mechanism of the underlying surface chemical reactions involved in the growth of gallium and indium nitride by MOCVD.

Next Generation Multicomponent Nanocatalysts: *in situ* Study of the Growth and Function

2011-123-R1

Elena V. Shevchenko, Jeffrey R. Guest, Julius Jellinek, Byeongdu Lee, Sungsik Lee, Xiao-Min Lin, and Tijana Rajh

Project Description

The goal is to explore, understand, and characterize the complex correlations among the size, composition, structure (both interior and exterior), thermal responses, electronic properties, and catalytic characteristics of multicomponent (e.g., mixed, core-shell, dumbbell-like) nanoparticles (NPs), as studied by a combination of chemical synthesis, *in situ* characterization, and theory/modeling/simulation techniques.

A main objective is to understand and characterize the synthesis conditions and mechanisms that define the composition and structure of the resulting multicomponent NPs and, on this basis, to synthesize novel multicomponent nanocatalysts with potentially superior characteristics. We focused on the nucleation and growth of nanosized core/shells and dumbbells, since understanding these mechanisms is critical for making progress in materials design.

Mission Relevance

This project is relevant to DOE's basic science mission. Catalysis is a key process in energy processing and in producing different types of chemical products. It has particular environmental significance, because it allows the efficiency of industrial processes to be increased. High-performance catalysts play a central role in energy conversion and storage technologies. The knowledge gained through this project should impact researchers' ability to design and synthesize catalytic nanostructures with superior performance, enabling them to avoid the time- and labor-consuming empiricism of current approaches.

FY 2012 Results and Accomplishments

We investigated the contributions of different parameters that control the synthesis of NPs by conducting *in situ* hard x-ray studies of the synthesis of multicomponent catalysts. We used simultaneous anomalous small-angle and wide-angle x-ray scattering (SAXS and WAXS) to determine the number and size of nanoparticles and the compositional distribution of atoms over the growth of nanoparticles. The *in situ* variation of the lattice parameter of either the shell or core metal due to alloying was monitored because it is directly related to the catalyst's performance. The primary types of NPs investigated involve ternary metallic core-shell and dumbbell-like systems (e.g., $CoPt_3/Au$, FePt/Au, Au/Fe_2O_3, $CoPd_2/Au$) and hybrid semiconductor-based photocatalysts (e.g., CdSe/CdS core/asymmetric shell with variable width of the shell decorated with Au).

The catalytic properties of the chemically synthesized NPs were tested in reduction and oxidation reactions. The issues addressed included (1) capping ligands that limit the availability of the surface of NPs for the reaction and can poison the catalysts and (2) the impact on possible sulfur-containing interfaces between the constituents in multicomponent NPs.

Theories, modeling, and simulations explored and characterized structural forms (both isomeric [defined by the geometric packing] and homotopic [defined by the placement of different types of atoms between the sites of a given geometric form] forms), energetics, thermal-stability-induced and temperature-induced structural and phase transformations, electronic properties, and chemical/catalytic characteristics of the multicomponent NPs (gas phase and in the environment; for example, deposited on supports) to be synthesized and explored experimentally.

In FY 2012, our accomplishments included:

- We systematically investigated the role of surface modification of Pt and $CoPt_3$ nanocatalysts in alkyne hydrogenation reactions and proposed the general explanation of the effect of surface ligands on the selectivity and activity of nanocatalysts by using experimental and computational approaches.
- We showed that the proper balance between adsorption energetics of alkenes at the surface of Pt and $CoPt_3$ NPs, as compared to that of capping ligands, defines the selectivity of the nanocatalyst for alkene in an alkyne hydrogenation reaction.
- We demonstrated that the addition of primary alkylamines to Pt and $CoPt_3$ NPs can drastically increase the selectivity for alkene from 0 to more than 90% with ~99.9% conversion. Increasing the primary alkylamine coverage on the NP surface leads to a decrease in the binding energy of octenes and to the eventual competition between octene and primary alkylamines for adsorption sites. When the coverage of catalysts with primary alkylamine is high enough, the alkylamines prevail, which prevents further hydrogenation of alkenes into alkanes. Primary amines with different lengths of carbon chains have similar adsorption energies at the surface of catalysts and consequently the same effect on selectivity. When the adsorption energy of capping ligands at the catalytic surface is lower than the adsorption energy of alkenes, the ligands do not affect the selectivity of hydrogenation of alkyne to alkene. On the other hand, capping ligands with adsorption energies at the catalytic surface that are higher than the adsorption energy of alkyne reduce the catalytic activity, resulting in low conversion of alkynes to alkenes (Figure 1).

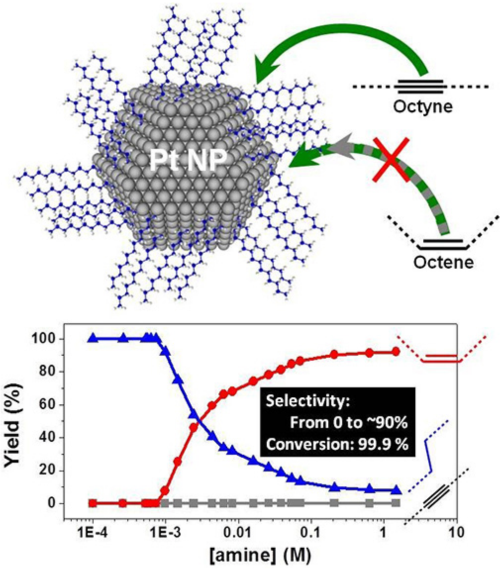


Figure 1. Yield of octane (blue line), octene (red line), and octyne (gray line) in hydrogenation reaction of 4-octyne in 3 hours as a function of octylamine concentration. (This sketch demonstrates that octyne molecules can be absorbed at the surface of Pt NPs when the concentration of surface ligands [octylamine] is high, while adsorption of octene does not take place.)

- In the example of alkyne hydrogenation using cubic and spherical Pt nanoparticles, we demonstrated that the effect of the ligands on the selective formation of alkene is significantly stronger than the effect of nanoparticle faceting.
- We obtained experimental data on the effect of surface modification with cations of different metals (Fe^{3+}, Co^{2+}, Ni^{2+}) for selective hydrogenation of C=O bonds versus C=C bonds in α,β-unsaturated aldehydes. We found a synergetic effect of metal cations and organic molecules (different from the case of alkyne hydrogenation) on the selective hydrogenation of C=O bonds.
- In our theoretical work, we explored the role of alloying Pt with transition metals, such as Co. Among the issues we addressed were the energetically preferred placement of Co within a Pt cluster (interior versus exterior) and the effect of Co on the adsorption energetics of citral. Citral (CH3-C(CH3)=CH-CH2-CH2-C(CH3)=CH-CH=O) is a molecule with two double -C=C- bonds and a C=O group. Geraniol (CH3-C(CH3)=CH-CH2-CH2-C(CH3)=CH-CH-OH) is used for flavors and as an aroma compound in perfumery. Geraniol is synthesized by reduction of citral. The goal is to selectively hydrogenate the CO group of citral and prevent full hydrogenation of the citral molecule. We found that Co atoms favor the interior sites, but they reduce the binding energy of citral to Pt sites irrespective of whether they occupy interior or exterior sites. The degree of reduction, however, is larger when Co is in the preferred interior sites (Figure 2). We are now exploring the role of doping a Pt_{55} NP with cations of transition metals (e.g., Fe^{+3} and Co^{+2}) as another means of affecting the adsorption energetics of citral.

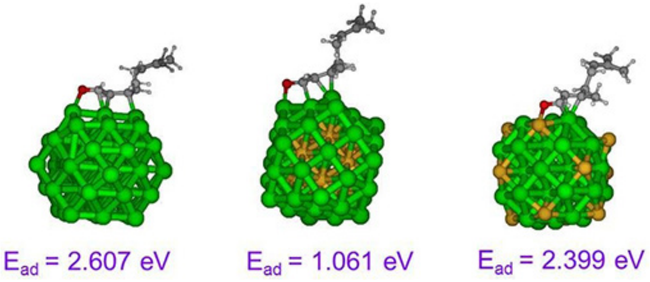


Figure 2. The preferred adsorption conformations and their energies for geranial citral on Pt_{55} (left) and $Co_{12}Pt_{43}$, with Co atoms in the interior and exterior of the 55-atom nanocatalyst. (In middle and right images, respectively, Pt is green and Co is brown.)

Proposed Work for FY 2013

In FY 2013, we plan to:

- Synthesize multicomponent Au/iron oxide and FePt/iron oxide;
- Study the surface modification for selective catalysis (e.g., hydrogenation of C=C groups versus C=O groups) via adsorption of metal cations, anions, and organic molecules;
- Conduct *in situ* CO oxidation;
- Develop the nanocatalyst/support system for gas-phase catalysis (e.g., Au/CeO_2, Au/SiO_2, Au/Fe_3O_4);
- Extend all studies to the neral isomer of citral;
- Explore the role of ligand modifiers (such as amines) in changing the adsorption energetics of citral and its hydrogenated products, with the goal being to use the amines as selectivity "knobs" in the hydrogenation of citral;
- Explore the role of cation dopants as selectivity regulators; and
- Explore the combined role of ligand modifiers (e.g., amines) and transition metal cations (e.g., Fe^{+3} and Co^{+2}) in regulating the selectivity of pure Pt and alloy Pt/Co nanocatalysts and extended surface catalysts.

Seminars

Shevchenko, E. (2013). "Design of Nanoparticles and Their Surfaces for Catalysis and Battery Electrodes." The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, October 30, 2012.

Shevchenko, E. (2012). "Nanoparticles for Catalysis and Batteries." University of Illinois at Chicago, Chicago, IL, May 17, 2012.

Inorganic Synthons: Toward Scalable Materials Design, Discovery, and Creation

2011-134-R1

Lynda Soderholm, Peter Chupas, Mercouri Kanatzidis, and John F. Mitchell

Project Description

In this project we seek a mechanistic approach for the directed syntheses of inorganic materials. At the core of our rational is a conceptual extension beyond atoms as core building blocks to inorganic functional groups — preorganized units call "synthons" — that self-assemble in molten or aqueous solution before crystallization. Synthons may take the form of well-defined fragments of covalent networks or merely exist as atomic correlations. If we can identify these preorganized bulk precursors and understand the general principles that guide their formation and condensation, we can move toward a mechanistic approach to the discovery and growth of new and targeted materials with energy relevance.

Mission Relevance

Our project fits directly under DOE's science mission because it addresses the "grand challenge" of controlling the structure of matter at the atomic level. The knowledge gained as a result of this project will effectively be used to rewrite textbooks on inorganic synthesis, paving the way toward directed creation of inorganic solids with the precision of organic functional group synthesis and the high yields of solid-state reactions.

FY 2012 Results and Accomplishments

Using our previously developed capability to probe air-sensitive materials as a function of temperature using high-energy synchrotron radiation, we were surprised by our observations that two different phases border the molten regime in a reaction of Cu in K_2S_3. This ability to nucleate different phases from a single reaction mixture is at the heart of materials by design, and our subsequent range of *in situ* reactions was performed to map the available phases. After we conducted Rietveld refinements of approximately 2,000 diffraction patterns over different temperatures and chemical compositions of Cu and Sn in polysulfide salt fluxes K_2S_3 and K_2S_5, we found the reaction space to be far richer than we imagined. In a single synchrotron scattering experiment, we found a variety of new phases, which was surprising because their formation mechanisms are novel. For example, our array of sequential Rietveld refinements uncovers the evolution of crystalline phases during an *in situ* reaction of Cu in K_2S_3 (Figure 1). This understanding of changing ion correlations offers a new route to metastable semiconductors.

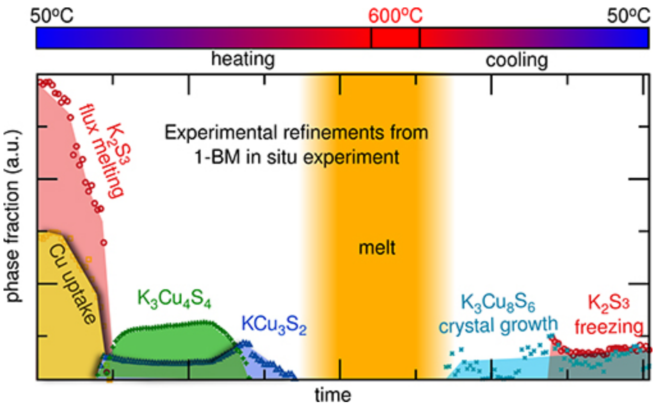


Figure 1. Sequential Rietveld refinements show the detailed evolution of phases during an in situ *molten salt flux reaction, with the novel metastable phase* $K_3Cu_4S_4$ *appearing in a narrow region upon heating only.*

Similarly unexpected results were uncovered in studies of aqueous transition-metal hydroxides as a function of sulfate concentration. The competition for the metal coordination environment between other metal cations and sulfate anions was influenced by solution conditions, resulting in correlations that also manifest themselves in the solid precipitates. As demonstrated in Figure 2, x-ray scattering experiments are critical to our newfound understanding of synthon development in these systems. Ion-ion correlations seen in the data correspond well with precipitates that form from the solutions. The theoretical component of our research is supporting our findings and providing insights into the energetics of synthon formation that will ultimately provide a route to predictive synthetic capabilities.

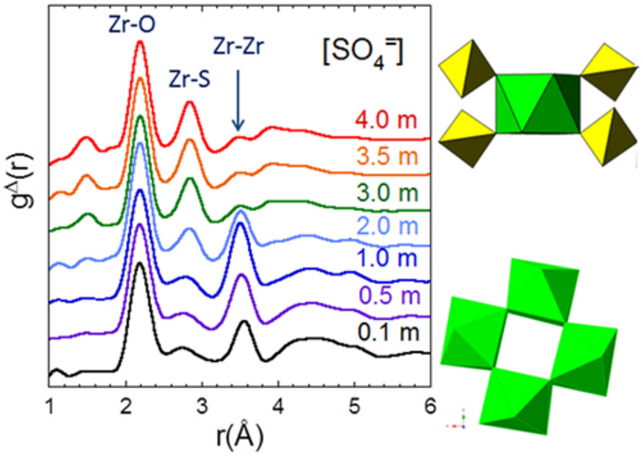


Figure 2. Peaks in Fourier transformed x-ray scattering data, attributable to atomic pair correlations, demonstrate the changing Zr speciation as a function of pH. Single crystal structures of solution precipitates reveal that the correlations persist into the solid state, thus providing information important for a mechanistic understanding of Zr-oxide phase formation.

Proposed Work for FY 2013

The development of the synthon concept for directed synthesis will continue with a two-pronged approach. Studies of the development of atomic correlations in chalcogenide melts and aqueous-oxide solutions are fully under way and are providing new information about their influence on materials syntheses. Solutes will be included in the chalcogenide melts to study synthon formation as a function of temperature and its impact on precipitate composition and structure. Transition metal oxide correlations in aqueous solution will be further monitored as a function of the solution conditions and choice of transition metal. We will continue our efforts to couple these experiments with computational studies of cluster growth in melts to determine synthons, establish additional pathways of synthons to transition metal structures, and begin exploring the role of solvent in structure growth.

Synthesis Science of Functional Layered Complex Oxides

2011-188-R1

John W. Freeland, Anand Bhattacharya, Jeffrey A. Eastman,
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Nenad M. Markovic, and Serge M. Nakhmanson

Project Description

Functional materials based on complex oxides offer new and exciting strategies for meeting many of our outstanding energy challenges. Materials theorists can now even design virtual crystals for specific applications and predict their properties. Unfortunately, synthesis of a new oxide material is typically difficult, particularly when there is a lack of quantitative feedback during growth. The goal of this project is to understand the growth of functional layered complex oxides by utilizing both computational studies of synthesis and experiments employing an oxide molecular beam epitaxy (MBE) system with *in situ* x-ray scattering and spectroscopy capability. The *in situ* oxide MBE system will be the first of its kind and will allow an unprecedented level of control over both stoichiometry and structure. The associated coupling of theory and experiment is expected to significantly advance both growth science and understanding of complex oxide phenomena as we harness these materials as model systems in the search for novel catalytic functionality.

Mission Relevance

This work is relevant to DOE's basic science mission. The aim of this project is to develop the "science of synthesis" approach for the case of layered oxide thin films. By merging theory and experiment, the goal is to move quickly down the path from prediction to synthesis of novel energy materials. Harnessing the ability to quickly isolate synthesis pathways will enable the study of novel materials for energy storage and conversion. In addition, this project involves the development of a unique capability at the Advanced Photon Source that, in the long term, will greatly benefit a wide community of users interested in oxide thin-film synthesis.

FY 2012 Results and Accomplishments

Layered oxide materials offer a broad range of functionalities, and the many recent advances in computational theory now allow the design of novel phases with potentially transformative properties in the field of energy technology. However, the main challenge is the ability to quickly isolate conditions for synthesis of novel materials, which is the goal of this project. Our approach combines three key ingredients: *in situ* characterization of the growth of layered oxides, application of theory of synthesis in close interaction with experiment, and systematic exploration of the relationships between complex oxide structures and electrocatalytic behavior.

In FY 2011, we redesigned and assembled the world's first in-situ ozone assisted MBE system in sector 33 on the Advanced Photon Source, began development of the theory framework to understand thin film synthesis, and developed the techniques for measurement of catalytic properties of oxide surfaces. In FY 2012, we continued this effort and fully integrated the reactive oxide MBE system into sector 33-ID of the Advanced Photon Source (APS). This system is a first of its kind at a synchrotron and is the centerpiece of the synthesis science portion of the program. To synthesize the complex composition for the class of novel materials, the MBE chamber accommodates multiple elemental sources with integrated shutters for layer-by-layer growth control.

We completed a study of MBE growth in the single-layer titanate Sr_2TiO_4, as a first step in the growth of more complex layered phases. The growth of layered Ruddelsden-Popper (RP) phases, $A_{N+1}B_NO_{3N+1}$, on the infinite layer case, ABO_3, poses a major challenge. Since the ABO_3 phase is often more stable, dynamic reconstructions can occur, and even though layers are deposited in a specific sequence, the end result is often different from that expected. For example, for growth of Sr_2TiO_4 on $SrTiO_3$, small deviations in local composition can lead to missing Sr_2TiO_4 layers, which become dynamically reconstructed into the $SrTiO_3$ phase. *In situ* studies of growth with quantitative x-ray probes allowed us to track the growth process step-by-step and, more importantly, identify in the growth sequence exactly where the growth occurs.

The RP phase for Sr_2TiO_4 is grown by repeated stacking blocks of SrO-SrO-TiO_2 on the substrate. In Figure 1, we show a layer-by-layer study of the crystal truncation rod (CTR) for the first four layers of the single-layer RP phase. After the growth of each complete layer, we stopped the process to examine the surface structure with x-ray scattering. While in the process of quantitatively analyzing the data, we were able to define the relative evolution of the CTR. We found that a unique stacking of the atomic planes on the substrate leads to a unique shape of the CTR.

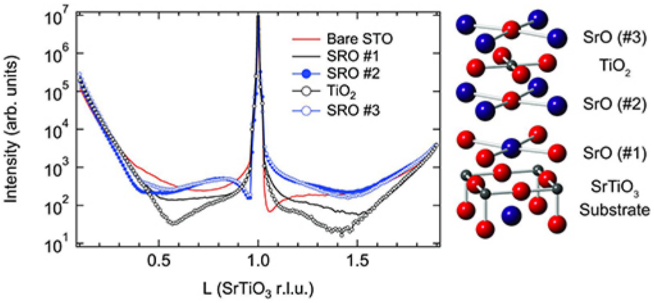

Figure 1. (Left) Layer-by-layer changes in the crystal truncation rod (CTR) scattering related to the lattice structure of the film. (Right) Deposited lattice structure for the initial growth of Sr_2TiO_4.

The data in Figure 1 show that for the first three layers (SrO #1, SrO #2, and TiO_2), the CTR evolves between different characteristic shapes consistent with the unique layer stacking. However, when the last layer (SrO #3) was grown, something unexpected happened: the CTR profile became nearly identical to the case of SrO #2. This result implies that the layer stacking for these two cases is the same, but the intended structure should be different. The only way to alter the stacking to make these two cases lead to the same lattice stacking is to move the TiO_2 down by one layer. This effectively adds one monolayer of $SrTiO_3$ to the substrate and returns to a case of two SrO layers on the surface.

Having obtained experimental details, we turned to the theory effort to understand the growth dynamics. We completed detailed calculations by using a spectrum of theoretical approaches (density functional, empirical potentials, and thermodynamics). The results for different layer stackings, shown in Figure 2, clearly show that the $SrTiO_3$ phase is much lower in energy than the layered phase. This difference offers the driving force for the dynamic reconstruction. To remediate, the theory actually proposed, a solution that has been verified experimentally. The TiO_2 layer on the surface will only move down by one layer, so if one grows three SrO layers rather than two, the system will dynamically reconstruct into the desired phase.

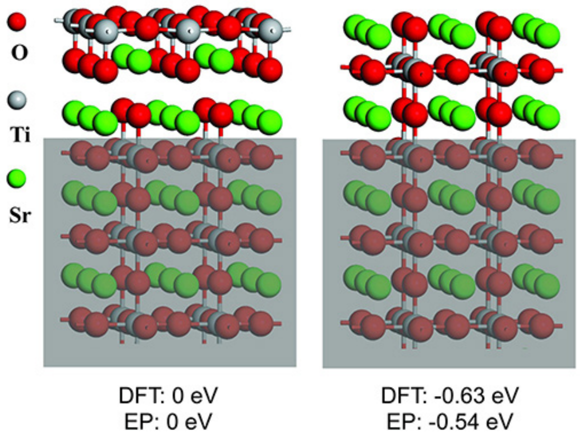

Figure 2. Energetics of different stacking orders on the surface of TiO_2-terminated $SrTiO_3$. These results show the driving force for the layer reconstruction seen in Figure 1.

Finally, to design complex oxide catalysts for the oxygen reduction reaction and oxygen evolution reaction, we have completed a study of epitaxial thin films of $SrRuO_3$ (SRO) on (100)-oriented niobium-doped strontium titanate and tracked both *in situ* activity and crystallographic structure with hard x-rays. The findings show that these systems are very reactive for water splitting but suffer from stability issues. Our *in situ* studies allowed us to better understand the structure and electronic properties *in situ* under catalytic conditions. This insight in the model systems allowed us to track directly the decomposition of the reactive phases to understand the growth process, which is the key first step in isolating how to maintain high reactivity in a stable phase.

Proposed Work for FY 2013

During FY 2013, we will finalize our experiments on the growth of non-polar titanates (Sr_2TiO_4) before extending the research into new layered phases. One of the main remaining issues to address is the dynamics of the reconstruction process. We will harness off-specular (diffuse) scattering to track island formation/coalescence during growth. The layered nickelates (La_2NiO_4) are the next compound of interest because of their interesting catalytic functionality. Growth of this phase, however, raises a new set of synthesis questions. For the previous case, the layers were charge neutral, but that is not the case here. The theoretical calculations show very different characteristics for layer rearrangements in this case. After synthesis, this system will be subjected to *in situ* catalysis studies. On the theory front, we will continue the development of synthesis models using molecular dynamics and kinetic Monte-Carlo methods. These methods will enable real-time theoretical modeling of the synthesis dynamics.

Seminars

Freeland, J. (2011). “Emergent Correlated Electron States at Surfaces and Interfaces.” Liebniz Institute for Solid State and Materials Research, Dresden, Germany, December 2, 2010.

Freeland, J. (2011). “Emergent Correlated Electron States at Surface and Interfaces.” Max Planck Institute for Solid State Research, Stuttgart, Germany, December 3, 2010.

Freeland, J. (2011). “Understanding and Controlling Phases of Complex Oxides.” Max Planck Research Department for Structural Dynamics, Hamburg, Germany, November 29, 2010.

Multiscale Computational Molecular Science

2011-197-R1

Gregory A. Voth

Project Description

The objective of this project is to develop novel coarse-grained (CG) and reactive molecular simulation methods that utilize rigorous statistical mechanics to describe the multiscale nature of chemical transformations in condensed phase systems. These methods will include a unique molecular dynamics method that extends molecular mechanics simulations to encompass chemical reactions. Additionally, new CG procedures are being developed to rigorously bridge resource-intensive *ab initio* simulations to large-scale molecular systems, enabling a more accurate description of molecular environments without resorting to empirical fitting. As a result, these methods retain predictive capability that can guide experiments. For the largest CG systems, new load-balancing algorithms are being designed and implemented to more efficiently utilize highly scalable computational resources. An example of a target system in this study is carbon dioxide (CO_2) sequestration by photosynthetic bacteria, a truly multiscale process involving the formation of protective protein shells called “carboxysomes” (Figure 1).

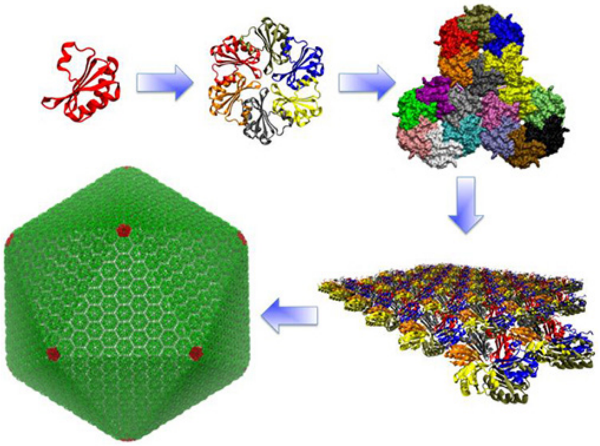

Figure 1. Illustration of the multiscale nature of the carboxysome shell structure constructed from basic protein building blocks. Carboxysomes play a key role in sequestering CO_2 in photosynthetic bacteria for the early stages of producing energy-containing compounds.

Mission Relevance

This project is relevant to DOE's missions in basic science and energy, as it advances the development of simulation tools to facilitate innovation and discovery. The continued development of energy conversion and storage systems is highly relevant to ensuring the leadership of the United States in energy storage technologies, as well as reducing the nation's dependence on oil. By combining the methods developed in this work, a consistent simulation tool is being created that will be capable of predicting materials properties relevant to engineering energy storage and conversion devices based on molecular structure, as well as complex molecular mechanisms.

FY 2012 Results and Accomplishments

Previous work in this project resulted in the development of force-matching algorithms to parameterize reactive models based on results of condensed phase electronic structure calculations in addition to creating efficient algorithms and strategies for their efficient calculation in molecular simulations. Building upon this foundation, in FY 2012, several advances were made in the development of novel force-matching algorithms that accurately parameterize multistate models to simulate reactive processes in condensed phase environments utilizing linear least squares algorithms. Multiple program (MP) and OpenMP parallelization strategies were combined in the simulation code for reaction simulations, named Rapid Approach for Proton Transport and Other Reactions (RAPTOR), leading to increased performance on a wide range of high-performance computing architectures. The MP algorithm was included in the Large-Scale Atomic/Massively Parallel Simulator (LAMMPS) code, making these advances accessible to the general user community. Two load-balancing strategies (hierarchical spatial subdivision and space-filling curves) were investigated for the efficient simulation of implicit solvent models in large CG simulations. All developed algorithms are being used for the multiscale reactive modeling of carboxysomes (Figure 1), which aid bacteria in sequestering CO_2 and can be used in the production of energy-containing compounds. An allocation of time on computing resources provided by the Oak Ridge Leadership Computing Facility (OLCF) through the DOE Advanced Leadership Computing Challenge (ALCC) support this work.

Proposed Work for FY 2013

Work will continue on the optimization of the new parallelization strategies in the RAPTOR and LAMMPS codes, targeting leadership-class computing resources. Considerable effort will be devoted to increasing the performance of RAPTOR to simulate multiple chemical reactions simultaneously by using algorithms designed over the past year, including a graphics processing unit (GPU) -based algorithm. A Hilbert space-filling curve approach will be implemented to enhance the performance of the CG code for simulations with implicit solvent models, utilizing an allocation of time on leadership computing resources provided by the Early Science Program at the Argonne Leadership Computing Facility. Investigations will continue into understanding the formation of carboxysome shells to capture CO_2 and their role in key enzymatic reactions to transform CO_2 into useful energy-containing molecules.

Fundamental Developments in Theory and Modeling of Nanoscale Systems and Phenomena

2011-198-R1

Julius Jellinek

Project Description

The field of nanoscience and nanotechnology represents a truly new research area. The principal novelty extends not only to the systems and phenomena at hand, but also to the fundamental concepts, methodologies, and techniques — both experimental and theoretical — needed to study and characterize them. By virtue of practical necessity, this state of affairs is well recognized in experimental studies of nanosystems — the very ability to perform them hinges on and forces the development of new, highly sensitive "nanoprobes."

Nevertheless, the overwhelming majority of theoretical explorations in the field still rely on concepts and methodologies originally developed for either the condensed phase or the gas phase of matter. These concepts and methodologies may not only be inefficient as applied at the nanoscale, but, more importantly, they may be limited or even inadequate for capturing, characterizing, and predicting novel properties and phenomena. Therefore, formulation of new fundamental theoretical concepts and methodologies and new theoretical tools of analysis and characterization that are specifically targeted at and tailored to nanoscale objects is central for the development of the entire field.

The goal of this project is to initiate and execute a well-defined program of exploratory theoretical research that aims at the development of such new concepts, methodologies, and analyses techniques in the general areas of dynamics and statistical mechanics of nanoscale (more generally, finite-size) systems.

Mission Relevance

This project falls under DOE's basic science mission. Because advanced materials are ubiquitous throughout all technologies underlying energy, environment, and national security, the fields of nanoscience and nanotechnology hold the potential of a truly revolutionary impact on all mission areas of the DOE.

FY 2012 Results and Accomplishments

In FY 2012, this project has resulted in three main accomplishments. The first is formulation of a general methodology for computation of *vibrational densities of states of arbitrarily anharmonic systems*. The knowledge of densities of states is essential as it forms the foundation for theoretical/computational characterization of thermodynamical and statistical mechanical properties of systems. Despite considerable effort over decades, the subject of densities of states of highly anharmonic systems remained one of the outstanding unsolved problems of statistical mechanics. The solutions offered were all approximate and/or applicable to systems with only a weak degree of anharmonicity. Progress in the first year of the project included replacing the harmonic frequencies by energy-dependent discrete sets of anharmonic frequencies and their associated (non-integer) degeneracies (both are obtained from the so-called power spectrum of a system generated by following its dynamical behavior) and developing a mathematical extension that allows for use of noninteger degeneracies.

Building on this progress in FY 2012, we completed the development of a new and exact methodology that allows for computation of vibrational densities of states for systems with an arbitrary degree of anharmonicity. This was accomplished in the frameworks of both classical and quantum mechanical formulations of physics. An important novel conceptual aspect of the new methodology is that it furnishes a *statistical* property — density of states — that is derived from the *dynamical* (i.e., actual time-dependent) behavior of systems at a given energy. As a consequence, in addition to equilibrium densities of states that correspond to "infinitely long" observation (simulation) times, the methodology also allows one to compute densities of states that correspond to finite time intervals and to analyze and characterize statistically finite-time, nonequilibrium properties of systems. This methodology was implemented algorithmically and coded. Work is in progress on applying it to characterization of energy-dependent (alternatively, temperature-dependent) dependent changes in properties of nanoscale systems, such as pure and alloy metal clusters of different sizes and compositions, which play a central role in modern technologies relevant to new and renewable sources of energy, sensors, biomedical uses, and other applications.

Figure 1 displays the vibrational densities of states computed for an Al_{13} cluster by using the new methodology and the traditional harmonic approximation. At high energies, the system behaves classically: the quantum and the classical densities of states coincide within both schemes. At low energies, the dynamics-based densities of states coincide with the harmonic ones. But as the energy of the cluster increases, the two begin to deviate substantially (by orders of magnitude) because of the anharmonic effects.

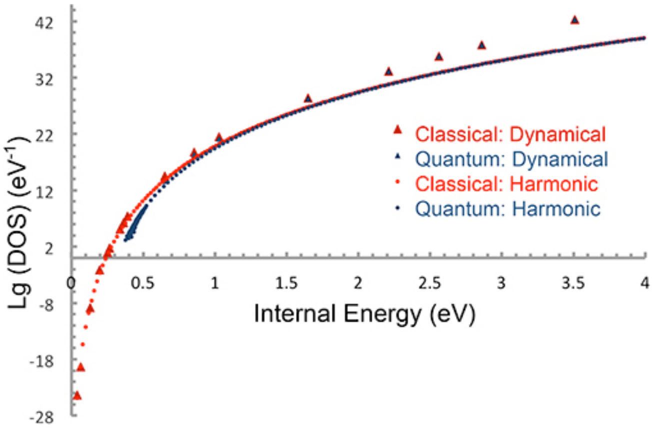

Figure 1. Classical and quantum densities of states (DOS) for Al_{13} as a function of its internal energy computed by using a harmonic approximation and the new dynamics-based methodology for anharmonic densities of states.

The second accomplishment was development of general analytical tools for analysis, understanding, and characterization of complexities in behavior of finite systems in terms of the behavior of their component subsystems. The goal here was to be able to identify parts of a system (e.g., groups of atoms), the dynamical behavior of which at a given energy is similar — we call these groups "classes of dynamical similarity" — and to characterize the behavior of the entire system in terms of the behavior of its classes of dynamical similarity. In the past, we introduced the notion of dynamical degrees of freedom as a powerful descriptor that allows one to group atoms into classes of dynamical similarity. As a new development, we have shown analytically that the distribution of characteristic frequencies underlying the dynamical behavior of any system at a given energy can be represented as a superposition of the distributions of frequencies of its classes of dynamical similarity (even more generally, of its parts for any partitioning of the system into parts), with the dynamical degrees of freedom of the classes (or parts) serving as the coefficients/weighting factors. This development expands the power of our methodology for analysis and characterization of dynamical behavior of systems in terms of behavior of their subsystems.

The third accomplishment concerned development of new methodologies for analysis and characterization of dynamical complexities in *heterogeneous* finite systems (e.g., systems consisting of more than one type of atom). In our earlier studies, we introduced the notions of mixing energy and mixing coefficient and derived general and rigorous formulas for their calculation. We applied these quantities to various equilibrium structures of bimetallic clusters and showed that the mixing coefficient is the quantity responsible for the stability ordering of structures that belong to a given class as defined by a number of common characteristics. As a new development, we extended the notion of mixing energy and mixing coefficient to arbitrary (including nonequilibrium) structures and introduced time-dependent mixing coefficients as a descriptor for analysis and characterization of the added complexity of dynamics in heterogeneous systems. The new methodology was implemented algorithmically, and work is in progress on applying it in molecular dynamics simulations of Ni/Al bimetallic clusters.

Figure 2 shows a graph of the mixing coefficient for $AlNi_{12}$ at low and high energies. The most stable structure of this cluster is an icosahedron with the Al atom in the center. At low energies, the Al atom remains encapsulated by the Ni atoms, and this behavior is indicated by the mixing coefficient that changes with time only slightly. At high energies, the Al atom can “escape” from the “cage” of Ni atoms and then return to it. These excursions are clearly indicated by the time evolution of the mixing coefficient at high energy.

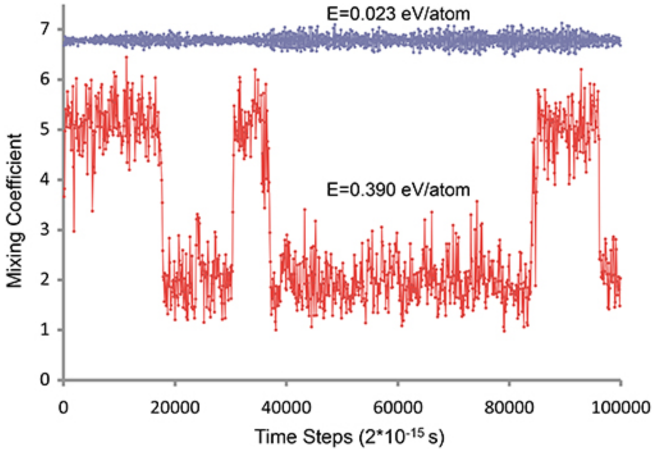

Figure 2. Mixing coefficient of $AlNi_{12}$ as a function of time at low and high energies.

Proposed Work for FY 2013

Our work in FY 2013 will focus on:

- Extending the new methodology for computation of anharmonic densities of states to vibrating *and rotating* systems, including arbitrarily floppy ones where the vibrations and rotations are strongly coupled;
- Developing an analysis of anharmonic densities of states of systems in terms of densities of states of their subsystems;
- Performing large-scale dynamical simulations of heterogeneous systems (e.g., Ni/Al alloy clusters) and characterizing their energy-dependent anharmonic densities of states, as a function of system size and composition;
- Carrying out an analysis of dynamical complexities of heterogeneous systems in terms of time-dependent mixing coefficient; and
- Combining the dynamical analyses based on dynamical degrees of freedom and the mixing coefficient.

Image Furnace Growth of Single Crystals

2011-199-R1

Kenneth R. Poeppelmeier

Project Description

In this project, our goal is to improve crystal growth capabilities, grow large single crystals of interesting materials, and understand how the crystal structure relates to the crystal properties. To grow crystals, we rely principally on the optical floating zone (FZ) technique; we combine this technique with the use of a flux for difficult-to-grow crystals. The focus is on growing crystals of non-linear optical (NLO) materials, although other materials of interest also will be investigated. We hope to achieve a better understanding of crystal structure and properties, how bulk and surface structures relate, and how the structure affects properties.

Mission Relevance

This project is relevant to DOE’s basic science mission. The fundamental knowledge gained and technical results of this project will be of interest to DOE, the Department of Defense (DoD), other state and federal agencies, and private industry for both basic and applied research and development (R&D) activities. From a basic R&D viewpoint, the crystal growing community will benefit from a better understanding of crystal growth as a result of the fundamental research conducted in this project. From an applied R&D viewpoint, the ability to produce large single crystals with NLO properties will benefit the development of shorter wavelength lasers. These lasers are used in a number of advanced spectroscopic techniques, including photoemission spectrometry, Raman scattering spectrometry, and scanning tunneling microscopy. These techniques are routinely used in catalysis and materials research. Furthermore, the development of shorter wavelength lasers will allow for data storage at higher densities than current Blu-ray technology.

FY 2012 Results and Accomplishments

Prior to FY 2012, we grew large, high-quality crystals of cuprous oxide, Cu_2O (Figure 1) and progressed in optimizing growth conditions. Interestingly, increasing the atmospheric O_2 concentration during growth decreases the number of Cu vacancies in the crystal. The opposite phenomenon would normally be thought to occur: increasing oxygen concentration would lead to decreased oxygen vacancies but increased cation vacancies. We hypothesize that the formation of CuO is responsible for the decrease in copper defects with increasing oxygen concentration, as explained by the chemical equation: $Cu_{2-x}O \rightarrow (1-x)\, Cu_2O + x\, CuO$. As CuO forms, it reduces the copper vacancies in the Cu_2O crystal. Cuprous oxide experiences an extremely long exciton lifetime, up to 13 microseconds, which makes it an ideal material for studying exciton behavior via a high-spatial-resolution exciton-mediated photovoltaic effect. For this purpose, Cu_2O has been cut to various facets and electrodes attached. Orientation is important since it determines optical selection rules. In addition, third harmonic generation was observed in the Cu_2O crystals at 630 nm from a 1,940-nm pump. Cu_2O is of interest for studying third harmonic generation without a second-harmonic-generation background.

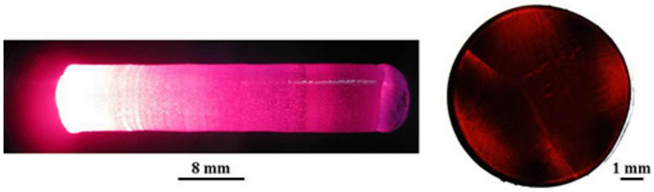

Figure 1. (Left) Cu_2O crystal cut on the left side and illuminated via a fiber light through the cut. (Right) Cu_2O crystal cut perpendicular to growth direction, showing a single grain boundary running from top left to bottom right.

In FY 2012, progress has been made in growing crystals of NLO materials and in understanding and improving crystal growth by using the optical FZ method.

We synthesized the inverse perovskites $K_3B_6O_{10}Cl$ and $K_3B_6O_{10}Br$, both NLO materials, in powder form. We found a KI-based flux that should be compatible with the FZ furnace hardware, grew a small single crystal of $K_3B_6O_{10}Cl$ from the KI flux in a crucible, and confirmed the structure via single-crystal x-ray diffraction.

We synthesized a new phase of $Li_6CuB_4O_{10}$ in the FZ furnace and grew crystals several millimeters in size. The crystals have a centrosymmetric crystal structure (space group P-1) with 1 formula unit per unit cell. This new phase is distinct from either of the two known phases of $Li_6CuB_4O_{10}$. We suspect that the phase transitions are related to the thermal history of the sample.

We grew crystals of $Co_{60}Cr_{28}Mo_7$ carbide and studied properties that are potentially suitable for use in artificial joints. We grew large single crystals (6 mm in diameter, several centimeters in length). The crystals exhibit a face-centered cubic (FCC) structure alloyed with Cr and Mo. The surface of the crystal contains multiple grains of $M_{23}C_6$ (M=Cr, Mo). Owing to this special surface chemistry, this material is of interest for hip replacements.

We studied Mg_2SiO_4 and Fe_2SiO_4 and grew small single crystals of Mg_2SiO_4 in the optical FZ furnace. These materials are of interest when comparing the properties of olivine minerals occurring on Earth (Forsterite, Mg_2SiO_4) with those occurring on extraterrestrial bodies (e.g., Fayalite, Fe_2SiO_4, on the Moon and Mars).

Proposed Work for FY 2013

In FY 2013, we will work to understand and control the phase changes in the $Li_6CuB_4O_{10}$ material and grow crystals of all three structures. We will grow single crystals of inverse perovskites from the KI flux in the FZ furnace. To determine the role that the alloy and carbide grains play in the corrosion of the material and their utility for an artificial joint, we will use $Co_{60}Cr_{28}Mo_7$ single crystals. We will grow large crystals of Mg_2SiO_4 and Fe_2SiO_4 and study their properties, in addition to studying exciton behavior and third harmonic generation in Cu_2O.

Seminars

Poeppelmeier, K.R., "Targeting Noncentrosymmetric Structures and Other New Materials." Indiana University at Bloomington, Bloomington, IN, January 17, 2012.

Poeppelmeier, K.R., "Targeting Noncentrosymmetric Structures and Other New Materials." University of Houston, Houston, TX, January 31, 2012.

Poeppelmeier, K.R., "Targeting Noncentrosymmetric Structures and Other New Materials." University of Buffalo, Buffalo, NY, February 17, 2012.

Novel Materials for Active Nanostructures

2011-200-R1

O. Daniel López and Liliana Stan

Project Description

In keeping with the current challenges to global energy sustainability, besides functionality, the new generation of piezoelectric devices (e.g., electromechanical systems) should also have compact dimensions, low power consumption, high efficiency, and increased reliability. Further miniaturization into the nanometer region presents great challenges in terms of micro-structuring techniques, fundamental effects, and material properties. The goals of the project are thus to fabricate and evaluate new-generation, high-performance active nanostructures incorporating novel thin film materials. The research builds on the ability to fabricate piezo- and ferroelectric thin films that are compatible with standard semiconductor processes. In particular, piezo- and ferroelectric thin films and their corresponding electrode materials will be grown mainly by sputtering, thereby creating functional structures for integration into nano-electrical and nano-mechanical systems.

One of the objectives of this project is the optimization of deposition conditions to maximize polarization while minimizing film thickness and controlling the residual stress and stress gradient in the entire film stack. The electrode materials will include metals and conducting oxides and will be optimized to maintain polarization while minimizing fatigue during operation. An important aspect of this project is gaining an understanding of phenomena governing the piezo- and ferroelectric response in active nanostructures. This information will guide the design and interpretation of nanoscale structures suitable for application in nano-electro-mechanical systems. Another objective of the project is the development of a variety of designs for testing and incorporation of the piezoelectric/ferroelectric materials into active nanostructure devices.

Mission Relevance

This project is relevant to DOE's basic science mission. The proposed research will develop a fundamental scientific understanding of nanoscale piezoelectric phenomena in active nanoscale electromechanical devices, with applications in high performance signal processing, communications, sensors, and nano-positioning actuators. The knowledge gained from the investigation of novel materials embedded in active nanostructures will be of interest to DOE, Department of Defense, and private industry for both basic and applied R&D.

FY 2012 Results and Accomplishments

In FY 2011, we installed, upgraded, and qualified the sputter deposition system acquired from AJA International, Inc. Our efforts led to a fully functional system, offering a variety of options with respect to deposition materials, substrate choices, and deposition conditions.

As an initial step on developing active nanostructures, in FY 2012, we worked on the optimization of the deposition conditions for the piezoelectric films and a variety of materials, including metals and conductive oxides, as electrodes. After successfully creating heteroepitaxial structures of $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT)/$SrRuO_3$ (SRO)/$SrTiO_3$ (STO) with good ferroelectric properties, we used the gained knowledge to integrate piezoelectric PZT with Si. In parallel with the study of the properties of the piezoelectric films as a function of deposition parameters and thickness, we dedicated special attention to the electrode materials. The electrode material is of primary importance for many reasons: it is crucial for nucleation-controlled growth of piezoelectric materials, must keep its electrical properties even after thermal treatment under oxidizing atmosphere, and has to be amenable for fabrication of devices.

We developed new processes for metal and conductive oxide film deposition, focusing on reducing their residual stress, which is known to greatly influence the quality of the devices. We explored different materials as bottom electrodes, including Pt/Ti, Ru, SRO, and $LaNiO_3$ (LNO). We studied the PZT phase-controlled growth dependence on the bottom electrode material. The Pt films grown on Ti/Si exhibited a strong (111) preferential orientation. We determined that the microstructure, preferred orientation, and ferroelectric properties of PZT films grown on Pt bottom electrodes depend strongly on the quality of the Pt which is dependent not only on the deposition conditions, but also on the adhesion layer beneath the Pt.

In parallel with improving the PZT/Pt/Ti/Si structures, we worked on investigating the use of conductive perovskite oxides, such as LNO as electrodes, because of their known advantage of decreasing the leakage current and polarization fatigue of the ferroelectric thin films. The PZT films grown on LNO/SiO_2/Si were found to have a preferred (001) orientation, proving that the LNO is a good candidate as a bottom electrode.

Besides PZT, we explored another piezoelectric material, AlN. This attractive piezoelectric material has high resistivity, high breakdown voltage, and high acoustic velocity, and it can be grown by the reactive sputtering technique at relatively low temperature, thus making it compatible with complementary metal-oxide semiconductor (CMOS) technology. We grew highly oriented (00l) AlN films on Pt/Ti/SiO_2/Si and Ru/SiO_2/Si. The piezoelectric coefficients of AlN films measured by piezoresponse force microscopy have values as high as 5.2 pm/V, which is the highest among currently reported values for AlN films.

Proposed Work for FY 2013

Proposed tasks for FY 2013 include the following:

- Continue to experiment with the growth conditions for the piezoelectric materials and multilayered stacks in order to improve their quality,
- Explore a variety of fabrication processes for achieving active nanostructures, and
- Proceed toward identification of scaling methods to allow large-scale integration of the active nanostructures.

Rare Earth Elements

2011-209-R1

John Hryn, Richard Brotzman, Xing Chen, Jeffrey W. Elam, Sam Jiang, Angel Yanguas-Gil, and Yuepeng Zhang

Project Description

The goal of this project is to expand the general knowledge and capabilities associated with rare earth elements (REEs), which have recently been the focus of increased interest by DOE and other agencies. Prompting this interest is the use of REEs in many applications that contribute to increased energy efficiency and environmental benefits and an anticipated near-term shortage. REEs are used in high-energy-product (BH) magnets (B is flux density and H is magnetic field strength) for automotive light-weighting and wind power turbine applications, in phosphors for lighting applications (particularly light-emitting diodes [LEDs]), and in other energy-related applications. This effort will allow us to combine capabilities in (1) magnet theory, nanomagnet synthesis, and nanomaterial processing to begin developing processes for synthesizing the soft magnetic phase of exchange spring BH magnets; and (2) rare earth chemistry and atomic layer deposition to develop highly energy-efficient phosphors for increased luminescence.

Mission Relevance

This project relates to DOE's energy security mission by enabling lightweight materials for automobiles and wind turbines. Current magnets for these applications depend on REEs such as neodymium (Nd) and dysprosium (Dy), supplies of which are decreasing. The proposed alternatives (samarium [Sm]-cobalt [Co] exchange magnets) are more energy efficient and readily available. Phosphors developed in this project would also improve energy efficiency in LED applications.

FY 2012 Results and Accomplishments

Research prior to FY 2012 focused on the development of colloidal methods to synthesize soft magnetic materials. Colloidal methods could not make iron (Fe)- or iron oxide (FeCo)-based nanomaterials with an aspect ratio greater than 1. However, a new electrospinning method was identified that was potentially capable of synthesizing high-aspect-ratio soft magnets.

In FY 2012, the project teams focused on the following two specific projects.

A. Magnets

We fabricated an integrated device that controls the atmosphere for electrospinning and heat treatment to enable fiber spinning and sample transfer between the electro-spinning device and heat-treatment furnace. High-speed rolling collects and aligns fibers and reduces fiber diameter by applying uniaxial tension. Electrospinning produces high-aspect-ratio nanofibers comprising a polymer (polyvinylpyrrolidone [PVP]) and metal salts [$Fe(NO_3)_3$ and $Co(NO_3)_2$].

As-spun fibers typically have a diameter >100 nm; final metal nanofibers/nanorods must be <10 nm for exchange-spring coupling, which implies that the diameter of as-spun nanofibers must be <30 nm; thermal oxidation and reduction processes reduce fiber diameters by 50–70%. Preliminary experiments indicate that solution viscosity has the greatest impact on as-spun fiber size. We used two thermal-treatment processes to produce metal nanofibers. Figure 1 shows Fe fibers after thermal reduction.

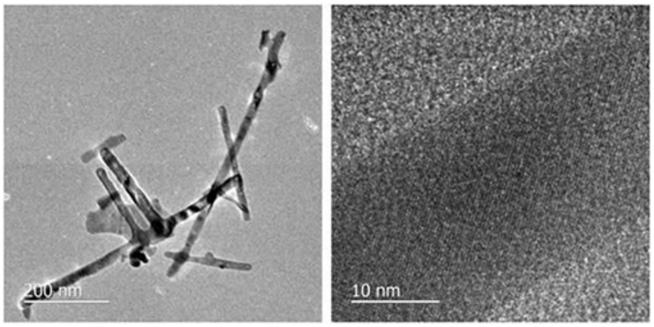

Figure 1. Transmission electron microscopy image of 20-nm Fe metal nanofibers. The nanofiber morphology enables magnetic shape anisotropy.

In FY 2013, we will receive funding from the Advanced Research Projects Agency – Energy (ARPA-E) to continue development of the core-shell approach to manufacturing the magnets.

B. Phosphors

We demonstrated control of dopant distribution for rare earth (RE)-doped materials through atomic layer deposition (ALD), controlling the saturation coverage of RE both in single oxides and as dopants in three different hosts. Our methodology uses ternary inhibitor/RE/O-source ALD cycles to tailor surface reactivity toward the RE precursor through functionalization with inhibitor moieties. We reduced dopant monolayer coverage by 70% with respect to the conventional ALD process for Er^{3+}:TiO_2, and conducted similar studies for Er:Al_2O_3 and Eu:Y_2O_3.

Working with collaborators at the Advanced Photon Source, we conducted x-ray photoelectron spectroscopy analysis of Eu:Y_2O_3 films to determine the presence of impurities, which produced results consistent with those for low-carbon oxide films. X-ray absorption studies of the Er edge of Er:Al_2O_3 samples produced results consistent with an absence of Er–Er clustering, showing efficient distribution of dopants in the host even in the absence of an inhibitor.

We synthesized Eu:Y_2O_3 phosphors with ALD on nanostructured scaffolds. Starting from nanoparticle substrates of both Al_2O_3 and Y_2O_3 (20–40 nm), we fabricated tens-of-micrometers-thick phosphor films without substantially increasing processing time with respect to the flat case (>100-fold reduction in processing time for an equivalent thickness). The typical process involved drop-casting nanoparticles in 1.5-cm-diameter disks that are subsequently coated by using ALD. Cross-sectional energy-dispersive analysis x-ray spectroscopy (EDAX) of Eu:Y_2O_3-coated Al_2O_3 substrates confirmed the complete infiltration of the substrates (Figure 2).

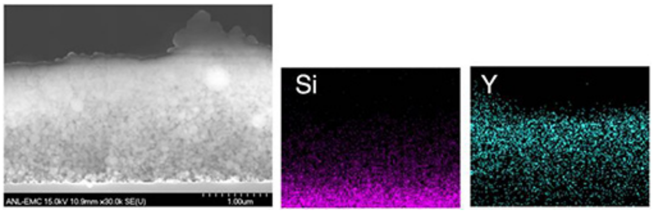

Figure 2. Cross-sectional EDAX of (a) Eu:Y_2O_3 phosphor film on Al_2O_3 nanoporous scaffold, (b) Si (substrate) and (c) Y concentration mapping.

Initial experiments on the growth of core Y_2O_3 shell Eu^{3+}:Y_2O_3 materials produced a total substrate area of 1.5–9.0 cm^2 and phosphor film thickness of tens of micrometers. The films present good mechanical properties as a consequence of the homogeneous coating of the Y_2O_3 cores, without any substantial increase in processing times.

Proposed Work for FY 2013

A. Phosphors

- *Preparation and characterization of RE-doped thin films with controlled dopant distribution using ALD:* We will focus on the action of betadiketonates as inhibitors to further control dopant distribution; efforts to date have involved mainly alkyl alcohols. We will prepare a systematic set of samples of Eu:Y_2O_3 with different cycle ratios by using acetylacetone as an inhibitor.
- *Preparation and characterization of core-shell nanoparticles and high-surface-area phosphors using ALD:* We will conduct photoluminesence measurements of Eu:Y_2O_3 films prepared on Al_2O_3 and Y_2O_3 scaffolds by using different inhibitors and ALD cycle ratios. These results will help us refine our novel methodology for low-temperature phosphor synthesis. In addition, we will determine the mobility of the dopants in the Y_2O_3 host. Studying the luminescence of the films as a function of the annealing temperature, we will characterize the mobility of the RE dopants on the Y_2O_3.
- *Scaleup of the fabrication process:* Depending on the success of the above task, we will scale up the synthesis processes for the case of Eu:Y_2O_3. Using the large bench reactor, we will scale the growth of core Y_2O_3 and shell Eu^{3+}:Y_2O_3 materials with a substrate area of 1.5–9.0 cm^2 and phosphor film thickness of tens of micrometers to a total substrate area of 200 cm^2.

B. Recycling

Nd-Fe-B magnets in spent hard drives are not generally recovered. We propose a novel recycling and recovery (R&R) strategy for RE-containing materials that takes advantage of the inherent chemical and electromagnetic properties of REEs. RE metals (most lanthanides) absorb large amounts of hydrogen to form RE hydrides. Hydride formation results in a large lattice expansion that fractures the RE metal — ultimately forming particulates. This process is termed hydrogen decrepitation and causes the RE magnets to disintegrate. Our R&R strategy focuses on hydrogenation to break apart the magnets to form particulates, followed by magnetic separation of the RE particulates, and recovery of the hydrogen and the pure REEs by means of thermal dehydrogenation and chemical extraction, respectively.

Polyelectrolyte Brushes in Multivalent Ionic Media

2011-217-R1

Matthew Tirrell

Project Description

The purpose of this project is to characterize the new structures formed and the new properties observed when polyelectrolyte chains are placed in media with oppositely charged multivalent ions. Polyelectrolytes in monovalent ionic media have repulsive interactions, exclusively; the range of these interactions can be tuned by using salt. Multivalent ions induce attractive forces through a set of effects related to the spatial disposition of ions relative to the polymer chains. During this project, we will conduct a quantitative experimental characterization and exploitation of these effects.

Mission Relevance

The project is tied to DOE's missions in energy and science. Polyelectrolyte applications are continuing to emerge and expand in novel materials, driven in part by a growing demand for polymeric materials that respond to environmental changes. Current efforts in multilayer formation and behavior, chemical gating, and drug delivery all exploit polyelectrolytes that respond to external stimuli, ranging from electrical and mechanical stimulation to environmental changes in pH and salt concentration. This increased interest necessitates a deeper fundamental understanding of the structure and properties of these complex materials. Although polyelectrolytes have been well studied in environments consisting exclusively of mono-valent ions, much less attention has been given to their behavior in the presence of multi-valent ions — despite the importance of multi-valent ions in many potential products and processes, such as energy storage, environmental technologies, and hybrid systems in synthetic biology. This work will provide one pillar of a new foundation for soft materials science that will contribute to future efforts in developing materials for energy and synthesis science. The work offers new opportunities in meso-scale science aimed at molecular engineering of polyelectrolyte-based materials.

FY 2012 Results and Accomplishments

This project began quite late in FY 2011. The time that year was devoted to preparing for FY 2012 work as a departure from earlier work [“Phase Behavior and Coacervation of Aqueous Poly(acrylic acid)-Poly(allylamine) Solutions,” R. Chollakup, W. Smitthipong, C.D. Eisenbach, and M. Tirrell, *Macromolecules*, **43**:2518–2528 (2010).] on a different synthetic system. In that work, we demonstrated that either fluid or solid complexes could be formed between oppositely charged polymers, and we delineated the boundaries between the two. Since we wanted to focus on the fluid complex formation (coacervation), we began investigating a system where such behavior was more common, which led us to the study of polypeptide systems under this LDRD project.

We examined the interactions between a series of oppositely charged polypeptide pairs by using isothermal titration calorimetry (ITC) in combination with turbidity measurements and optical microscopy. Polypeptide complex coacervation was modeled as a sequence of two distinct binding steps by using an empirical extension of a simple ITC binding model. Complex coacervation in all probed systems was found to be endothermic — essentially, an entropy-driven process. Increasing the screening effect of the salt on the polyelectrolyte charges diminishes their propensity to interact, leading to a decrease in the observed energy change and coacervate quantity. The pH plays an important role in complex formation because it affects the degree of ionization of the functional groups. Plotting the change in enthalpy with temperature allowed us to calculate the heat capacity change (ΔCp) for the interactions. The ITC revealed that complex coacervation is promoted when higher total polymer concentrations or polypeptide chain lengths are used.

Mixing oppositely charged polyelectrolytes in aqueous solutions may result in the formation of polyelectrolyte complexes (PEC). In this portion of the study, we investigated phase separation and complex coacervation of polypeptides. We prepared phase diagrams as a function of polybase content and salt concentration by using the critical salt concentrations required to extend the coacervate to the solution boundary. In addition, we examined the effect of molecular weight on the complex formation for the P(L-Lysine) (PLys)/P(l-glutamic acid) (PGlu) system and prepared a phase diagram. By determining the water content of the coacervate phase under various conditions, we found that the salt content and stoichiometry of the mixed polyelectrolytes have a significant effect on the coacervate composition.

We performed a systematic study of the interfacial energy (gamma) of polypeptide complex coacervates in aqueous solution by using a surface forces apparatus. Poly(L-lysine hydrochloride) (PLys) and poly(L-glutamic acid sodium salt) (PGA) were investigated as a model pair of oppositely charged weak polyelectrolytes. Two phases in equilibrium evolved: a dense polymer-rich coacervate phase and a dilute polymer-deficient aqueous phase. Capillary adhesion, associated with a coacervate meniscus bridge between two mica surfaces, was measured upon separation of the two surfaces. This adhesion enabled us to determine the gamma at the aqueous/coacervate phase interface. The gamma of these polypeptide coacervates was separately found to decrease with both increasing salt concentration and decreasing polypeptide chain length. In most cases, gamma measurements were found to be very low, <1 mJ/m^2. Biocompatible complex coacervates with low gamma have a strong potential for applications in surface coatings, adhesives, and the encapsulation of a wide range of materials.

Proposed Work for FY 2013

During the next fiscal year, we will focus on new, self-assembled structure and properties obtainable via polyelectrolyte complexation. In particular, we will study micelle and ordered phase formation in block copolymers where one block is a neutral polymer chain, such as polyethylene glycol, and the other block is either an anionic or cationic polypeptide. Our overall aim is to relate the phase behavior we discovered in homopolypeptide systems to self-assembly in block copolymer systems. We believe that these self-assembled systems will produce interesting new soft materials with self-healing properties and tunable elastic moduli. We have begun to develop the synthetic chemistry, based on anionic polymerization, to produce this new class of materials.

Membrane-Bound, Broad-Spectrum, Photo-Driven Protein Devices

2012-204-N0

Stephan Rosenkranz and Suzanne G.E. te Velthuis

Project Description

This project involves building a broad-spectrum bio-battery by using several membrane-bound, photo-driven proteins and peptides. Because a homogenous membrane cannot satisfy the lipid environment required by all of these proteins and peptides, we propose to use topographically controlled substrates to drive phase separation of lipids into distinct membrane domains. The topology control will not only create distinct environments, but it will also be a means of controlling where these proteins and peptides are localized in a single membrane.

We are studying how lipid mixtures respond to the imposition of topographical, microfabricated, patterned supports. The resulting patterned membranes will then be used to fabricate bio-inspired materials (light-harvesting devices for efficient generation of electricity) that utilize proteins (photo-driven proteins). The first objective is to investigate the dynamics and organization of model multi-lipid membranes on well-defined, microfabricated surfaces by imposing specific curvature patterns on the substrates. This work will allow us to develop the biophysical mechanism by which lipid membranes organize. It will also allow us to develop two-dimensional fluid platforms with well-defined spatial variation in dynamics and composition. The second objective is to incorporate photo-driven proteins into the heterogeneous lipid environment. The final objective is to optimize the optical properties of the device. Therefore, the proposed research involves the following tasks:

1. Fabricate silicon and quartz substrates with different topographical features and forming a lipid membrane over the substrate,
2. Introduce both natural and synthetic proteins into the system and show that they conform to the patterned lipid environment, and
3. Tune the optical properties of the lipid-protein composition/chemistry to enhance the photon absorption efficiencies.

Mission Relevance

DOE Basic Energy Sciences (DOE-BES) is very interested in research on the use of bio-molecular materials for energy because such research is one of the core activities in the Division of Materials Sciences and Engineering, which explores the use of molecules, methods, and concepts of biology to create novel materials and processes with significance for energy generation.

FY 2012 Accomplishments and Results

During FY 2012, we achieved the following milestones:

1. Characterization of lipid monolayers at the air-water interface by using the spin-echo resolved grazing incidence scattering (SERGIS) technique.

   SERGIS is a novel technique in which a polarized neutron beam is scattered at grazing incidence from the surface of a film, allowing characterization of in-plane structures. The technique relies on using changes in the polarization of the neutron beam to detect small changes in scattering angle. Experiments were performed using the OFFSPEC beamline at the ISIS pulsed neutron and muon source, Rutherford Appleton Laboratory, United Kingdom.

   One way of depositing a lipid film on a substrate is to conduct a series of Langmuir Blodgett/Langmuir Schaefer depositions. The transfer may disrupt large-scale features; thus, it was important to determine whether order exists at a smaller scale and whether it would persist in the transfer to a substrate. Although modeling showed that the experiment was feasible, instrument, as well as sample environment, complications resulted in unreliable results. We have allocated beam time at ISIS to repeat these experiments. Figure 1A shows a lipid monolayer at the air-water interface composed of a mixture of dipalmitoylphosphatidylcholine (DPPC) and dimyristoylphosphatidylcholine (DLPC). These domains are micrometers in size and are severely disrupted when transferred into a substrate in the range of 10–30°C.

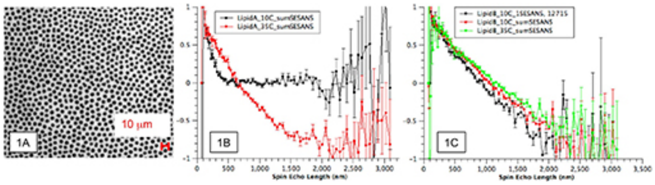

Figure 1. (1A) A monolayer of DPPC and DLPC at a 1:1 molar ratio at the air-water interface for T=10°C. Image from Professor Perez-Salas Lab at UIC (unpublished). (1B) Polarization as a function of spin echo length for lipid stacks of mixtures of DPPC and DLPC at a 1:1: molar ratio on a hydrophilic surface (lipid A) and (1C) on a hydrophobic surface (lipid B).

2. Characterization of lipid multilayers on hydrophilic and hydrophobic surfaces by using the SERGIS technique.

   By using a spin-casting technique, we made about 50 stacks of lipid layers on hydrophobic, as well as hydrophilic, surfaces. The SERGIS technique showed no feature change as a function of temperature at 100% relative humidity for the films on hydrophobic substrates. On the other hand, on a hydrophilic surface, there were clear changes in domain size as a function of temperature, with clear reversible behavior (see Figures 1B and 1C). The signal itself was also affected by an instrumental artifact, making quantitative analysis challenging. Specifically, the neutron beam polarization was modified due to a small magnetic field in the instrument, which was not completely compensated for during tuning of the instrument before the measurement. Further measurements are planned for FY 2013.

3. Characterization of block-copolymer nanopatterned films by using small-angle neutron scattering (SANS).

   It is possible to form nanometer-size domains of regularly spaced patches of polymethylmethacrylate (PMMA) and polystyrene (PS) block-copolymers by using very thin films. Their size and arrangement depends on the amount of time the films are exposed to acetone. SANS was used to detect the size and order of the PS-PMMA patches as a function of acetone treatment and the molecular weight of the polymers. The domains were much larger than what could be measured by using SANS. However, an indication of their existence was clear: the intensity curve started to rise at very low angles for the largest molecular weight. We did not detect a change in domain size as a function of acetone treatment. This finding was surprising, because the domains were expected to grow and rearrange with exposure time to acetone vapor. As an extension of that work, we tried controlling the PS-PMMA domain or patch size by reducing the molecular weight of the polymers; however, we did not get enough SANS signal because these lower-molecular-weight polymer films were much thinner (i.e., the lower the molecular weight, the thinner the film). We obtained a SANS signal only for the largest-molecular-weight polymer. We will pursue using SERGIS to study these very thin films because we found that the technique was able to detect domains in similarly thin films of lipids.

Proposed Work for FY 2013

During FY 2013, we will focus on (1) characterizing and understanding the film (wetting/dewetting) and phase behavior of mixed lipid membrane stacks on hydrophilic and hydrophobic surfaces, (2) characterizing and controlling the patch size of nanopatterns made from PMMA-PS copolymer thin films, and (3) tuning the optical properties of the lipid-protein composition/chemistry to enhance photon absorption efficiencies.

20-kV/10-A 4H-SiC Vertical Trench Field-Controlled Thyristor (VTFCT)

2012-208-N0

Krishna Shenai and John Hryn

Project Description

Silicon (Si) has been demonstrated to limit the performance and reliability of power MOSFET (metal oxide semiconductor field-effect transistor) switching and amplifier technologies. Wide bandgap (WBG) materials, such as silicon carbide (SiC) and gallium nitride (GaN), are being investigated to replace Si for high-power electronic switching and amplifier applications. WBG semiconductors are preferred for high-power, high-temperature electronics because their electrical and thermal characteristics are superior to those of Si. Their widespread application has been hindered, however, as a result of a high density of crystal defects. The project goal is to show that WBG material inadequacies can be overcome with proper design and fabrication techniques, laying the foundation for WBG implementation. The project scope is to:

- Model and characterize power semiconductor materials for a 20-kV/10-A SiC VTFCT;
- Conduct research to advance crystal growth technologies for WBG semiconductors;
- Demonstrate device-quality gate dielectric material for SiC; and
- Test 20-kV/10-A SiC VTFCT for high-voltage transportation and grid applications for performance and reliability, conduct system testing, and establish specifications for the power switching device.

Mission Relevance

The project is tied to DOE's mission in energy security. The proposed 20-kV/10-A gate-controlled SiC thyristor would have a transformational impact on next-generation power semiconductor materials and devices and on power electronics systems. It would enable this technology to be integrated into the conventional alternating-current electrical grid, as well as the direct-current micro-grids. Specific technologies affected would be next-generation hybrid and all-electric transportation systems and standalone electrical power sources. This new research area would thrive on advanced power semiconductor devices and power electronics converters, and it would integrate sensor networks and wireless technology. DOE considers WBG semiconductor materials a "keystone" technology in the following areas: switches, nonlaser diodes, laser diodes, solar cells, converters, communications, and light-emitting diodes (LEDs).

FY 2012 Results and Accomplishments

The project began with less than two months remaining in FY 2012. The two major accomplishments were setting up the test laboratory and identifying specific technology barriers and the needs of the device to be developed in this project. The laboratory set up included a micromanipulator and testing/modeling computers in preparation for our FY 2013 work.

Proposed Work for FY 2013

Two tasks are planned. In Task 1, we will model and characterize power semiconductor materials for a 20-kV/10-A SiC VTFCT. An experimental test and modeling infrastructure will perform real-time, high-speed computations on a 20-kV/10-A SiC VTFCT. Computer-aided design tools will include (1) Silvaco tools for power semiconductor process and device simulation, (2) power semiconductor material synthesis and microstructure analysis tools from ESI–North America, (3) power converter design and analysis tools from Synopsis and Cadence Design Systems, and (4) radio frequency (rf) power amplifier design and analysis tools from Agilent Technologies. WBG semiconductors and devices will be characterized by using a current-voltage and capacitance-voltage measurement system that can perform:

- Detailed wafer-level and package characterization up to 30 kV and 1 kA;
- Specialized application-level accelerated stress testing, including single electron burn-out (SEB);
- dV/dt (change in voltage/change in time) and avalanche testing;
- Temperature profiling of actively biased semiconductor chips; and
- Wafer-level defect mapping by using ultra photoluminescence spectroscopy (UPLS).

The test/measurement infrastructure will take rf power device and amplifier measurements up to 18 GHz. The Naval Research Lab is currently growing 2-in., defect-free bulk and epitaxial SiC and will supply material for device fabrication and testing. We will develop designs for rugged, high-power switching and amplification devices.

In Task 2, we will conduct research to advance crystal growth technologies for WBG semiconductors (i.e., the bulk and epitaxial growth of SiC and GaN power semiconductor materials). We will evaluate three crystal growth techniques: chemical vapor deposition (CVD), solution growth, and hydrothermal growth at NRL. Key objectives are to:

- Reduce the crystal defects by two orders of magnitude in bulk and epitaxial materials;
- Increase the growth rate by a factor of two; and
- Demonstrate device-quality, thick (>100 micrometers) homo-epitaxial films that can be used to fabricate a >20-kV class of power devices.

Growth parameters will be optimized by using computational fluid dynamics (CFD) ACE, thin film microstructure will be studied by using CFD-TOPO software, and wafer-level defect mapping will be performed by using UPLS with potassium hydroxide (KOH) etching. Material characterization will include Raman spectroscopy and x-ray diffraction based on synchrotron radiation. Switch device architectures and process simulation will be developed, and materials produced at NRL will be characterized.

Atomistically Informed Mesoscale Modeling for Advanced Electrical Energy Storage Systems

2012-209-N0

Larry Curtiss, Olle Heinonen, Dmitry Karpeev, and Dieter Wolf

Project Description

The currently used Li-ion battery technology is based on oxidation or reduction of Li that involves intercalation of Li into a solid electrode without changing the electrode matrix structure. Because of inherent limitations in the potential energy and power densities of Li-ion technologies, there is much interest in finding systems that go beyond them. Among these are systems based on the reversible formation and destruction of chemical bonds at an electrode surface (sometimes called a "precipitation-dissolution reaction"), resulting in the formation of crystalline, nanocrystalline, or even amorphous or polymeric reaction products. A major challenge in developing these systems is being able to understand and predict the processes involved in electrochemical growth and the formation of the oxide or sulfide reaction products.

This project focuses on developing a mesoscale approach for modeling electrochemical crystal growth and dissolution at an electrode upon electrochemical cycling. Based on the application of phase-field theory and informed by separate atomic- and electronic-level simulations, this mesoscale approach will begin to capture at least some of the reversible microstructural processes that occur during discharging and charging at the cathode of, for example, Li-air batteries that will help to enable these new battery systems.

Mission Relevance

This project is relevant to DOE's missions in energy and science. This theoretical and computational project addresses key challenges associated with bridging scales in hierarchically structured materials and with developing Li-air batteries. It is relevant to DOE's mission to develop advanced electrical energy systems that can help the nation attain energy independence through alternative energy sources. It also addresses DOE's interest in developing new advanced computational methods for simulating at the mesoscale. The underlying mechanisms seen in the simulations will help researchers interpret and understand existing microstructure-level experimental observations and likely help them predict novel (not yet observed) phenomena. The new modeling approaches can be used not only to advance beyond Li-ion technologies but also to significantly improve the energy density and cycle life of current Li-ion technologies important to DOE.

FY 2012 Results and Accomplishments

The project began in August 2012 with the development of the pair potentials needed to simulate the lithium oxides that are formed during the operation of the Li-air battery. Mesoscale modeling of the electrochemical processes involved during charge and discharge of the Li-air battery require input from molecular dynamics simulations of lithium oxides. We assessed various types of potentials for use in modeling and found that it will require inclusion of many body effects because of the covalent nature of the bonding present in the Li_2O and Li_2O_2 oxides and the different types of bonding arrangements.

Proposed Work for FY 2013

Our objective is to determine numerous parameters in the governing phase field equations in mesoscale modeling from either atomistic- or electronic-structure calculations. We will accomplish this objective by conducting molecular-dynamics simulations for Li_2O_2 surfaces and nanostructures based on realistic interatomic potentials. For predominantly ionic oxides, such potentials typically have the Buckingham form coupled with a shell model that incorporates the polarizability of the oxygen ion cores and any charge transfer associated with covalency, resulting in nonintegral ion charges. We will use the potentials that are developed to determine the energies, structures, and point-defect properties of free surfaces; from this information, a Wulff construction can be performed to predict the nanoparticle shape as a function of their size. In all the surface calculations, we will focus on the electrostatics of charged and dipolar surfaces. The comparison with the energies and structures obtained directly from the electronic structure calculations will provide an important test of the validity of the underlying interatomic potentials.

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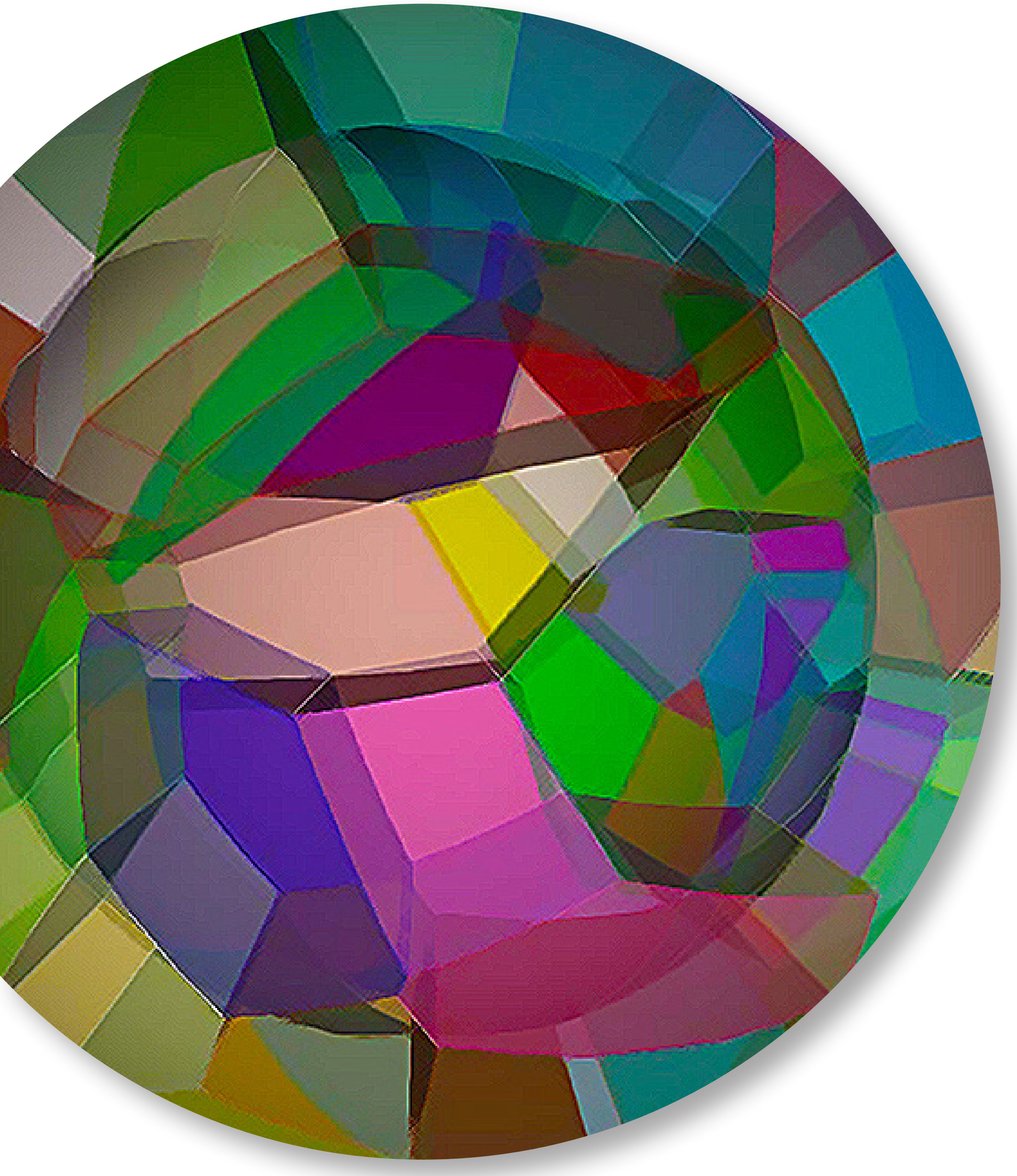
NATIONAL SECURITY



Molecular Characterization of Spore Coat Proteins

2010-093-R2

Daniel Schabacker and Paul Raptis

Project Description

There is a critical need for methodologies that generate a detailed signature of a biothreat agent (BTA). Genetic analysis alone cannot provide a full description of a BTA; information on how the material was prepared, by whom, and the resources available to the operator cannot be obtained by genetic means. Obtaining useful information of this type will require novel methods that provide a signature of the BTA that is highly sensitive and detailed enough for attribution. In some scenarios, the signature must be sufficiently reliable to withstand legal challenges in court. The proteome, which is the set of expressed proteins in a given type of cell or an organism, is the most appropriate source of molecular signatures. The goal of this project is to develop a novel forensic methodology specific to BTA attribution, through proteomic signatures, that will provide detailed information regarding the methods used to culture, purify, and store the BTA. This information can help identify not only the specific organism used, but also the facilities used in its preparation and the technical sophistication of the operator. *Bacillus anthracis* spores, which cause anthrax, are the model organism for this research.

Mission Relevance

This project supports the national security mission of DOE to reduce the global danger from weapons of mass destruction by enhancing the capability to attribute a BTA to individuals or organizations. This approach is an innovative improvement on previous spore analytic methods because of its molecular separation and protein chip fabrication technologies and the manner in which they are integrated into a single system. The methodology is particularly well suited for security missions because it combines sensitivity with a highly robust, semi-automated platform that does not require a specialized laboratory or expensive mass spectral analysis. This project is also relevant to the Defense Intelligence Agency (DIA) and the Science and Technology (S&T) program of the Department of Homeland Security (DHS).

FY 2012 Results and Accomplishments

The initial year of this research focused on developing the methods required for generating robust proteomic signatures. The signatures must be reproducible because they will be the basis of a signature library used for competitive analyses. To this end, we worked with Dr. Adam Driks, an expert in *B. anthracis* at Loyola University Medical Center, in developing a standard operating procedure for spore purification and protein extraction. It became clear during this process the resolution provided by our system is able to discern even slight variations in sample preparation. Initial signatures of *B. anthracis* cultured in liquid or solid media provided ample evidence that our methods were sound. To further elucidate differences in the proteins expressed, going beyond solely protein expression, biochips were used to characterize the expressed proteins. For example, sugar-binding lectins were used to generate interactive signatures that identify variations in glycosylation of the proteins, providing additional signatures supporting attribution.

The second year of this research focused on refining the methods required for generating reproducible proteomic signatures. Because of the high sensitivity and resolving power of our system, we determined that slight variations in the proteomic signature will be present even in identical spore preparations of *B. anthracis*. This variation has not been characterized or even identified in current lower-sensitivity/lower-resolution proteomic tools. We characterized this inherent variation to better understand our processes and to remove this non-informative signature variation from our analysis. We also expanded our analysis to non-sporulating bacteria, such as *E. coli*. Initial analysis of *E. coli* preparations resulted in extremely similar (practically identical) signatures between replicates. Comparing *E. coli* proteome signatures from two growth media proved that our technological approach can provide extremely reproducible data while differentiating growth conditions.

In FY 2012, the project focused on generating *B. anthracis* spore proteome signatures under two growth conditions to confirm that we are able to differentiate between growth conditions. We continued characterizing the inherent variation in *B. anthracis* spore preparations to remove non-informative signature variations from our analysis. Identification of proteins within discriminating fractions was accomplished. Additionally, the process of creating software and algorithms for automated comparative analysis was undertaken, resulting in a custom program for compilation of varying datasets, automated generation of dendrograms for determining nearest neighbors, statistical analysis by using quantile normalization, and principal-component analysis. By using this new software, two unknown samples were correctly attributed to the growth media used for their preparation.

This work resulted in the following invention/patent:

- Schabacker, D. and A. Driks, “High Resolution Characterization of Biological Matrices,” invention report submitted October 2010, and Patent Application No. 61/466,396 filed March 2011. [ANL-IN-10-082].

Seminars

Pravecek, T., D. Schabacker and A. Driks (2010). “Microbial Forensics and Signatures.” Air Mobility Command, Scott Air Force Base, IL, February 4, 2010.

Schabacker, D. (2012). “Forensic Proteomics.” Interagency Microbial Forensics Advisory Board (IMFAB) led by the White House Office of Science and Technology Policy (OSTP) and FBI. FBI Operational Response Center, Fredericksburg, VA, June 27, 2012.

Schabacker, D. (2012). “Forensic Proteomics.” Defense Intelligence Analysis Center (DIAC), Joint Base Anacostia-Bolling, Washington DC., January 19, 2012.

Schabacker, D. (2012).”Microbial Forensics – Beyond DNA.” Defense Threat Reduction Agency (DTRA) HQ, Fort Belvoir, VA, November 9, 2011.

Schabacker, D. and T. Pravecek (2010). “Characterizing Biological Matrices Through Proteomic Signatures.” Air Force Research Laboratory, Dayton, OH, May 13, 2010.

Schabacker, D. (2010). “An Ultrahigh Resolution Method for Identification and Attribution in Microbial Forensics.” Private Meeting, Quantico, VA, October 15, 2009.

Schabacker, D. (2010). “Method for Characterizing Protein Signatures in Food Technology.” National Center For Food Safety and Technology, Summit-Argo, IL, November 6, 2009.

Data Encryption and Compression for Cybersecurity Applications

2011-027-R1

Alexander Heifetz and Paul Raptis

Project Description

Compressive Sensing (CS) is a recently introduced algorithmic paradigm for performing numerical optimization computations. Our study constitutes a non-traditional application of CS to the problem of data encryption and compression. The objective is to evaluate the feasibility of applying a CS approach to encryption and compression of nuclear spectral data collected during wide area screening. In our study, the data bank will consist of a large number of one-second nuclear background spectra measured with a sodium iodide (NaI) scintillation detector-spectrometer in air. Using the L1-Magic software package to implement the CS protocol, we hope to demonstrate secure and robust encryption/decryption of nuclear spectral data.

Mission Relevance

This project is relevant to DOE’s mission in national security. It responds to national security exploratory research in radiation sensing. New challenges in radiation sensing involve the compression and encryption of large volumes of nuclear spectral data collected in wide area screenings or searches for a missing source. We plan to develop compressive sensing (CS) algorithms that perform simultaneous compression and encryption of data for high speed and secure transmission.

FY 2012 Results and Accomplishments

The NaI nuclear detector is most frequently used in wide area screening and search for missing source applications because of its fast response and relatively low cost. A modern NaI detector measures gamma radiation in the energy range of 0–3 MeV by using 1,024 spectral channels. Thus, the measurement to be encrypted is a vector with 1,024 elements, all of which are integers. Gamma-ray spectra measured in air always contain background counts because of the ubiquitous presence of radioactive isotope ^{40}K and the daughter products of the natural decay series of ^{238}U, ^{232}Th, and ^{235}U primordial isotopes on earth. Measurements made with the NaI detector in air consist of one-second samplings of the nuclear background. Because of the low signal-to-noise ratio, one-second background spectra measurement vectors do not display distinct isotopic spectral lines. An example of a typical one-second background spectrum measurement vector is shown in Figure 1.

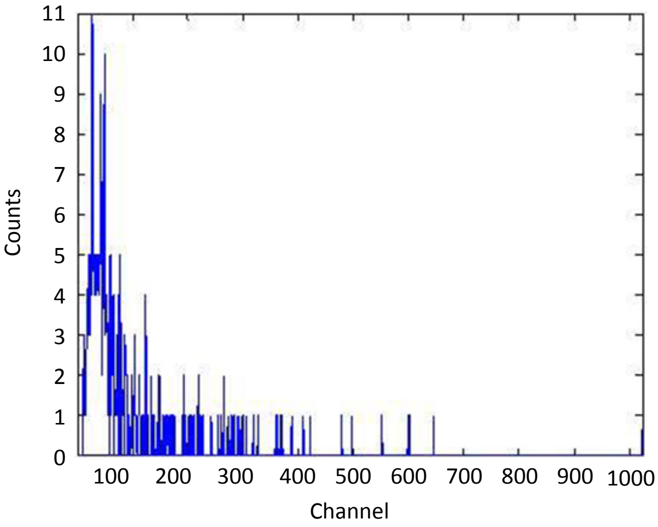


Figure 1. One-second background spectrum measurement vector of 1024 channels.

To demonstrate the isotopic structure of an urban nuclear background, Figure 2 displays the background spectrum integrated over 1,026 seconds. The spectrum in Figure 2 shows recognizable isotopic lines of ^{40}K, ^{232}Th, and daughter products of ^{235}U/ ^{238}U.

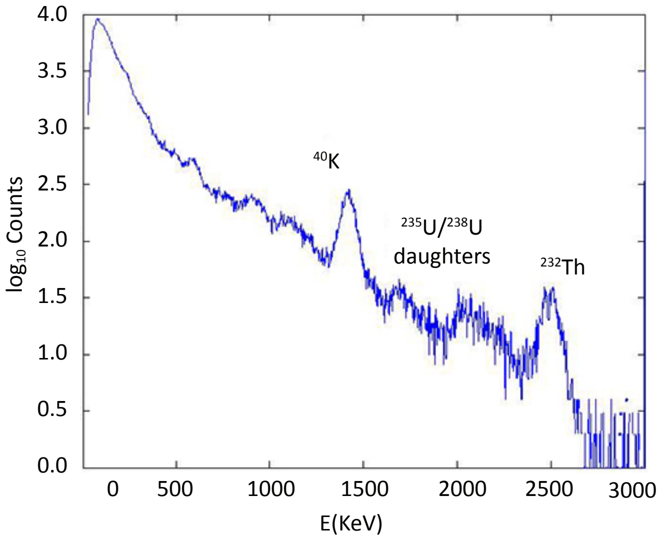


Figure 2. Integrated log-linear plot of counts vs. energy of the background spectrum. The space of 1,024 channels is linearly mapped to the energy space of 0–3,000 keV.

The objective of this project is to demonstrate that one-second spectra continuously acquired with a NaI detector can be compressed and securely encrypted with CS for transmission over an unprotected low-bandwidth channel. The projection matrix generated by CS for encrypting and compressing the signal serves as the encryption key, which is known ahead of time to both sender and receiver. Although an eavesdropper can potentially intercept the signal, without the knowledge of the encryption key, the eavesdropper is unable to read the encrypted message. Under the CS protocol, the receiver should be able to reconstruct the signal with minimal loss of the original information. One metric of reconstruction fidelity is that the spectral lines in Figure 2 are well preserved in the reconstructed signal.

To evaluate CS capability in encryption and compression of nuclear spectral data, we conducted a series of numerical experiments by using the L1-Magic software package implementation of the CS method. First, we demonstrated essentially lossless reconstruction of the encrypted/compressed signal of Figure 1. The calculated difference between the original and reconstructed signal was observed to be negligible, and algorithm run-time was less than one second. To investigate the encryption strength of CS, we simulated a scenario in which an eavesdropper intercepts the encrypted signal of data shown in Figure 1. In this hypothetical scenario, the eavesdropper does not have the encryption key, so he or she attempts to perform a blind reconstruction of the intercepted signal by guessing the CS matrix. Our numerical experiments have shown that the eavesdropper's reconstructed signal has no resemblance to the original signal. Therefore, we confirmed that CS should be secure against a brute-force attack.

To investigate the limits for data compression and reconstruction reliability with CS, we tested the stability of the reconstruction for different compression ratios. Numerical experiments showed that there is a fairly sharp transition from the region where reconstruction fails to converge to the region where reconstruction converges. The transition occurs at approximately 40% sampling rate of the original signal. In addition, several sporadic instabilities occur after the transition threshold to the region of convergence is crossed. Limits of compression with CS, transitions from large to small errors, and numerical instabilities are not well understood in CS theory and should be the subject of future investigations.

To be useful in a practical scenario, the CS method should be capable of repeatedly generating different encryption keys (projection matrices), all of which result in stable reconstruction of the encoded message. To test the stability of the reconstruction, we conducted a set of 500 repeated trials in which different projection matrices (all giving a 50% compression ratio) were generated to perform CS coding and decoding of the original signal in Figure 1. We observed that signal reconstruction converges in each trial.

Finally, we simulated a target scenario in which a sequence of 600 one-second nuclear spectra is encoded by the sender and then decoded by the receiver. The same projection matrix/encryption key was used for encryption of all 600 one-second spectra. Although the majority of reconstructions converge, a few reconstructions fail. Understanding the reasons for convergence failure requires further investigation. The integrated reconstructed spectrum of the 600 one-second spectra is very similar to the integrated background spectrum displayed in Figure 2. The spectral peaks that correspond to the isotopic lines of ^{40}K and ^{232}Th and the daughter products of ^{235}U/ ^{238}U are clearly visible. In search for a nuclear source or wide area screening applications, processing of nuclear spectra is usually automated by using radioisotope identification (RIID) algorithms. One way of validating a CS approach to encryption/compression of nuclear data is to compare the performance of an RIID on the original and reconstructed spectra.

Proposed Work for FY 2013

During FY 2013, we will investigate CS compression and encryption performance limitations and reliability. In addition, we will compare the performance of CS-based methods with existing data compression (e.g., entropy coding) and encryption (e.g., RSA Encryption). The specific issues to be addressed in this work include:

- Limits of compression with CS, sudden transitions from large to small errors in signal reconstruction, and numerical instabilities;
- Reasons for reconstruction convergence failure (either stochastic or deterministic); and
- Benchmarking of CS-based methods performance against other existing compression and encryption methods.

The results obtained during our research will enable us to develop algorithms, to analyze performance limitations, and to evaluate performance comparisons of CS-based algorithms and existing state-of-the-art methods for data encryption and compression.

Architectures and Algorithms for Protecting Sensitive Information in Mobile Wireless and Sensing Environments

2011-109-R1

Mobile Device Vulnerability Research

2011-214-R1

Charlie Cattlet and Rajesh Sankaran

Project Description

In these projects, our goal is to investigate cyber security and privacy vulnerabilities associated with mobile devices, along with the mechanisms for detection and prevention of attacks. We examine the security (and privacy) of the device and, in particular, focus on privacy with respect to the location of the device and, by extension, the location of the user. The work has involved the evaluation of existing location service architectures and the development of an experimental, privacy-preserving architecture.

Mission Relevance

These projects are relevant to DOE's national security mission. Argonne, its sister laboratories, and DOE, as well as other federal agencies, are increasingly reliant on mobile devices for mission-critical applications and services, while hosting visitors who are typically carrying at least one such device. Understanding the risks and potential protective measures is essential to our cyber security.

FY 2012 Results and Accomplishments

During FY 2012, we focused on the combined objectives of these two projects; specifically, we explored vulnerabilities associated with the use of mobile devices and particularly related to sensors, in the context of both commercial devices (smartphones, tablets) and increasingly common urban sensors that interact with people and mobile devices, such as air quality sensors or accelerometers. Accelerometers, in particular, relate to an emerging genre of mobile devices for health monitoring (such as those associated with the popular "quantified self" movement).

Building on the FY 2011 work with mobile wearable sensing devices, we demonstrated a wearable accelerometer sensor, highlighting the ease with which even simple analysis can detect activity type based on accelerometer results at 1-s intervals over 8 h (Figure 1). We evaluated communication security of the BodyMedia FIT armband, Jawbone UP, and the FitBit, finding, for example, that the FitBit device will transmit username and password in cleartext via RF (radio frequency) wireless any time it detects a FitBit base unit, using that unit's Internet connection to report device activity to the FitBit website. Such vulnerabilities may be innocuous in terms of present-day content (activity data). However, as devices become more advanced (e.g., adding GPS), the data become more sensitive, and the propensity of users to reuse passwords means that the captured fitness-device password could endanger other user accounts.

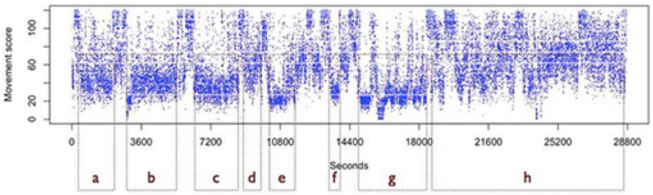


Figure 1: Wearable-accelerometer trace over 8 hours at 1-second intervals, illustrating the ease with which simple analysis can detect activity type. During intervals (a)–(g), the subject was seated during lectures; intervening intervals correspond to movement between rooms and an extended break (between [e] and [f]). Interval (h) corresponds to a reception.

Students from the Art Institute of Chicago (SAIC) collaborated on a project that used air quality (NO_2, CO, temperature, humidity) sensors, GPS, and on-board data cache in a package that could be attached to a bicycle. Several units were built and students developed tools to visualize the device (and thus user) movement and associated air quality measurements.

We have been exploring ideas combining mobile phones and 802.11 WiFi technologies toward tackling two broad challenges in indoor spaces — (privacy-preserving) navigation and ventilation efficiency. We developed techniques for privacy-preserving indoor location estimation and indoor population detection. An accurate indoor location system based on the ubiquitous 802.11 networks will provide a strong foundation for precise indoor navigation applications. Likewise, the ability to estimate the population density and distribution in a building will help facility managers in planning ventilation and temperature regulation. Additionally, an understanding of the building occupancy density will help first-responders better plan and monitor evacuation and other public safety application strategies. To these ends, we worked to develop a new technique to compress 3D volumetric building data annotated with parametric values quantifying electromagnetic properties of the building materials. The representation format was developed with the goal of being manipulated in systems with limited memory and processing power (e.g., mobile phones and PDAs). New algorithms, based on the 3D model, for calculating electromagnetic signal strength of WiFi waves propagating through the building were explored.

Several enterprise 802.11 WiFi access points modify the strength of the wireless signal they transmit based on the number of wireless users connected to them. WiFi users compete with each other for bandwidth when using the shared wireless resource. Generally, the increase in the number of users reduces the amount of data a single user can upload or download. By manipulating the strength of the wireless signal, the WiFi access points can increase or decrease the size of the space around them where users can connect wirelessly. This strategy is comparable to people changing the loudness of their voice toward modifying the space around them where others can hear. The signal strength manipulation allows the access point to control the number of connected users and extend to them the required upload and download speeds consistently. The indoor population estimation research exploits this attribute of the access points toward understanding user distribution. Through non-invasive recording of changing transmission signal strengths of the WiFi access points by using mobile phones in optimal locations in a building, the technique being developed estimates the number of wireless users in the proximity of an access point. This estimate is then further extended to the number of occupants in an area of the building.

Proposed Work for FY 2013

In FY 2013, we plan to continue to pursue privacy-preserving mobile and urban sensing architectures and applications. Additionally, we will be working to understand the privacy and security issues associated with data collection modes being used by the City of Chicago, including sensor networks and access to mobile phone location data.

Multilevel Optimization Tools for the Simulation, Detection, and Mitigation of Cyber Attacks

2011-121-R1

Sven Leyffer, Todd Munson, Scott Pinkerton, and Ilya Safro

Project Description

We are developing a set of next-generation mathematical models and computational techniques to simulate, detect, and mitigate attacks on networks of computers. The main objectives are to enable network operators to better detect attacks, quantify the attack spread, and explore the trade-offs between threat levels and operability of the system. The detection of attacks includes the enhancement and extension of existing machine learning tools in order to detect cyber threats. We are developing computationally fast intrusion-detection techniques that are robust to outliers and/or manipulation by an adversary.

In addition, we are developing techniques that allow network operators to choose a minimal set of computing resources that must be shut down to mitigate the effect of a cyber attack. Our tools allow operators to keep the operability of the network at maximum while reasonably containing the threat.

Mission Relevance

This project is relevant to DOE's national security mission. Attacks on the nation's cyber infrastructure impose an increasing cost on DOE and the nation. In the first half of 2009, for example, the Department of Defense spent more than $100 million repairing damage caused by cyber attacks.

FY 2012 Results and Accomplishments

In FY 2011, we formulated several alternative network optimization problems that are based on mathematical models of the spread of epidemics in biological networks and developed a first version of a solver for optimal response to cyber attacks, network response, and multilevel network algorithms.

In FY 2012, we developed a strategy for designing fast methods of response to cyber attacks and infection spread on complex weighted networks. In these networks, nodes can be interpreted as primitive elements of the system, and weighted edges reflect the strength of interaction among these elements. The proposed strategy belongs to the family of multiscale methods, the goal of which is to approximate the system at multiple scales of coarseness and to obtain a solution of microscopic scale by combining the information from coarse scales. In recent years, these methods have demonstrated their potential for solving optimization and analysis problems on large-scale networks. We developed an optimization problem that is based on the SIS (susceptible – infectious – susceptible) epidemiological model. The objective is to detect the network nodes that have to be immunized in order to keep the level of infection in the system low.

We introduced novel formulations for optimally responding to epidemics and cyber attacks in networks. In our models, at a given time period, network nodes (e.g., users or computing resources) are associated with probabilities of being infected, and each network edge is associated with some probability of propagating the infection. A decision-maker would like to maximize the network's utility by keeping as many nodes open as possible, while satisfying given bounds on the probabilities of nodes being infected in the next time period. The model's relation to previous deterministic optimization models and to both probabilistic and deterministic asymptotic models was explored. Initially, we formulated a nonlinear integer program with high-order multilinear terms. We then proposed a quadratic approximation that provides a lower bound and feasible solution to the original problem and can be easily linearized and solved by standard integer programming solvers. We also devised a novel application and extension of cover inequalities (i.e., a set of cuts or valid inequalities that are added to strengthen the formulation) to speed the solution by using standard solvers.

Proposed Work for FY 2013

Having laid the groundwork by developing a set of deterministic tools for intrusion detection and attack response, we will use the final year of the project to incorporate the treatment of uncertainties into these models by developing and testing robust approaches. In particular, we will develop approaches to handle uncertainties and possibly corrupted data by concentrating on the following goals:

1. Develop new efficient and scalable solvers for sparse support-vector machines (SVMs). This work includes the development of new active-set approaches that can be effectively warm-started for screening data on the basis of augmented Lagrangian filter methods recently proposed by the principal investigator.
2. Develop models and solution approaches for robust intrusion detection under uncertainty and adversarial manipulation. This task includes testing the newly developed sparse SVM approaches with regard to manipulated data.
3. Formulate and solve a model for network response within the robust optimization framework to allow infection and transmission probability estimates to vary within a user (i.e., network operator) region of uncertainty.
4. Integrate the multilevel optimization approach with the newly developed network-response model to enable robust response models.

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SUSTAINABILITY ENERGY PRODUCTION AND USE

Novel Power System Operations Methods for Wind-Powered Plug-In Hybrid Electric Vehicles

2010-044-R2

Jianhui Wang, Mihai Anitescu, Audun Botterud,
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Project Description

This project addresses how power systems can incorporate large amounts of wind power and a high penetration of plug-in hybrid electric vehicles (PHEVs) into their operations; from a few days-ahead planning to real-time operations. We propose to develop a novel stochastic security-constrained unit commitment and dispatch algorithm for power system operations, as opposed to using the traditional deterministic method, which does not consider the uncertainties in wind power generation and PHEV charging and/or discharging.

Mission Relevance

This project is relevant to DOE's missions in environment and energy because it supports DOE's strategic goal of promoting a low-carbon environment by enhancing transmission reliability through advanced power system operations and large-scale stochastic optimization. It also supports the DOE Office of Electricity Delivery and Energy Reliability's strategic goal to improve the protection and restorative capability of national critical energy infrastructure components and supply. Our proposed approach may significantly improve the bulk power system's operation and planning by lowering the system's cost, reducing blackouts, improving social welfare, and advancing research on power-system and large-scale computing. The proposed method can leverage the benefits of new energy sources and applications without compromising the reliability and security of power system operations.

FY 2012 Results and Accomplishments

In FY 2011, we developed a new unit commitment model that can simulate the interactions among PHEVs, wind power, and demand response (DR). We also reported [Liu et al., 2012] on using a stochastic unit commitment model that considers the coordination of thermal generating units and PHEV charging loads, as well as the penetration of large-scale wind power. Results show that a smart charging pattern can reduce a power system's operating costs and compensate for fluctuations in wind power. We implemented a stochastic unit commitment (UC) and energy dispatch (ED) formulation by using the Illinois transmission system and solved it with a new hybrid parallel version of our solver, Parallel Interior Point Solver (PIPS). The Illinois grid contains about 2,000 transmission nodes, 2,500 transmission lines, 900 demand nodes, and 300 generation nodes. Time horizons of up to 24 hours were used. This stochastic UC/ED problem is the largest one that has ever been solved. The problem contains 1.4 billion variables. A strong scaling efficiency of 96% was obtained on 32 racks (131,072 cores) of the "Intrepid" Blue Gene/P system at Argonne. Solution times of less than an hour were achieved. We also conducted an initial review of current operating reserve requirements in U.S. electricity markets and of the assumptions for operating reserves that were used in some wind integration studies. Furthermore, we conducted an initial investigation of how to derive a demand curve for operating reserves [Zhou and Botterud, to be published].

Continuing from our FY 2011 work on PHEVs, in FY 2012, we particularly looked into how PHEVs can be integrated with microgrids. Microgrids have emerged as a relatively new and promising solution to restructuring the current energy infrastructure and ensuring the reliability of energy supply. Unlike other controllable loads, electric vehicles can be connected to the distribution system anytime and anywhere, according to the customers' preference. The uncertain parameters (e.g., charging time, initial battery state-of-charge (SOC), start and/or end time) associated with vehicle charging make it difficult to predict the charging load. Therefore, the inherent uncertainty and variability of the charging load have complicated the operations of distribution systems. To address the operational challenges associated with the uncertainty of vehicle charging, we proposed a model predictive control (MPC) -based energy and power dispatch approach. The proposed model minimizes the expectation of the operational cost while minimizing the power losses. Case studies were performed on a modified Institute of Electrical and Electronics Engineers (IEEE) 37-bus test feeder. The numerical simulation results demonstrated the effectiveness and accuracy of the proposed MPC-based energy and power dispatch, considering the uncertainty of vehicle charging. We also came up with a stochastic energy scheduling method in microgrids with intermittent renewable energy resources. The case studies showed the effectiveness of the proposed method.

As for the work on electricity market simulations, we analyzed how demand dispatch — combined with the use of probabilistic wind power forecasting — can help accommodate large shares of wind power in electricity market operations. In a case study of the power system in Illinois, we found that both demand dispatch and probabilistic wind power forecasting can contribute to the efficient operation of electricity markets with large shares of wind power.

On the stochastic optimization side, we found that stochastic optimization can yield much more consistency in revenue adequacy and revenue neutrality than deterministic optimization when applied to power grid market clearing procedures. Existing deterministic approaches introduce severe biases in prices that distort the representation of the spot market in forward markets. This destroys revenue neutrality, which is a property that allows market participants to achieve stable revenues. When revenue neutrality is not achieved, market participants face highly volatile revenues and a high degree of uncertainty; leading to speculation and resource withholding. We demonstrated that stochastic optimization is able to better represent spot market behavior, and thus it leads to revenue neutrality. We demonstrated this behavior in small test problems and in the Illinois grid system. We also found evidence that stochastic optimization ameliorates strong volatility and inefficient spreads of prices and welfare across the network. The models currently include storage models, which have been shown to increase the value of stochastic optimization as recourse actions become less expensive. The developed market models are currently being translated into the parallel stochastic optimization system PIPS to understand scalability effects.

This work resulted in the following awards:

1. Victor Zavala won a DOE Office of Science Early Career Award as a result of his research.
2. Mihai Anitescu, Victor Zavala, and Emil Constantinescu were members of a multi-organization team that won one of the multi-million dollar Office of Science Mathematical Multifaceted Integrated Capability Centers, which was partially attributed to their research.

Research will continue on this project with the funding provided by the mentioned awards and new funding from the DOE OE Smart Grid R&D program.

Probing Catalytic Transient Intermediate in Ultrafast Time Domain

2010-167-R2

Di-Jia Liu, Lin X. Chen, and Michael Harpham

Project Description

Catalyst development has traditionally been a time-consuming process. For practitioners in the field, catalyst synthesis often is regarded as "black magic" based on years of experience and know-how. To design catalysts rationally, it is vital to gain insight about the catalytic intermediate in the excited state, so the improved active site will have a lower potential barrier. Various sophisticated characterization tools are presently available; however, there is still an amazing lack of fundamental knowledge about catalytic reaction pathways at the molecular level. To catch the catalyst "in the act," a characterization method must be in a time domain relevant to the molecular processes.

The objective of this project is to explore and develop time-resolved spectroscopic techniques, such as optical and x-ray transient absorption spectroscopies (OTA and XTA) and terahertz (THz) spectroscopy, for the investigation of the time-dependent behavior of model catalytic systems and catalysts relevant to energy and environmental applications. The goal is to introduce new ultrafast techniques that break the current time barrier for catalyst characterization and to initiate a new frontier in structural and dynamic studies in catalysis.

Mission Relevance

This project is relevant to the DOE missions in energy and the environment. Catalytic processes account for nearly 20% of the U.S. gross domestic product, and they impact more than 20% of all industrial products. Catalyst technology is widely applied in clean and affordable energy production, as well as in environmental control and mitigation. All are directly linked to DOE missions. This project aims to develop innovative tools to promote better understanding, design, and discovery of catalyst materials.

FY 2012 Results and Accomplishments

In prior years, we focused on the time-dependent structural-electronic behaviors of the transient states of several organometallic compounds by using OTA and XTA methods. These compounds were selected because their photo-excited intermediates mimic representative catalytic transition states during photo or thermal excitation. Two systems we extensively studied via a series of laboratory and synchrotron x-ray experiments include (fulvalene) tetracarbonyl diruthenium and triruthenium dodecacarbonyl.

Our research in FY 2012 involved the comprehensive analysis of the data acquired from the XTA experiment on the transition intermediates of (fulvalene) tetracarbonyl diruthenium $Fv[Ru\ (CO)_2]_2$ during its photo-isomerization reaction. The $Fv[Ru\ (CO)_2]_2$ is a novel organometallic compound developed at the University of California at Berkeley. The $Fv[Ru\ (CO)_2]_2$ can store photon energy from sunlight through molecular structural transformation from the cis- to the trans-isomer. The trans-isomer can be reverted back to the cis-configuration through catalysis while releasing the stored energy in the form of heat. Computational modeling predicted the thermal energy release of ~20 kcal/mol upon reversal. Our team initiated the investigation of the $Fv[Ru\ (CO)_2]_2$ isomerization mechanism by using a time-resolved x-ray absorption spectroscopic approach. Through a joint effort with researchers at Northwestern University, the University of California at Berkeley, Massachusetts Institute of Technology, the University of North Carolina, and Chalmers University of Technology, we successfully elucidated the photo-storage steps in $FvRu_2$ through a combined ultrafast XTA, infrared spectroscopic, and density-functional-theory computational study. We found that the complex (shown in Figure 1) captures sunlight, which causes an initial Ru–Ru bond rupture to furnish a long-lived triplet biradical configuration that will reach a crossing point upon thermal activation (middle) into the singlet manifold en route to the thermal storage isomer. This study revealed the exciting possibility of using $FvRu_2$ as a medium to store solar energy in a bottle and release it thermally via catalysis.

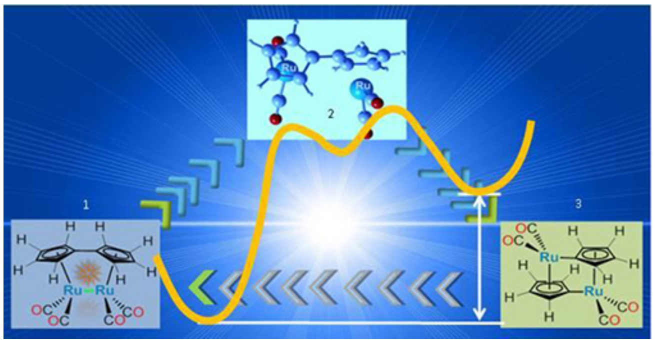


Figure 1. (1) The sunlight-harvesting (fulvalene) tetracarbonyl diruthenium Fv[Ru (CO)$_2$]$_2$ (2) undergoes an Ru–Ru bond rupture on photoexcitation to furnish a long-lived triplet, which requires thermal activation to reach a surface crossing point (3) to enter the singlet surface en route to its isomer. This isomer functions as an energy storage material. During the reverse reaction, the energy stored in the chemical bonds is released as heat.

We also completed a study of another organometallic system, triruthenium dodecacarbonyl [$Ru_3(CO)_{12}$], which is a compound known for homogeneous and heterogeneous catalysis. The tri-ruthenium nuclear core bonded by multiple carbon monoxide groups renders this complex a unique model in understanding the dissociation of carbon monoxide from the metal cluster. This material also can be used as a photocatalyst for olefin isomerization and can catalyze the water-gas shift reaction when complexed with 2, 2' bipyridine. We completed both experimental and data analyses of the time-resolved x-ray absorption spectroscopic study on this system.

In addition to the x-ray experiment, we designed and produced a THz system that could be used as a generic, non-photon trigger source for the study of thermally induced catalytic processes. We completed the THz system in FY 2012 and successfully obtained the THz pulse. The system is now used for the study of gold nanoparticle catalysis.

Seminars

Chen, L.X. (2012). "X-ray Transient Absorption Spectroscopy: A Decade and Beyond." Washington State University, Pullman, WA, November 29, 2011.

Harpham, M.R., M.W. Mara, J. Huang, A.B. Stickrath, X. Zhang, K. Attenkofer, G. Jennings, D.-J. Liu and L.X. Chen (2011). "Ultrafast X-ray Studies in Catalysis: Progress, Challenges and Perspectives." 2011 Advanced Photon Source Center for Nanoscale Materials Electron Microscopy Center Users' Workshop, Argonne, IL, May 2–5, 2011.

Nanoscale Architectures for Energy Storage

2010-188-R2

Tijana Rajh, Mahalingam Balasubramanian, Ralu Divan, Jeffrey Greeley, Christopher S. Johnson, Nenad M. Markovic, Subramanian Sankaranarayana, Elena V. Shevchenko, and Vojislav Stamenkovic

Project Description

In this project, our aim is to develop novel nanoscale electrode materials that will lead to the development of affordable and efficient rechargeable batteries. Whereas rechargeable Li-ion batteries offer the highest energy density of any present battery technology, there are still a number of limitations, such as cost, safety, and service life. Thus, the discovery, investigation, and development of a sustainable system that can provide an alternative choice to Li-ion batteries are essential for further advancement of energy storage materials. Sodium-based batteries are attractive, because of the promise of low cost associated with the abundance of sodium and enhanced stability of non-aqueous battery electrolytes because of the lower operating voltages. In our research, we focus on obtaining a fundamental understanding of chemical and physical processes that occur in nanoscale electrodes and electrode-electrolyte interfaces, to improve the performance of the electrode materials for both Li-ion and Na-ion batteries. From these initial considerations, we are designing optimal electrode materials operating with transporting ions having different diameters and valence states. Current focus is on polyvalent ions, such as Mg^{2+}, Ca^{2+}, or Be^{2+}, that can provide the higher energy densities needed for the development of compact batteries.

Mission Relevance

This project is in support of DOE's energy mission of fundamental research on electrical energy storage with a link to new energy technologies or technology roadblocks. This project provides an interdisciplinary environment in which both basic and applied research are simultaneously directed at the research challenge facing energy storage.

FY 2012 Results and Accomplishments

In prior years, we developed nanoscale electrodes in the forms of nanotubes (TiO_2, FeO_x; o.d.: 50–60 nm), nanoribbons (V_2O_5, MnO_2; 8–12 nm in diameter), and hollow nanoparticles (Fe_2O_3; 5 nm) for Li- and Na-ion batteries. We found that nanostructured electrode materials have advantages over bulk materials for rechargeable batteries and can achieve (1) high energy (10^2–10^3 Wh/kg) because of efficient electronic and ionic transport properties, (2) high power (10^2–10^4 W/kg) enabled by large contact area, and (3) good cycle life (~600 cycles) because of high mechanical strength at nanoscale to accommodate volume change during operation. We also found that that hollow nanostructures contain a very high concentration of cation vacancies that can be efficiently utilized for Li intercalation without structural change and can operate like solid-state solutions with ~100% Coulombic efficiency and excellent stability.

We also showed that open frame layered structures are optimized to accommodate for large-volume Na ions by adjusting the layer spacing upon exposure of a reduced layered structure to a high concentration of Na ions. The electrostatic attraction of electrochemically altered oxide layers provides a strong driving-force for the diffusion of a large concentration of transporting ions into open layer frameworks. This consequently leads to ordering of the overall structure, with the appearance of both short-range order within the layers and long-range order between the layers. Upon deintercalation of sodium, the long-range order is lost, while the intralayer structure is still preserved. Inducing ordering of nanomaterials in operando allows realization of the highest possible electrode capacity by optimizing the balance of electrostatic forces. Molecular dynamics (MD) and density functional theory (DFT) calculations with a classical interaction potential were employed to obtain insights into the dynamic properties of Li ion transport in anatase and amorphous titania.

In FY 2012, we investigated the high-pressure stability and compression behavior of cubic TiO_2 phases with varying Li concentrations under quasi-hydrostatic conditions. These TiO_2 nanotube anodes demonstrate self-improving capacity, high rate capability, and surprising stability. *In situ* synchrotron x-ray diffraction was performed at pressures of up to ~60 GPa (typical pressure limit range for most phase transitions observed for bulk/nano TiO_2) at ambient temperature, by using a diamond-anvil cell. We correlated the experimental observations with molecular dynamics simulations in order to elucidate the role of Li ions in the stability of c-TiO_2.

We found that the structural stability of c-TiO_2 is enhanced with increasing Li concentration, and this phenomenon is explained by a vacancy-filling mechanism — the applied pressure drives the interstitial Li ions to the cation vacancy sites in the oxide interior, leading to significant improvement in structural stability (Figure 1). Experimental and theoretical studies on the compositional dependence of stability and compressibility in lithiated c-TiO_2 show that Li concentration plays a critical role in dictating the stability of the lithiated TiO_2. Our finding suggests that, although surprisingly stable, the c-TiO_2 nanotube electrode is most vulnerable in the delithiated discharged state (up to 17.5 GPa). It is important to note that in battery electrodes, large atomic rearrangements and high stress are expected at the highest Li concentration gradient. The observed vacancy-filling mechanism suggests that the enhanced stability of c-TiO_2 electrodes is a consequence of a pressure-initiated ordering at the sites subjected to the highest local stress. These findings could benefit the optimization of battery electrodes and show that high cationic vacancy content in cubic materials assists in accommodating electrode stress and improving their long-term stability for Li-ion battery operation.

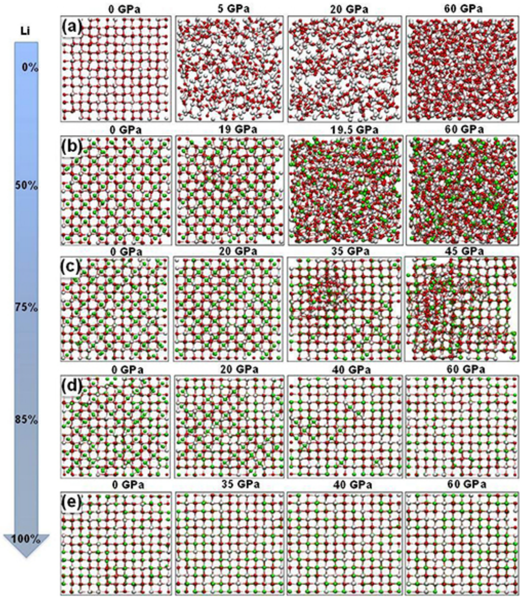


Figure 1. Structural transition under pressure for (a) delithiated, (b) 50% lithiated, (c) 75% lithiated, (d) 85% lithiated, and (e) fully lithiated c-TiO_2 at different pressures. Red spheres, O; green spheres, Li; and white spheres, Ti.

Hollow nanoparticles of Fe_2O_3 that are grown by using the Kirkendall effect also contain very high concentrations of cation vacancies that can be efficiently utilized for reversible Li intercalation without structural or electronic changes to the iron. Cycling in a high voltage range results in high capacity (up to 218 mAh/g), ~100% Coulombic efficiency, superior rate performance (133 mAh/g at 3,000 mA/g), and excellent stability (no fading at fast rates during more than 500 cycles). Cation vacancies in hollow Fe_2O_3 nanoparticles are also found to be responsible for the enhanced capacity in the conversion reactions in Li-ion battery in which more than one electron transfer occurs per transition metal host atom. We monitored *in situ* structural transformation of hollow Fe_2O_3 nanoparticles by synchrotron x-ray adsorption and diffraction techniques that provided us with a clear understanding of the lithium intercalation processes during electrochemical cycling.

Process Engineering Research for Scalable Energy Storage Materials

2010-191-R2

Gregory Krumdick, Ilias Belharouak, Ralph Brodd, and Young Ho Shin

Project Description

The objective of this project is to conduct process engineering research to demonstrate scalable process development for energy storage materials. Process engineering research is needed to identify and resolve process and material constraints on the development of scalable processes for energy storage materials (that is, advanced battery chemistries). As the chemistries get more complex in order to achieve multiple performance goals for both mobile and stationary applications, parallel process engineering research is required to ensure that the materials can be consistently and cost-effectively manufactured in high-volume applications.

Mission Relevance

This project is relevant to DOE's energy mission. Scientists in battery materials programs across the DOE complex refer to "scale-up" as the synthesis of battery materials in gram quantities, but this is done in multiple, time-consuming, small-scale runs. No DOE laboratory has the capability to scale up currently developed battery materials (primarily lithium-ion-based batteries) to the kilogram and tens of kilograms quantities that would support the transition of these technologies to industry. Moreover, neither DOE nor industry has a systematic engineering research capability or program for identifying and resolving constraints to the development of a cost-effective process technology for the high-volume manufacture of these advanced materials.

FY 2012 Results and Accomplishments

In FY 2011, the scale-up of an electrolyte additive ANL-RS2 was completed. This additive prevents cells from going into thermal runaway when accidentally overcharged, preventing a potential fire. The cathode material scaled in this project was designed to work in conjunction with the previously scaled electrolyte additive.

In FY 2012, we completed scaling up the cathode materials process and system design. Scale-up involved modifying the bench-scale process chemistry to allow for the continuous production of the composite. A primary issue identified with regard to the 4-L system was the fact that before particles reached steady state, they continued to grow past the optimal size. A mixture of particles formed, the sizes of which were both larger and smaller than optimal, with an average particle size of 28.2 μm at steady state. We identified and tested a technique to overcome this issue and allow for continuous processing. Five kilograms of spherical precursors with a narrow particle size distribution and smaller average particle size (7.8 μm) and a tap density of 1.49 g/cc (cm^3) were prepared to attempt to minimize fracturing during the cell fabrication process. Results of tests of a coin cell — which is a small battery (typically found in a watch) that is used as a simple way to test the electrochemical performance of a battery material (basically the smallest battery you can easily make and test) — showed that cycle and cycling or C-rate performances were good (Figure 1). 1C and 2C were 195 and 180 mAh/g. C/3 was kept over 190 mAh/g for 100 cycles. Ten percent capacity loss occurred between 21 and 94 cycles.

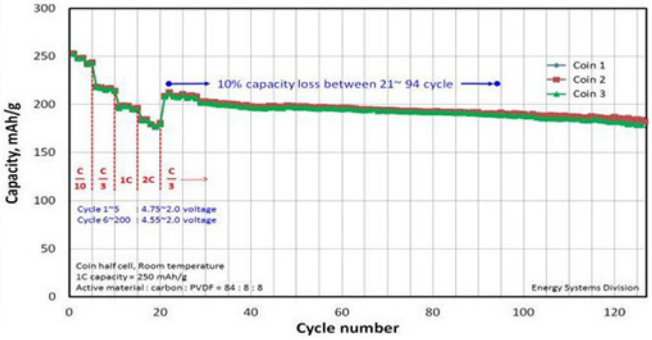


Figure 1. Coin cell test: rate performance and cycle life (C/3).

We developed a mini pilot-scale (4-L) assembly for cathode materials development and then further scaled it to 20 L. We finished optimizing the carbonate process for synthesizing $Li_{1.14}Mn_{0.57}Ni_{0.29}O_2$ on the 4-L system and then began work on scaling it to the 20-L system. Finally, we completed our review of the process with regard to its ability to be integrated into manufacturing operations. We found that the new particle-size control technology developed was compatible with a continuous reaction system. This technology enables the continuous production of this cathode material, rather than batch production. The integration process was reviewed relative to each level of scale-up.

Microscopic Building Blocks of a Better Lithium-Ion Battery

2010-192-R2

John F. Mitchell and Qiyin Lin

Project Description

Lithium-ion batteries are at the state of the art for deployed electrical energy storage platforms, finding use in applications ranging from power cells for laptop computers to the electrical drive train of plug-in hybrid electric vehicles, such as the Chevrolet Volt. Moving Li-ion batteries toward the higher capacities, better cycling performance, and higher power densities that are necessary for widespread deployment of mobile storage stands as both a technical and scientific challenge. We are approaching this challenge from a very fundamental standpoint, creating well-defined crystalline substrates with which the key processes in charging and discharging batteries can be studied in pristine forms, isolated from extrinsic effects found in powders and composites. Specifically, we aspire to grow the highest quality single crystals of canonical cathode materials (e.g., $LiCoO_2$, $LiFePO_4$), understand their intrinsic electronic and ionic transport characteristics, explore their performance in real-world as well as idealized battery environments, and correlate performance with underlying processes (e.g., Li-ion diffusion in the bulk and at the surface of the crystal, structural changes during charging). The outcome of such studies is expected to enable improvements of today's Li-ion cathode materials, as well as inspire the design of next-generation Li-ion cathodes with improved functionality.

Mission Relevance

Expanding the role of energy technologies that can reduce fossil-fuel dependence and enhance U.S. energy security is a critical mission activity of the DOE. Research in advanced electrical energy storage materials platforms directly targets this mission.

FY 2012 Results and Accomplishments

During FY 2010 and FY 2011, we successfully grew single-crystal specimens of $LiCoO_2$ and $LiFePO_4$ by using flux methods and began electrochemical characterization of these samples. We then developed a principally new method for growing extremely high quality crystals of $LiCoO_2$, delithiating them chemically, and exploring the structure of the material. The high electrical resistivity is consistent with simple pictures of the electronic structure of $LiCoO_2$ and furthermore argues that these defects are essential for effective charging. Because of this high resistivity, we were unable to electrochemically delithiate these defect-free crystals. Instead, we chemically removed Li and followed the process *in situ* with x-rays. In this way, we were able to demonstrate that the crystals can be delithiated without decomposing or breaking into polycrystalline form. Furthermore, this x-ray technique allowed us to monitor the Li concentration over time, allowing us to selectively choose important compositions for electrical characterization. A significant outcome of this phase of the work was a convincing demonstration of (1) defect-free $LiCoO_2$ crystals that reveal the intrinsic, highly insulating nature of this material and (2) strong evidence for inhomogeneous delithiation on the macroscale.

During FY 2012, studies of the electrical properties of the Li_xCoO_2 system were completed by characterization of the chemically delithiated vapor-grown single-crystal specimens prepared in the previous year. Specifically, the first systematic study of electrical transport in single crystals in the metallic regime x ~0.7 was performed, and the variation of the metal-metal transition with composition was mapped as a function of composition (Figure 1). Study of multiple samples of nominal composition x = 0.7 demonstrated a weak variation in the transport characteristics, presumably arising from chemical inhomogeneity. Correlation of this composition dependence with the single-phase ($x \leq 0.6$) and bi-phasic ($0.6 \leq x \leq 0.7$) composition ranges demonstrated that details of the transport physics will depend strongly on the composition and Li uniformity. Summarizing the effort on vapor-grown crystals, the successful vapor-phase growth of highly insulating and presumably highly defect-free crystals provides a stringent baseline for understanding the intrinsic properties of $Li_{1.0}CoO_2$. Successful delithiation of such crystals demonstrated that they can serve as model systems, providing access to measurement of anisotropies of conductivity and other properties relevant to understanding and improving Li-ion transport functionality.

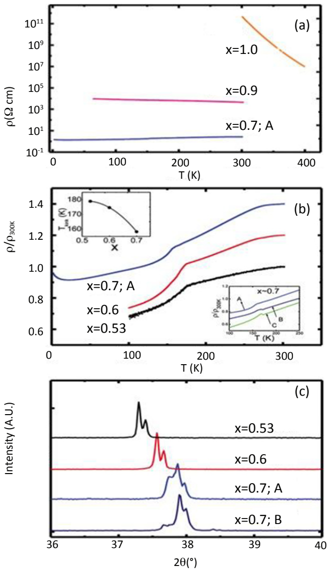


Figure 1: Temperature dependence of electrical resistivity for chemically delithiated Li_xCoO_2 crystals in the range $0.7 < x < 1.0$ (a) and $0.5 < x < 0.7$ (b). Data in (b) have been normalized to room temperature to facilitate comparison; curves for x=0.7 (A) and x=0.6 have been offset by 0.4 and 0.2, respectively, for clarity. Upper inset in (b) shows the composition dependence of the electrical anomaly near 170 K. Lower inset in (b) compares the behavior of three nominally x=0.7 specimens; (c) shows the evolution of x-ray diffraction patterns with composition, highlighting the change from multiphase (x > 0.6) to single-phase (x < 0.6).

Atomistically-Informed Mesoscale Simulation of Gradient Nuclear-Fuel Microstructure

2010-196-R2

Dieter Wolf and Michael J. Pellin

Project Description

In this project, we will incorporate the effects of temperature and stress and their gradients across nuclear fuels into an atomistically informed mesoscale phase-field modeling framework. Gradients in temperature and stress across a fuel pin provide the driving forces, for example, for thermo-migration of voids and gas bubbles, directional grain growth, and alloy-species migration. All of these adversely affect the thermo-mechanical behavior. Incorporation of temperature, stress, and their gradient effects into a mesoscale model requires knowledge of the underlying atomic-level processes involved in radiation damage, including defect clustering. These processes will be elucidated by molecular dynamics (MD) simulations. The mesoscale model to be developed under this project will subsequently also be applicable to other materials for energy, such as advanced electrical energy storage devices.

Mission Relevance

This project is relevant to DOE's energy mission, particularly in nuclear energy. Because traditional nuclear-fuel performance simulations are based on incorporated empiricism, they have little predictive capability in regimes for which no test data exist (e.g., under transient conditions in the reactor). The same holds for simulations of materials degradation under irradiation and in corrosive environments. The first step toward making these simulations more predictive is to incorporate materials microstructure into engineering performance codes. Next-generation fuel-performance codes, based on a materials-science/nuclear-engineering scale-linkage approach, will ultimately provide higher-fidelity predictions of overall system performance. In addition, they will begin to enable predictions of fuel and safety performance under transient conditions and thus provide a valuable modeling tool for the development of more reliable and safer nuclear materials.

FY 2012 Results and Accomplishments

During the first year of this project, we developed a new MD approach for the simulation of radiation damage by direct insertion of Frenkel pairs into the crystal lattice. This approach was then used to perform MD simulations on uranium dioxide (UO_2) and cerium dioxide (CeO_2) under ion irradiation in order to investigate the degree to which ceria can be used as a surrogate material for the investigation of radiation damage in UO_2. Specifically, we (1) determined the kinetics of the clustering of irradiation-induced point defects and the initial formation of the extended defects and (2) compared the clustering mechanisms in the two materials.

A unique aspect of this approach to simulating radiation damage is the ability to insert vacancies and interstitials (so-called Frenkel pairs) on only one sublattice at a time, rather than simultaneously on both (as is the case in the conventional radiation-damage experiments and simulations). With this capability, we could identify the atomic-level mechanism of dislocation-loop formation. Remarkably, our simulations revealed a self-healing response of the perfect crystal to the radiation-induced defects. In fact, the lattice responds to point defects created during irradiation with the spontaneous creation of new point defects. These new "structural defects," with a negative energy of formation, neutralize the radiation-induced point-defect cluster by screening its long-range Coulomb potential, thereby lowering the overall energy and localizing the damage.

In FY 2013, we incorporated the key insights gained from our previous MD simulations of the effects of irradiation on defect clustering into our mesoscopic phase-field computer code for microstructure evolution in nuclear-fuel materials. In particular, the code was extended to include the coupling between stress, temperature, and the related gradient terms as driving forces for microstructure evolution. Incorporation of this coupling requires simultaneous solution of the phase-field equations and stress calculation on an evolving, adaptively refined mesh. The numerical solution of this highly coupled problem was achieved by using elements of the publicly available FEniCS software package. The FEniCS project is a collection of free software with an extensive list of features for automated, efficient solution of partial differential equations. The project involved a collaborative effort between research groups from Simula Research Laboratory, University of Cambridge, University of Chicago, Texas Tech University and KTH Royal Institute of Technology.

Controlled Heterogeneity of Materials for Energy Applications

2010-197-R2

Marius Stan, Zhi-Gang Mei, and Di Yun

Project Description

Materials for energy applications, such as nuclear fuels and electrical batteries, are multicomponent ceramics or metals that are subjected to extreme radiation, temperature, and chemical environments during their manufacture, use, and storage. Changes in composition and micro (nano) -structure cause the properties to evolve with time and can severely impact performance. However, the heterogeneous character of the materials — that is, the presence of multiple phases with distinct properties — makes it difficult to understand and control their properties. In this work, we will develop theoretical models of heterogeneity and perform advanced transport simulations to understand and control material properties during synthesis and operation. Moreover, we hypothesize that, in some instances, controlling heterogeneity can lead to improved material properties, thereby creating the framework to develop materials that are "heterogeneous by design." To this end, we will develop theoretical and computational tools for the analysis of heterogeneity at the microscale and nanoscale levels in nuclear fuels (e.g., uranium oxide [UO_2]). Then, by performing simulations of heat, chemical, and electrical transport for a variety of heterogeneous features (e.g., point defect clusters, pores, gas bubbles, and cracks), we will identify the optimal nano (meso) -structure and assist with the design and synthesis of new materials.

Mission Relevance

This project, which is relevant to DOE missions in energy and science, opens a new area of research focused on materials that are "heterogeneous by design." This endeavor has the potential to accelerate the development of new materials for a variety of applications beyond nuclear energy and energy storage. The project fosters theoretical and computational work to generate new models, methods, and algorithms. This research will result in innovative design experiments that can transform the understanding of materials, thus moving materials science from observation and analysis to prediction and control. All these features benefit both basic and applied scientific research and support the DOE Office of Science and Office of Nuclear Energy missions and strategies. This project will also serve as the basis for a multiscale (e.g., atomistic, mesoscale, and continuum) high-performance materials simulation program at Argonne that is relevant to DOE programs and resources, such as the Nuclear Energy Advanced Modeling and Simulation Program, the Center for Electrical Energy Storage, and the Argonne-directed Center for Exascale Simulation of Advanced Reactors.

FY 2012 Results and Accomplishments

This project began in August 2010. In FY 2010, we defined the relevant geometry and boundary conditions for the coupled finite-element-method (FEM) simulations of heat transport and chemical species diffusion in porous materials.

In FY 2011, we set up a simulation domain that consisted of a cylindrical UO_2 fuel pellet and steel cladding separated by a helium gap. We used the software COMSOL Multiphysics, which provides an ideal tool for studying coupled phenomena and allows for mesh refinement in 3-D (three-dimensional) configurations. In this fuel element, we solved for the coupled equations that describe thermal expansion of the fuel pellet and steel cladding, heat transport, and oxygen diffusion. The fuel pellet and steel cladding were allowed to expand freely in the radial direction. We placed a disc-shaped void (1 mm diameter, 0.1 mm thickness) in the UO_2 pellet to simulate the effect of a macroscopic defect. The heat transport simulation showed that the presence of the void changed the local temperature by more than 100 K.

In FY 2012, the study focused on the effect of heterogeneous porosity on the thermal conductivity of the oxide nuclear fuel (UO_2). As opposed to common 1-D (one-dimensional) and 2-D (two-dimensional) studies, this work provided quantitative information about the role of porosity in a 3-D geometry that represents a segment of the oxide fuel element. The porosity correction factor (PCF) was defined as the thermal conductivity of the porous fuel divided by the thermal conductivity of the fully-dense fuel and was determined by a method that involves the temperature profiles in the two fuel types.

The results confirmed that uniform porosity changes the temperature profile, especially toward the edge of the pellet. The decrease in the PCF was significant and approximately linear, with a slope of 10 K per volume-percent (vol. %) porosity. The PCF was strongly influenced by the shape of the pores, with platelet pores having a much stronger impact than spherical pores. A comparison of the simulation results with the Maxwell-Eucken model gave a shape factor $\sigma = 1.5$ for the spherical pores and $\sigma = 3.5$ for the platelets. At a fixed total porosity of 2.74 vol. %, the size of the pores (80–140 µm) had a weak effect on the centerline temperature and the PCF.

The FEM simulations provided information about the effect of heterogeneity on thermal and chemical transport at the continuum and mesoscale. To improve the understanding of how heterogeneity impacts material properties at lower length and time scales, we started density functional theory (DFT) calculations of defect formation in UO_2. The initial calculations were performed on Argonne servers to include FUSION (MCS) and CARBON (CNM), and they involved a uniform distribution of defects, such as vacancies and interstitials.

Proposed Work for FY 2013

We will further study the effect of the size distribution, position, shape, and orientation of voids on the heat and chemical transport in UO_2. Subsequently, we will analyze this information to ascertain the optimal distribution. In addition, we will approach mesoscale from atomistic simulations, such as DFT and molecular dynamics. This method will enable us to determine the impact of the heterogeneous distributions of defects on continuum properties, such as thermal conductivity and chemical diffusivity.

Seminars

Stan, M. (2011). “Materials Discovery and Design.” Illinois Institute of Technology, Chicago, IL, March 28, 2011.

Stan, M. (2012). “Bridging the Micro and Macro Scales.” Massachusetts Institute of Technology, Cambridge, MA, March 20, 2012.

Stan, M. (2012). “Multi-scale Computational Microscopy.” University of California Santa Barbara, Goleta, CA, April 16, 2012.

Stan, M., B. Mihaila, A. D. Andersson, P. Cristea, S. Y. Hu, C. Ramirez, V. Tikare, P. Turchi and M. Samaras (2010). “Integration of Simulation Techniques for Nuclear Fuels.” F-Bridge School, Karlsruhe, Germany, Sep. 28–October 2, 2010.

Near-Term Spent Nuclear Fuel Disposal Using Accelerator Drive System

2010-201-R2

Rod Gerig, Yousry Gohar, Jerry Nolen, Peter Ostroumov, and Mark Williamson

Project Description

The objective of this multi-discipline project is to characterize and develop an innovative approach for disposing of the spent nuclear fuel (SNF) inventory of the United States. The proposed system is intended to use neutrons to transmute/fission the minor actinides, which eliminates the long-term radiotoxicity of the SNF.

Mission Relevance

Our proposed system provides a disposal solution for SNF and thus supports DOE's missions in energy and the environment. This system significantly reduces the required geological repository capacity for nuclear waste and eliminates the need for a large storage facility, such as Yucca Mountain.

FY 2012 Results and Accomplishments

Prior to FY 2012, we identified major parameters for the system. For the accelerator required to drive the neutron production target, we selected a continuous wave superconducting proton linac with a beam energy of 1 GeV. For the engineering study phase, a beam power of 5 MW is appropriate, while for the production facility, a beam power of 25 MW is required. End-to-end beam dynamics simulations were done to determine the number and types of superconducting cavities required, along with initial estimates of the liquid helium refrigeration and RF power supply specifications. An initial cost study for the two versions was conducted. The cost study identified potential subsystems where savings could be realized with an "industrialization" of the fabrication that may be appropriate for such a large-scale project. It was determined that the 5-MW linac would be based on existing technology and is "project ready." For the 25-MW linac, R&D is needed for the RF couplers, where the requirements are beyond the present state of the art but not considered potential showstoppers.

The spallation target was designed to produce neutrons from the interactions of the high-energy protons with a high-atomic-number target material. Liquid metal targets were selected because they have several design advantages. Both windowed and windowless target designs are under consideration. In the MEGAPIE experiment, in which we were collaborators, a liquid lead-bismuth eutectic spallation target at the Paul Scherrer Institute in Switzerland, demonstrated the operation of the target design with a solid window for 0.8-MW beam power.

Mobile fuel forms with transuranic materials without uranium were considered in this work, to avoid the issues of solid fuel forms and to eliminate the minor actinides and the long-lived fission products of the SNF. Liquid metal (lead-bismuth eutectic or liquid lead) and molten salts (Flibe, etc.) are the fuel carrier materials.

In FY 2012, two approaches were analyzed for disposing of the 70,000 metric tons of expected U.S. SNF inventory by the year 2015; these are based, respectively, on the use of external (homogenous configuration) and internal (heterogeneous configuration) cooled blanket design configurations. The heterogeneous blanket configuration utilizes a larger plutonium fraction and generates about 2.6 GWt. Optimization analyses for the physics and the thermal hydraulics were performed to generate a reference configuration for the mechanical engineering design concept. Two mechanical configurations were investigated. The heterogeneous and the homogenous configurations are being compared to select a reference configuration. Physics studies were performed to define the blanket reflector material and dimensions in order to develop the plant configuration. Shielding analysis was started to define the shield materials and dimensions, which are required for the mechanical design concept development.

Progress was made on developing schemes for reprocessing lead slurry fuels. A small stream of the slurry is withdrawn from the accelerator-driven system (ADS) and processed quickly to separate a suitable fraction of the fission products and recycle 99.9% of the actinides. Make-up actinides are added to the stream and the reconstituted fuel is returned to the ADS.

Proposed Work for FY 2013

In FY 2013, the reference design point will be selected, and the corresponding plant configuration and parameters will be defined.

Several options are being explored for the mobile fuel form of the transmuter, including a particle fuel (oxide or intermetallic) dispersed in a liquid metal coolant and a molten salt fluid fuel-coolant system. Key to success of the system are the definition and demonstration of viable fuel cycle technologies that allow for efficient recovery of minor actinides from SNF, optimum performance of the transmuter system, and fission product recovery.

Engineering design of the required higher-power couplers was initiated during FY 2012 and will be the main task for FY 2013.

The Rational Synthesis of Kinetically Stabilized, Higher-Order Inorganic Materials for Catalysis

2010-202-R2

Adam Hock and Theodore Krause

Project Description

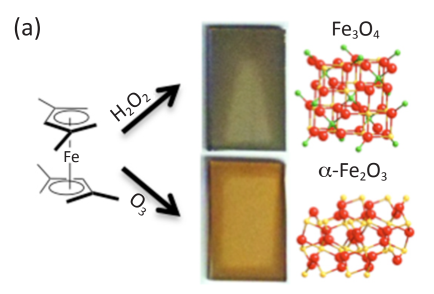
There are major challenges to large-scale adoption of solar energy as a significant contributor to our energy sources, whether the photon energy is used to generate electricity directly (photovoltaic devices) or to drive chemical reactivity (photoelectrochemical devices). Preparing catalytic materials in a pure state, with control over both the atomic positions and metal oxidation state, is one of the most difficult challenges. Because the properties of a given material rely upon exquisite tuning of those features, we are working to achieve just that synthetic control. We have discovered a system in which we can control both the crystalline arrangement and oxidation state of a metal at low temperatures. Low-temperature synthesis is ideal for incorporation into inexpensive devices, together with low-cost substrates such as organic polymers. Specifically, we are exploring photocatalysts for solar water splitting.

Mission Relevance

This project aligns with DOE missions to support basic science, fortify energy supplies, and ensure energy security. Well-controlled synthetic methods to tailor composition and produce structurally engineered materials will lead to more efficient solar devices. Finally, dramatic improvements in light-driven catalysis will help shift the United States to a renewable solar-based chemical feedstock economy.

FY 2012 Results and Accomplishments

Our initial target for photon harvesting materials was a mixed tantalum oxygen/nitrogen material, TaON. In FY 2011, we prepared several Ta complexes with remarkable thermal stability, a challenge for reactive Ta complexes. Unfortunately, the complexes were not volatile under typical atomic layer deposition (ALD) conditions. In parallel with this work, we sought to target other potential materials, such as hematite (α-Fe_2O_3), a promising candidate for solar water splitting. In FY 2012 we discovered a highly reactive Fe precursor grew thin films with peroxide, as well as ozone, as the oxygen source. The resulting iron oxides were different materials, with the oxygen source controlling the amount of Fe oxidation. The precursor is in the 2+ state and we achieve *selective* oxidation of 2/3 of the Fe with peroxide, all of it with O_3 to produce crystalline Fe_3O_4 and α-Fe_2O_3 at 120°C (Figure 1a). This result is remarkable not only for the crystallinity of the films, but also for the control over iron oxidation state. Furthermore, we observed virtually no growth with H_2O. These results indicate that the well-defined surface chemistry between the precursor and various oxygen sources work in tandem to control iron oxidation state and crystalline phase.



(b)

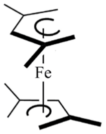
Iron Precursor	Oxidant	65°C	120°C	Phase (120°C)
	H_2O_2	0.4	0.6	Fe_3O_4
	O_2	0.2	0.3	not determined
	O_3	0.5	0.9	α-Fe_2O_3

Figure 1. (a) ALD of two different iron oxide thin films made from a common iron(II) precursor by varying the oxygen source. (b) Iron oxide growth rates (Å/cycle) under saturation conditions using different oxygen sources at 65 and 120°C.

We systematically evaluated the Fe system growth and properties, which indicate deposition occurs via ALD and not chemical vapor deposition (CVD). Furthermore, this rationally designed organometallic iron(II) precursor contains ligands previously unused for vapor deposition. We used the low temperature and faster growth rates to fashion photoelectrochemical devices as efficient as previously reported devices, but with much quicker fabrication times (Figure 1b). We are currently investigating the mechanism of this unique reactivity and looking to extend this methodology of controlled metal oxidation to other complex oxides.

Proposed Work for FY 2013

We will explore the mechanism of this novel oxidation state control during ALD synthesis and incorporate other heteroatoms into our deposition strategies. We expect to prepare and analyze metal oxysulfide films and study their properties. We anticipate that we could couple the improved photon absorption properties of S-doped TiO_2 to our Fe material through a film stack grown by ALD. Such a device would have improved photon-harvesting and photocatalytic abilities relative to existing technology. These results will drive research into ALD-synthesized multilayer films for photon-harvesting catalysis.

Spin and Charge Dynamics in Oxide Heterostructures

2010-204-R2

Olle Heinonen

Project Description

This project increases our fundamental understanding of spin and charge dynamics in oxide and magnetic heterostructures through modeling and theory closely coupled to experiments. Much of the work is aimed at understanding charge transport and spin transfer torque in structures that can readily be integrated with conventional semiconductor-based electronics. The magnetic behavior in patterned magnetic thin films is also investigated. In such structures, competing interactions from interfaces and geometries give rise to rich phenomena. A smaller part of the research is aimed at studying the effects of defect motion on charge transport in metal/oxide/metal nanostructures through modeling. The goal is to investigate in a broad context, how oxygen defects affect the behavior of oxide heterostructures.

Mission Relevance

The project supports the DOE-BES mission to advance energy efficiency through use-inspired R&D on new materials for information storage. In particular, the research is relevant to the development of low-power electronics. The project also addresses challenges articulated in the September 2012 BESAC report “From Quanta to the Continuum: Opportunities for Mesoscale Science" by studying how nanoscale building blocks can be combined into macroscale systems with new properties inherently derived from the interactions between those building blocks.

FY 2012 Results and Accomplishments

In previous years, the dependence of resonance frequencies on current and temperature in magnetic tunnel junctions was studied with researchers at the University of Gothenburg. Some key results were linear dependence of a component of current-induced spin transfer torque and the effect of Joule heating on the magnetic interactions in the tunnel junction. Together with University of Gothenburg researchers, we also elucidated the detailed nano-scale magnetization structure in artificial spin-ice lattices by using micromagnetic modeling, in conjunction with imaging by means of aberration-corrected Lorentz transmission electron microscopy.

The main accomplishments in FY 2012 were (1) elucidating the interactions between resonant modes in spin torque oscillators, (2) investigating the resonant modes of topological defects in an artificial spin-ice lattice, and (3) advancing fundamental understanding of resonant dynamics of magnetic vortices in coupled discs.

The magnetization dynamics in magnetic tunnel junctions and in nanocontact spin torque oscillators were studied in collaboration with researchers at the University of Gothenburg, Sweden. In these devices, spin transfer torque from the conduction electrons to a magnetic layer in the structure can lead to magnetic oscillations. We have shown that interactions between different resonant modes can lead to mode-hopping. Further studies of metallic nanocontact spin torque oscillators showed that the spectral linewidth of the oscillations, that is, the broadening of the oscillation frequency, can have a temperature dependence that is non-monotonic and complicated. By using our coupled-mode theory, we showed that the mode coupling leads to additional interactions between power fluctuations and phase fluctuations in the oscillators. In certain regions, these interactions can lead to prolonged power fluctuations, which in turn amplify phase fluctuations, leading to an enhanced linewidth.

With collaborators at the Max Planck Institut, the Peter Gruenberg Institute, and The Centre National de la Recherche Scientifique (CRNS), the resonant dynamics of a square artificial spin-ice lattice was studied by using micromagnetic simulations. This lattice supports topological defects, so-called Dirac monopoles and Dirac lines. We first calculated the resonant frequencies in a defect-free reference state of the lattice. We then inserted defects and calculated the resonant frequencies of the lattice with defect configurations. The calculations showed that the defects give rise to specific signatures in the spectrum that are localized in both frequency and space. The local nature of the resonances leads to intriguing possibilities of manipulating the spectrum for use in low-power storage and logic applications.

The magnetization in 1-µm-diam discs forms a vortex, with the magnetization in the circumferential direction (Figure 1). At the center, there is a core where the magnetization points out of the plane. The dynamics of two such overlapping discs were studied with fellow researchers at Argonne. Experiments showed that the resonant frequency of the coupled discs depends very strongly on the direction of an in-plane field and is asymmetric in the field direction, with two branches for which the frequency is split. Micromagnetic modeling showed that the asymmetry is caused by whether the cores are pushed closer or farther apart by the applied in-plane static magnetic field, while the split is caused by different polarities (the direction of the core magnetization).

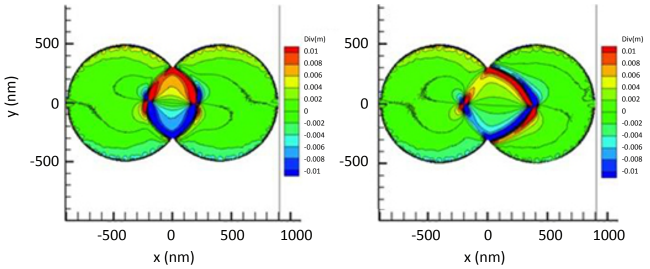


Figure 1. The magnetic charges of two discs with the cores at close points for same (left) and opposite (right) core polarities. The volume magnetic charge density (divergence of the magnetization density) is indicated by Div(m).

Proposed Work for FY 2013

The consequences of coupled modes in spin torque oscillators and magnetic tunnel junctions will continue to be explored, in particular the effect of finite temperatures as well as the implications for noise in tunnel junction sensors. The dynamics of topological "meron"-structure stacked discs will be studied. To date, results show a dramatic change in the resonant spectrum as a result of the topological deformation caused by a weak interlayer interaction.

First-principle calculations will be used to study oxygen defects in metal/metal oxide/metal heterostructures. Optimization of the codes for Blue Gene platforms (started in FY 2012) will continue, with subsequent applications to Pt/NiO/Pt systems.

Seminars

Heinonen, O. (2011). "Spin Torque in Magnetic Tunnel Junctions." University of Minnesota, Minneapolis, MN, October 25, 2010.

Heinonen, O. (2010). "Spin Torque in Magnetic Tunnel Junctions." Nordforsk Nanospintronics Workshop, Norrkoping, Sweden, September 22–24, 2010.

Heinonen, O. (2010). "Spin Torque in Magnetic Tunnel Junctions." Deptartment of Physics, Case Western Reserve University, Cleveland, OH, September 9, 2010.

Heinonen, O. (2012) "Magnetization Dynamics, Mode Hopping, and Coherence in Magnetic Tunnel Junction Spin-torque Oscillators." Seagate Technology, Minneapolis, MN, December 16, 2011.

Heinonen, O. (2012) "Spin Torque and Magnetization Dynamics." California Nanosystems Institute, Santa Barbara, CA, January 23, 2012.

Improved Catalytic Performance by Applying Electrochemical Control

2011-210-R1

Stefan Vajda

Project Description

This project aims at using an interdisciplinary approach to explore the effect of electrochemical potential on the activity of small cluster-based catalysts supported on novel carbon-based materials. The effort emphasizes the controlled synthesis of atomically precise metal, metal alloy, and metal composite clusters by using synthesis techniques developed at Argonne that are based on gas-phase physical cluster fabrication. The work also includes state-of-the-art characterization to allow a more thorough understanding and improved design of the new materials.

Mission Relevance

The research is tied to DOE's missions in energy and science. The project involves design of new catalytic materials through optimization of their size and composition at the sub-nanometer scale and fine-tuning of their properties via electrochemical potential. The work represents a fundamental new approach to solving energy-related problems by identifying environmentally friendly and efficient catalysts for the production of fuels and improved energy storage.

FY 2012 Results and Accomplishments

We performed an extended series of tests on the stability and electrochemical activity of size-selected cobalt, palladium, and nickel clusters and characterized their chemical composition before and after reaction. We also studied the thermal stability of select promising cobalt/support combinations at elevated temperatures both in inert gases and in an oxygen-containing atmosphere. We chose ultrananocrystalline diamond (UNCD) film, as well as a variety of oxides (e.g., iron oxide [FeO_x], zinc oxide [ZnO], titanium dioxide [TiO_2], and magnesium oxide [MgO]), as support materials for these studies. To avoid agglomeration of clusters upon deposition, we deposited clusters at an atomic coverage as low as 0.1 monolayer. X-ray absorption spectra revealed that, after their exposure to air, the as-deposited clusters turned into oxides. X-ray scattering data revealed the high stability of the clusters; they withstood thermal treatment for several hours without noticeable signs of agglomeration/size change.

Next, we examined the activity of the clusters in an electrochemical cell, under oxygen evolution reaction conditions, as a function of metal (oxide), cluster size, and composition of the support. Figure 1 shows the strongly size-dependent activity of sub-nanometer size clusters. Interestingly, the smallest-size 4-atom clusters seem to heal the support by quenching the activity of the active sites in UNCD; this reaction may extend the lifetime of the support. The activity of the larger clusters places them among the best-performing electrocatalytic materials reported to date. X-ray characterization indicates that, in terms of size as well as oxidation state, the sub-nanometer clusters are stable. To our knowledge, this is the first demonstration that subnanometer clusters can be used under harsh electrochemical conditions and that the performance of the electrocatalyst can be tuned by varying the cluster size and composition of the support.

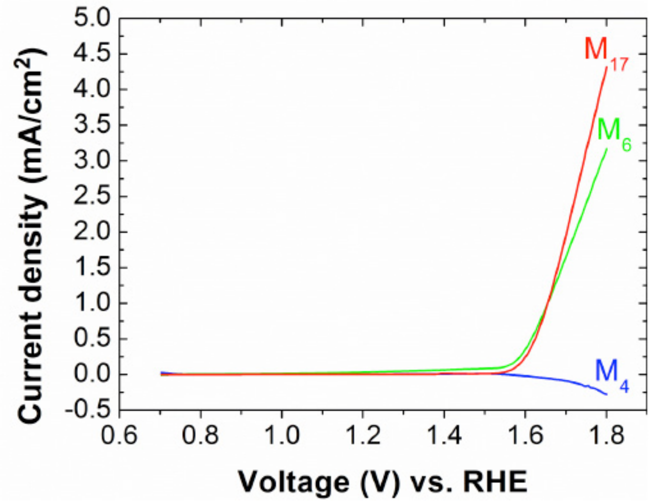


Figure 1. Performance of size-selected clusters on UNCD showing background corrected (i.e., after subtraction of the current of the blank UNCD support) currents normalized for the cluster covered area. (RHE = reference hydrogen electrode.)

During FY 2012, we designed a special *in situ* reaction cell that allows us to apply an external electric field under gas-phase heterogeneous conditions. The initial test of the apparatus, performed in the presence of water vapor, shows that the charge/oxidation state of the clusters can be tuned by applying an external field; the results are reflected in the electrocatalytic performance of the clusters: as a function of the external electrical bias applied, we observed a change in catalytic activity and selectivity.

Proposed Work for FY 2013

We will extend the studies conducted thus far to identify the most promising clusters and support materials by optimizing the size and composition of the clusters, as well as the composition and morphology of the support materials. We will also continue our studies of the effect of the external electric field on the yield and selectivity of the catalyst as a function of cluster material, cluster size and shape, and field strength.

Research and Development of Advanced Energy Storage Methodologies

2011-212-R1

Dieter M. Gruen

Project Description

Materials breakthroughs are required in storage and conversion methodologies to help bring about the large-scale, economical use of sustainable energy sources. Both of these areas can benefit substantially from new research and development (R&D) efforts in nanocarbon materials. As a result of pioneering work in the field of nanocarbons, which culminated in the discovery of ultrananocrystalline diamond (UNCD) films, we are developing a new class of mechanically and thermally stable, highly electrically conducting nanocarbon materials. The materials consist primarily of hollow polyhedral stacks of 5–7 graphene sheets enclosing volumes of 300–500 cubic nanometers. These unique nanocarbon structures have the potential to function as high-performance cathodes in lithium-air batteries; thus we have measured the storage capacity of this material in a cell. We discovered that the high storage capacity, near 5-kWh/kg carbon, when coupled with the temporally remarkably stable electrochemical potential (3.38–2.8 V), warrants detailed study to enable us to optimize the performance of such cathodes. The considerable challenges that must be overcome to make lithium-air batteries viable include, but are not limited to, controlling the porosity of the electrode for higher storage capacity, designing catalysts for improving the charge and discharge kinetics, developing electrolytes that resist the aggressive chemical environment of the cell and reduce the overpotential, and preventing lithium dendrite formation.

Experiments conducted during this project will yield data on new nanocarbon material called ultrananocrystalline graphene (UNCG). Specific results will include the clarification of the interrelationship among capacity, discharge current, and voltage, which will enable the optimization of the performance of this material. In addition, the project will result in high-resolution transmission electron microscopy (HRTEM) characterization of UNCG composition, synthesis conditions, and annealing temperatures. The research is also expected to result in the correlation of (1) the details of the carbon nanostructure with the location, confinement, and composition of the discharge product; and (2) the details of the reaction of lithium peroxide (Li_2O_2) with electrolytes, the carbon support, and encapsulated catalyst particles.

Other important outcomes of the project will be findings from an evaluation of the stability of various electrolytes, particularly ionic liquid electrolytes, with respect to attack by Li_2O_2; identification of electrochemical intermediates and gaseous charging products; and determination of the effect of electrolytes on the morphology of electrodeposited lithium.

An important question concerning the use of ionic liquids as electrolytes involves the preservation of high diffusion coefficients, which are compromised by structuring effects due to the presence of lithium ions. As a result of the proposed research, we expect to gain an understanding of the effect on the overpotential of bringing manganese dioxide (MnO_2) into more intimate contact with Li_2O_2 by making use of the unique nanostructure of UNCG. On the basis of this understanding, we will be able to maximize the overall efficiency of energy storage in lithium-air batteries.

Mission Relevance

The proposed project is relevant to DOE's missions in energy and national security. When coupled with a new generation of electrolytes, bulk nanocarbons are expected to advance the search for high-capacity rechargeable lithium-air batteries. The prosperity and, indeed, the survival of our complex technological civilization depend on the availability of economical energy. In particular, energy in the convenient form of electricity is highly desirable and in demand in ever-increasing amounts, making the project particularly interesting to several national laboratories that are conducting R&D on sustainable energy efforts in general and on problems related to storage and generation in particular. This project will help to create novel storage materials that are expected to demonstrate breakthrough performance characteristics, which will be of high value to DOE, the nation, and the international community.

FY 2012 Results and Accomplishments

Quantitative studies were carried out on the growth kinetics of the catalytic reaction of methane at 1,000–1,200 K with nanoparticles of cubic silicon carbide (SiC). Our earlier work revealed that this reaction results in the formation of graphene layers surrounding the SiC particles.

The follow-on work conducted during FY 2012 was designed to elucidate the growth mechanism of this highly unusual and important reaction that results in graphene formation at very moderate temperatures. These extensive studies involved taking weight gain measurements after exposure of SiC nanopowders to methane for periods ranging from minutes to many hours. Detailed analysis of the data revealed a layer-by-layer growth mechanism and first-order growth kinetics. A very important conclusion of this study is that the number of graphene layers can be closely controlled — to within 1 or 2 monolayers in a range of 1 to 20 layers — by varying the length of time the reaction is allowed to proceed. The number of graphene layers deposited was monitored quantitatively by using HRTEM.

We also completed quantitative studies to investigate sulfur sequestration in 20-layer graphene on SiC powders. These highly porous materials sequester up to three times their weight in elemental sulfur and are potentially of interest in energy storage applications for lithium/sulfur batteries. Very limited studies have been carried out on these substances to determine their storage capacity using the MACCOR battery and cell test facility, which is designed to measure the current-voltage (IV) characteristics of a coin cell as a function of charge/discharge time. The results of these studies are fragmentary and do not lend themselves to interpretation in terms of cell efficiency.

This work resulted in the following invention:

- Gruen, D., "High Performance Lithium/Sulfur Batteries by Optimizing the Pore Connectivity, Size and Volume or Ordered Mesoporous Nanocarbons." Invention report filed December 2011. [ANL-IN-11-130].

Biofuel Chemical Kinetic Experiments to Advance the Modeling of Advanced IC Engine Combustion

2012-203-N0

S. Scott Goldsborough

Project Description

The objective of this project is to initiate a research program to acquire the necessary experimental data that are of sufficient fidelity and minimal uncertainty that will help researchers understand and model the decomposition and oxidation pathways of next-generation biofuels at conditions relevant to combustion engines. Advanced low-temperature combustion (LTC) regimes are of particular interest. Accurate, predictive combustion models are necessary to reliably design next-generation fuels and future engines that can meet mandated fuel economy and emission standards while reducing development times and costs for new configurations. Biofuels could enable carbon-neutral energy utilization.

In this project, a unique rapid compression machine (RCM) will be designed, fabricated, and validated. An RCM is being pursued because it can create and maintain well-controlled, elevated temperature and pressure environments (e.g., T = 600–1100 K, P = 5–80 bar), where the chemically active period preceding autoignition can be monitored and probed via advanced *in situ* and *ex situ* diagnostics. The ability of RCMs to use wide ranges of fuel and oxygen concentrations — that go from ultra-lean to over-rich (e.g., equivalence ratio = 0.2 to 2.0+) and span dilute to oxy-rich regimes (e.g., O_2 = 5 to >21%) — gives them advantages over other laboratory apparatus, such as shock tubes and flow reactors, for which complications can arise under such conditions. The RCM will have an integrated gas sampling and gas chromatograpy/mass spectrometry (GC/MS) analytic unit to resolve the stable intermediate molecules that form during ignition processes. A novel aerosol fueling system will also be fabricated in order to prepare gas-phase fuel + oxygen + diluent mixtures of involatile, diesel-representative fuels. We expect that the distinctive features of this apparatus will allow critical data for emerging biofuels and other fuels to be acquired.

Mission Relevance

This project is relevant to DOE's missions in energy and science. This project simultaneously addresses DOE goals of increasing national energy security through renewable fuel development and reducing transportation sector emissions and fuel consumption. It is directly related to the advanced biofuel mandates defined in the Energy Independence and Security Act (EISA) of 2007. The project specifically responds to the critical need to optimize the combustion behavior of biofuels while also ensuring that biofuels produced from non-agriculture-based biomass are compatible with the combustion characteristics of petroleum-based fuels. This research addresses the need to integrate the efficient production of biofuels with the design of highly efficient and ultra-low-emission engines. Historically, combustion regimes (and thus overall engine designs) have been dictated by feedstock-defined fuel properties. By concurrently tailoring fuel properties and engine performance, the full potential of the energy source (fuel) and conversion device (engine) can be realized.

The success of this project will provide a link between established combustion programs at Argonne sponsored by DOE: DOE's Office of Science Basic Energy Science (SC-BES) programs and DOE's Office of Energy Efficiency and Renewable Energy Vehicle Technology Program (EERE-VTP). At the highest levels of DOE, significant efforts are under way to connect fundamental and applied research; combustion science and technology is ready for improved interactions. An example is the Predictive Simulation for Internal Combustion Engines (PreSICE) initiative. Both the U.S. Department of Defense and National Science Foundation have a significant interest in biofuels and combustion chemistry in general; the ability to provide accurate combustion data and models for alternative fuels is very relevant to them.

FY 2012 Results and Accomplishments

This project started late in the fiscal year. The new machine was designed (Figure 1), and a safety review of it is under way. A series of reduced-order models for the RCM were developed, and some were validated by using detailed simulations (e.g., computational fluid dynamics) and comparison with experimental data from existing facilities shared by collaborators. The intent is to describe the physical processes that occur during experiments. The models will be used to provide insights into the operational characteristics of the apparatus and reduce uncertainties associated with the experimental data and modeling of the chemical kinetic processes.

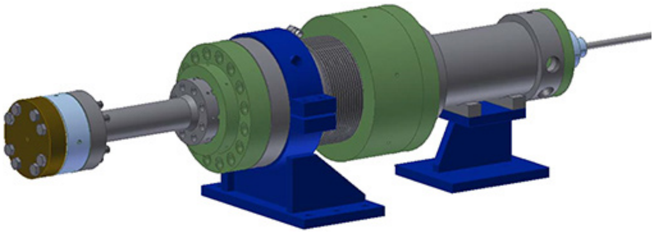


Figure 1. Schematic of the RCM.

Proposed Work for FY 2013

The RCM will be fabricated and its components tested. Experiments with "model" fuels will be conducted to validate its operation and assess the performance of the reduced-order, physics-based models. iso-Octane is an example of a "model" fuel where a significant database for this currently exists in the literature, and it is currently being used as a test specimen for the International RCM Workshop. Measured ignition delay times will be compared against published data, and pressure-time records will be compared to the RCM Workshop database. Reduced-order models will be evaluated by using measurements from the new machine, including reaction chamber, hydraulic and pneumatic pressures, and instantaneous piston position.

Seminars

Goldsborough, S.S. (2012). "Autoignition Studies to Support Advanced Engine and Fuel Co-development." University of Leeds, Leeds, UK, July 3, 2012.

Goldsborough, S.S. (2012). "Future Fuels for Future Engines: Applications with RCMs." Combustion Chemistry Centre, National University of Ireland Galway, Galway, Ireland, November 24, 2011.

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Goldsborough, S.S. (2012). "Combustion Behavior of Transportation-relevant Fuels." Center of Tailor-Made Fuels from Biomass, RWTH Aachen University, Aachen, Germany, January 26, 2012.

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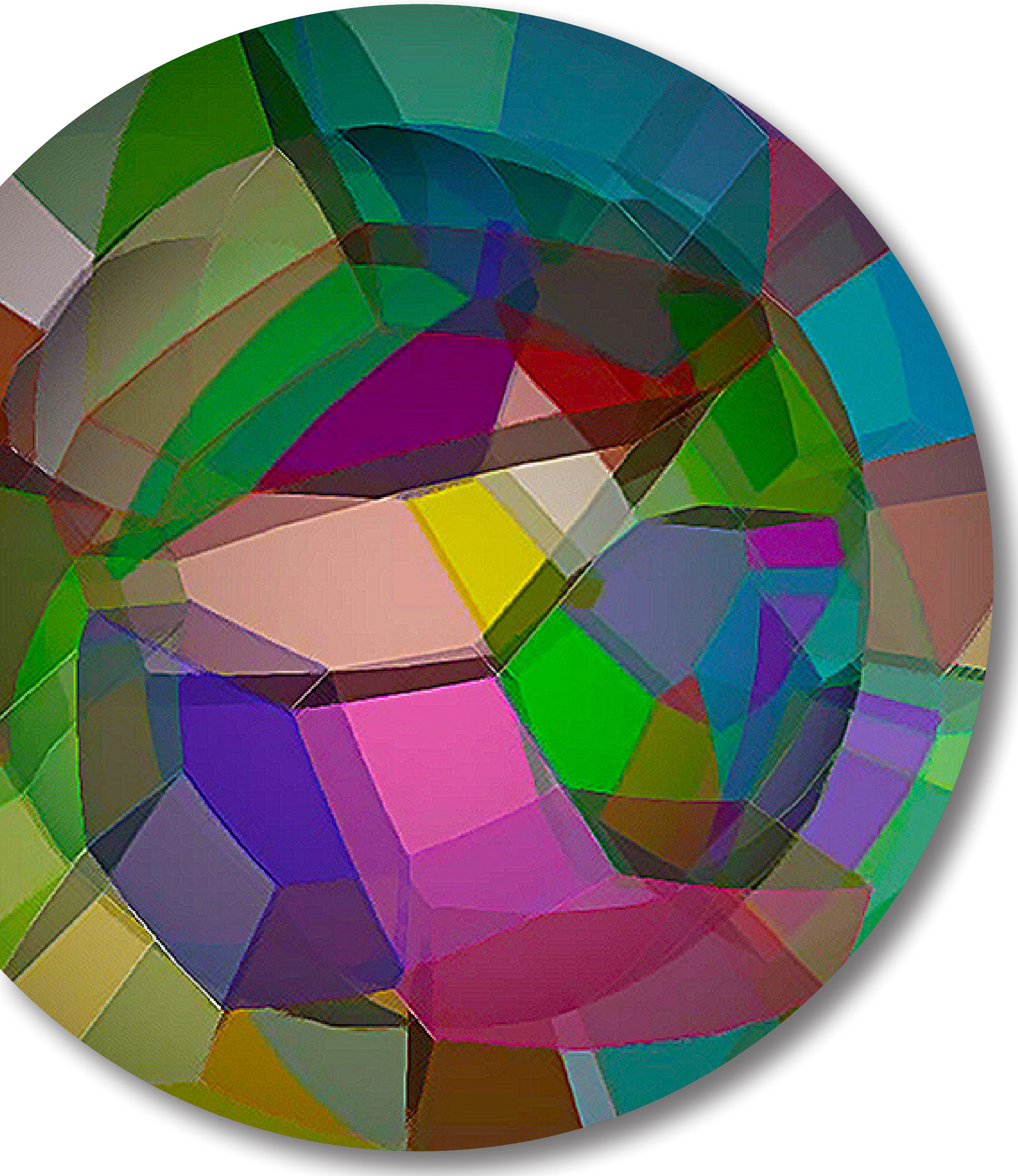
OTHER NOVEL R&D



Multifunctional Polymers for Regulating Membrane Function

2011-202-R1

Millicent A. Firestone and Simonida Grubjesic

Project Description

The goal of this work is to design and synthesize biologically inspired multifunctional polymers that target selected signal transduction pathways and induced changes in biomembrane structure and function. The main objectives of the proposed work are (1) to generate synthetic polymers that interact with natural (living) systems in a predictable fashion by regulating natural communication pathways and (2) to harness the fundamental principles of quorum sensing for the dynamic assembly and reconfiguration of materials. Ultimately, this research will help establish the link between synthetic polymer-induced changes in biomembrane physicochemical characteristics and cell biochemistry. If this connection can be successfully made, these findings will represent a significant advance in using synthetic polymers for the inhibition/regulation of chemical communication and signal transduction.

Mission Relevance

This project is relevant to DOE's basic science mission. The research focuses on addressing one of the DOE-identified grand challenges in soft materials, "design principles for the synthesis of self-assembled materials." In this multidisciplinary research project, basic physical sciences (synthesis and characterization of bioactive polymers) are coupled with life sciences. This scientific effort offers the unique opportunity to advance soft materials research and further enhance the biomolecular materials effort directed at solving energy-related challenges.

FY 2012 Results and Accomplishments

Prior work examining the insertion of non-functionalized polymers into model membranes formed the basis for the current work.

We synthesized and characterized polymers that regulate chemical communication (quorum sensing) between prokaryote cells. Triblock copolymers that intercalate into lipid bilayers, producing a poly(ethylene oxide) (PEO) surface coat, were found to function as a barrier against pathogen adsorption. Chemical tailoring of the copolymer by appending phosphate groups on the terminus of the PEO blocks was found to regulate the *Pseudomonas aeruginosa* quinolone signal (PQS) biochemical pathway, thereby shifting the behavior of bacteria from that of a lethal pathogen to an indolent colonizer.

We investigated meso- and nano-scale interactions between the chemically modified block copolymers and model biological membranes by means of small-angle x-ray scattering studies performed at the Advanced Photon Source. These studies revealed that the terminally appended charged phosphate moieties significantly alter polymer membrane (lipid bilayers) interactions (Figure 1). Specifically, the terminal phosphates caused greater extension of the PEO blocks into the aqueous phase. The reduction in lateral PEO block entanglement and physical cross-linking causes loss of macroscopic gelation. The expanded PEO blocks will most certainly affect the barrier function of the polymer. We predict that the phosphate-functionalized polymers may not prevent bacterial association on cell surfaces as well as the hydroxyl-terminated polymers. The ionization state of the phosphate groups was determined to be pH dependent. At high pH, the phosphate moiety is fully deprotonated (i.e., in the diacid form), and thus PEO chain extension can be minimized. At low pH, a fully protonated state is achieved that causes the greatest expansion of the PEO chains. While the lipid bilayer polymer interactions are altered by the ionization state of the phosphate groups, they were determined to substantially attenuate the virulence of *P. aeruginosa*, thereby demonstrating that delivery of an organophosphate serves as an effective exogenous nutrient and imparts anti-virulence characteristics to the polymer.

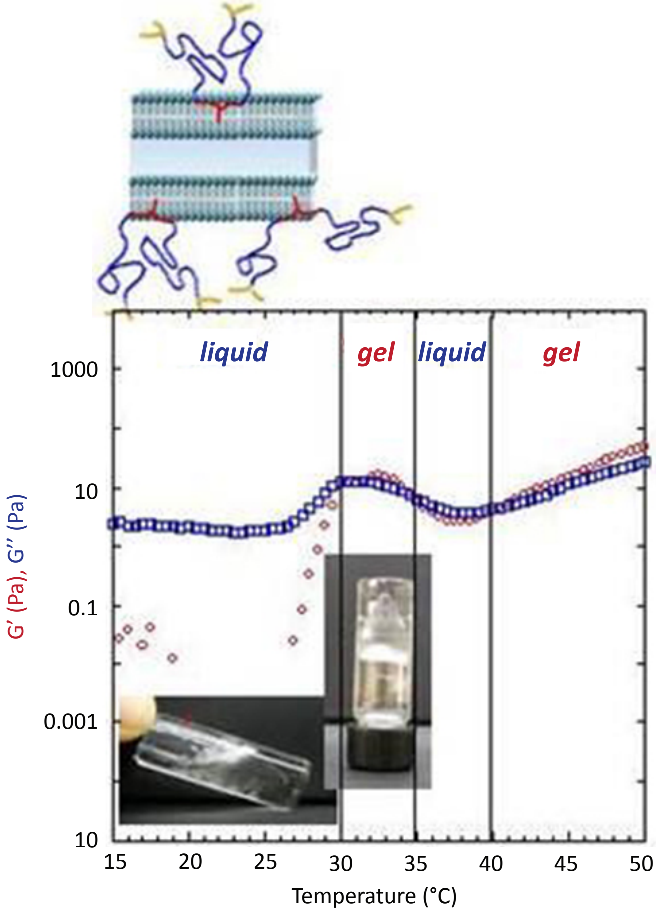


Figure 1. Grafting terminal phosphate groups reduces block copolymer – lipid bilayer interactions. The figure shows the dynamic rheological profile of the polymer's temperature dependence within a model membrane. Phosphate end groups serve to diminish laterally crosslinked ethylene oxide (EO) blocks.

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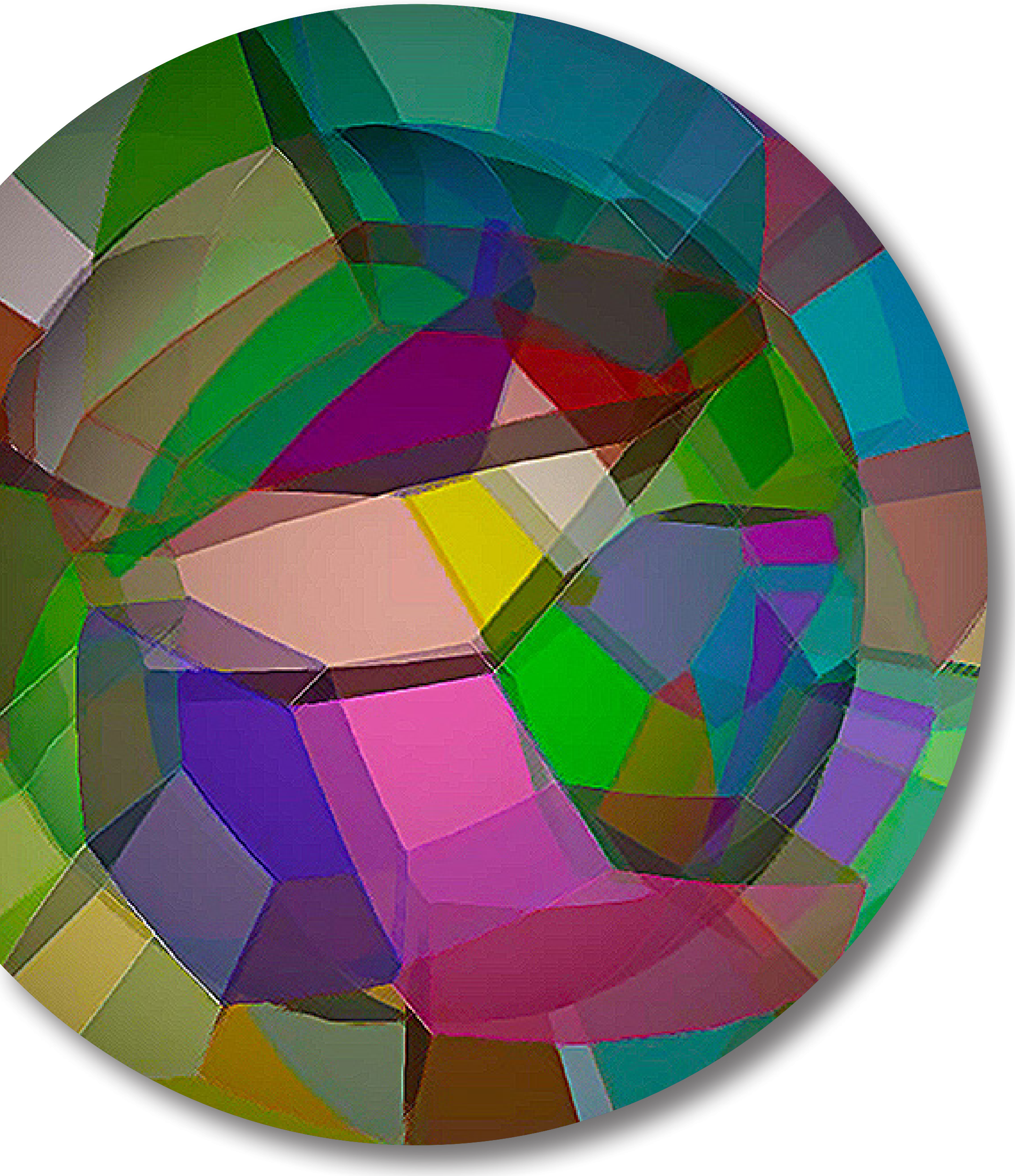
APPENDIX



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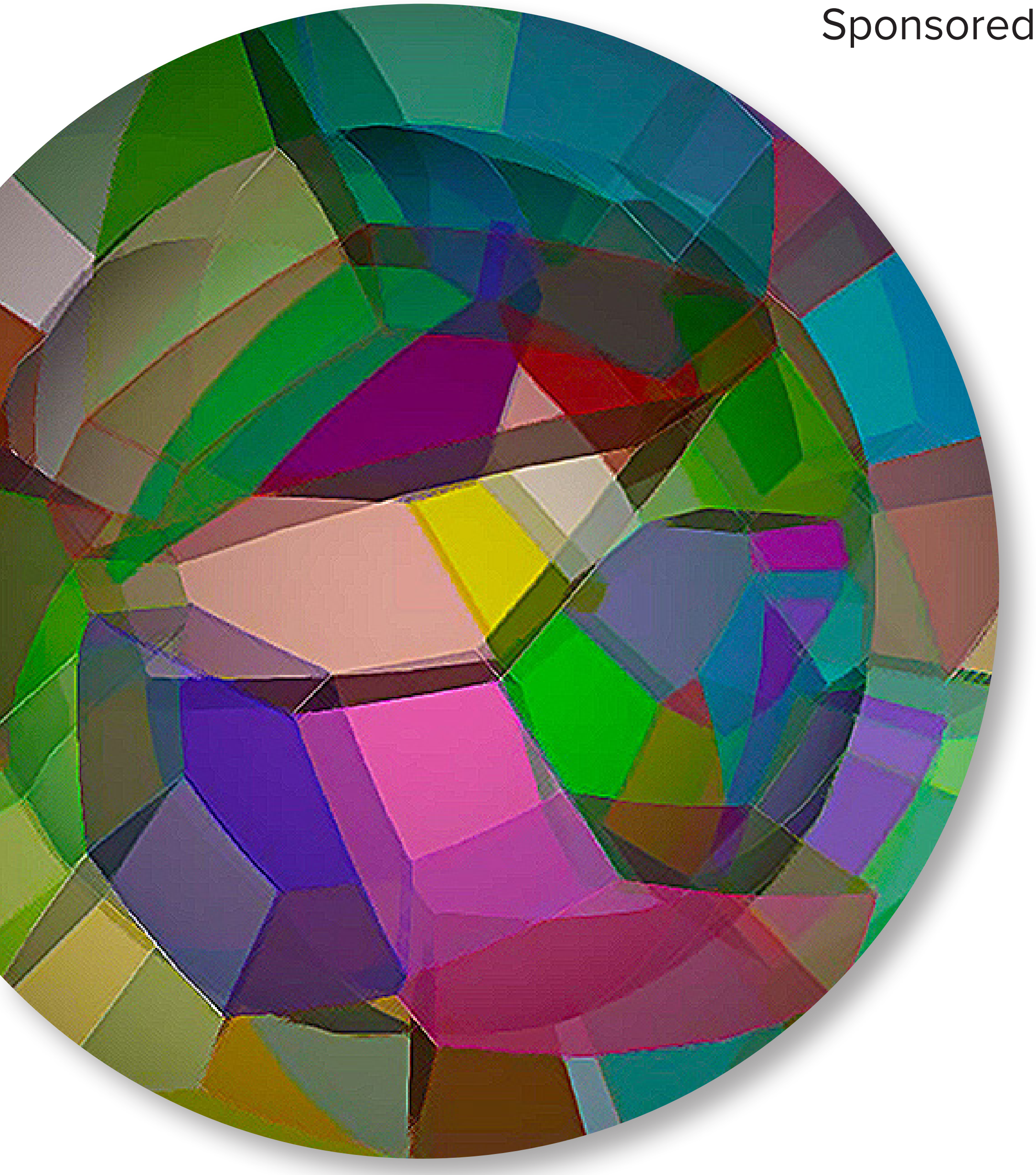
INTELLECTUAL PROPERTY EVENTS OCCURRING IN FY 2012

(As a Result of LDRD Projects
and Subsequent Related
Sponsored Research)



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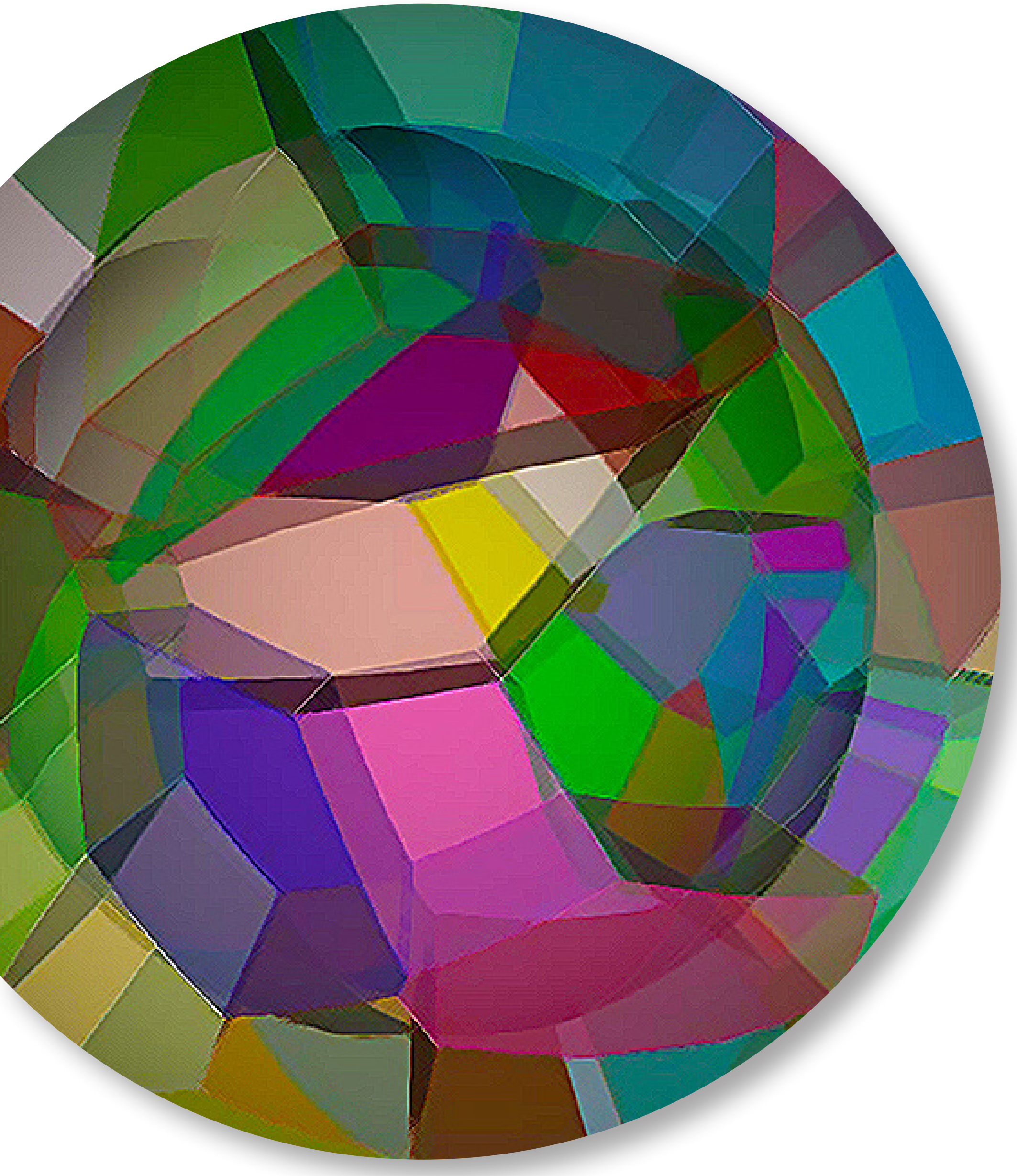
(Derived from LDRD Projects Active in FY 2012)



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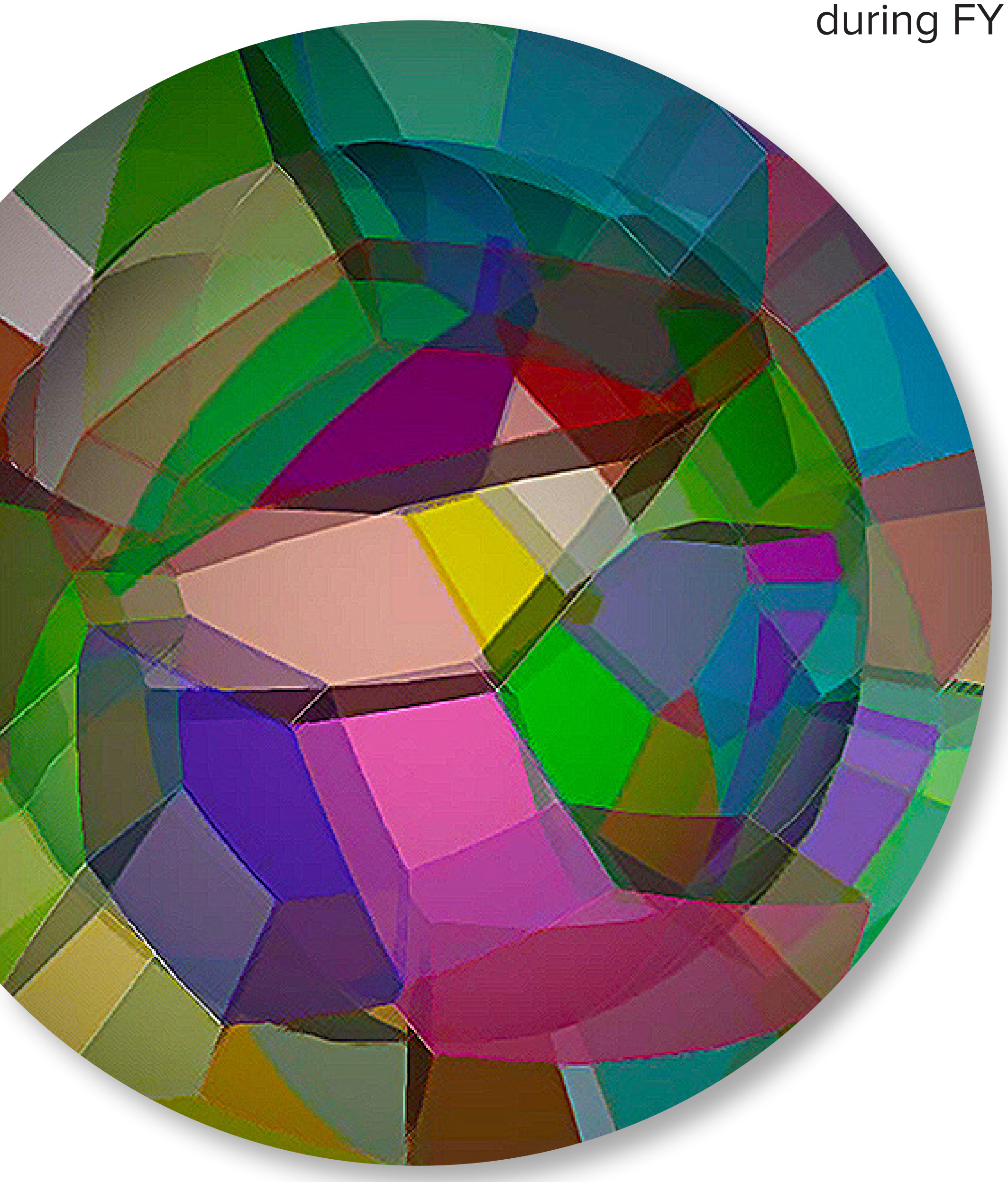

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*Note: For information regarding projects listed here, see annual reports from previous years. *Indicates refereed publication*

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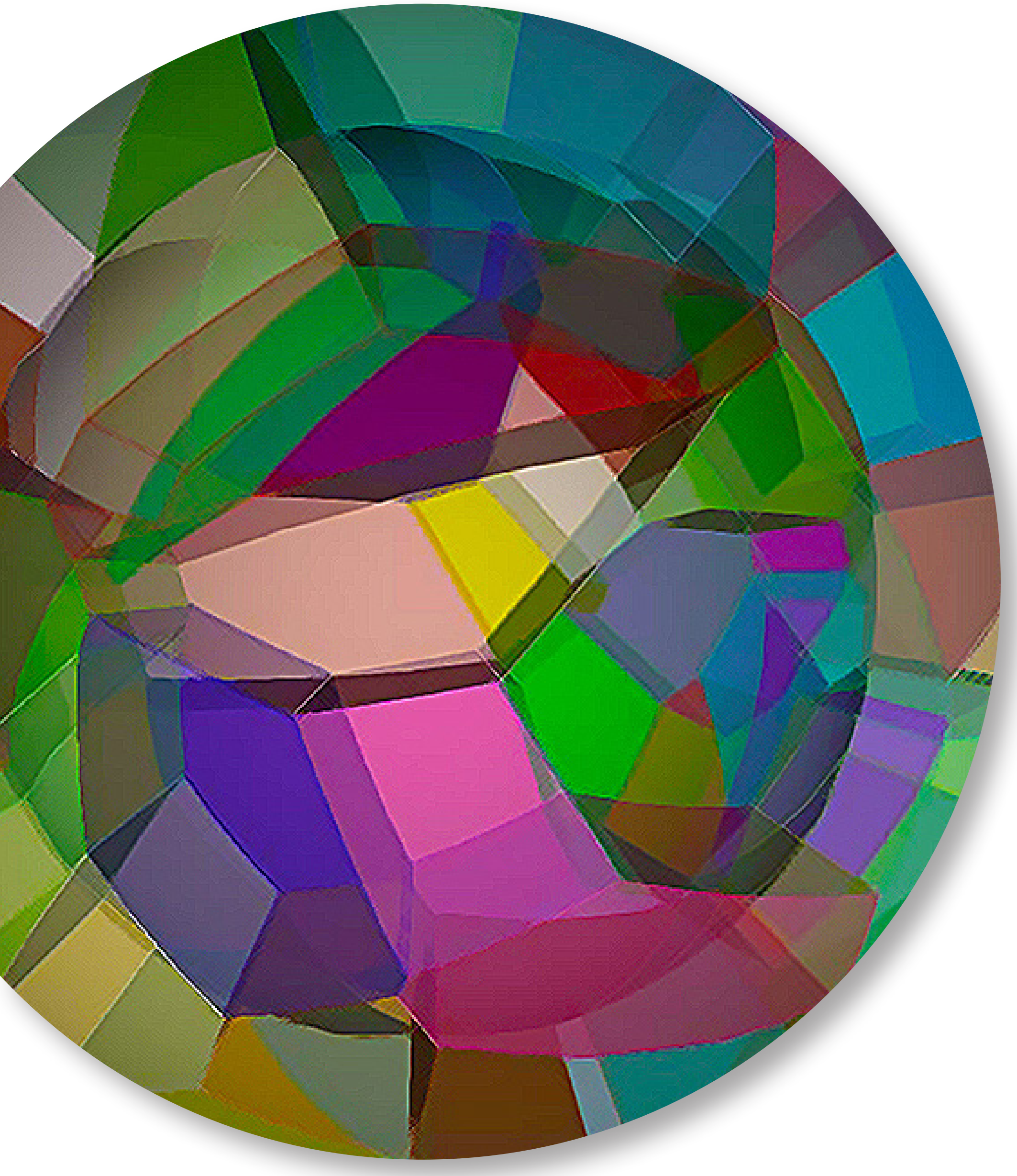

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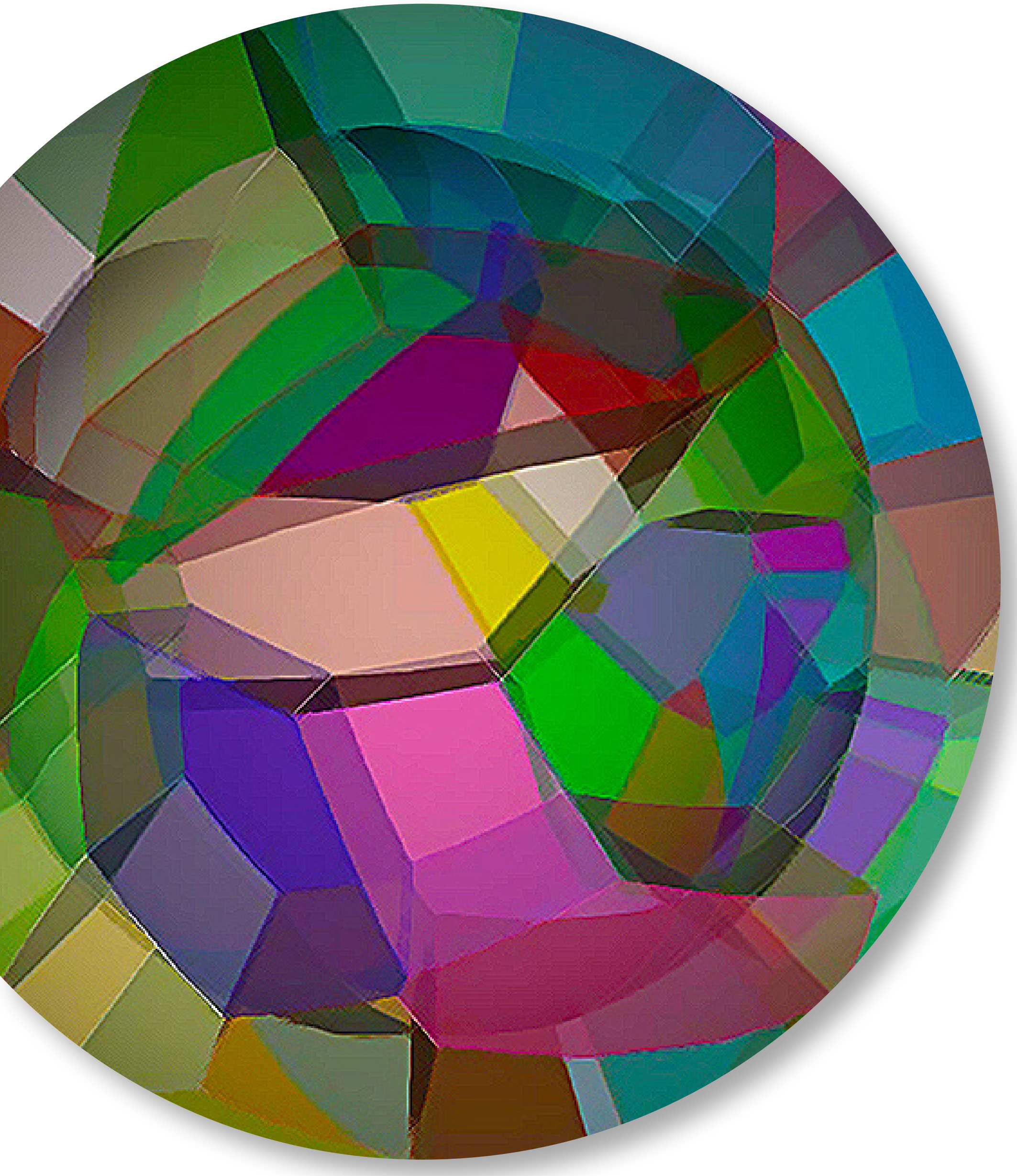

FY 2013 New Start Projects

LDRD #	Project Title	Lead Investigator
2013-013	Improving the Stability of Rubisco Activase, the Weak-link, in the Biological CO_2 Fixation Machinery	Phani Pokkuluri, BIO
2013-016	Spin-based Thermal Power Generation	Axel Hoffmann, MSD
2013-022	Superlubricious Carbon Films Derived from Natural Gas for Home-Refueling Applications	Ali Erdemir, ES
2013-035	Extreme Optomechanics	Matthew Pelton, CNM
2013-036	Development of Near-Field Enhanced Terahertz Pump X-ray Probe Techniques for Ultrafast Control of Strongly Correlated Materials	Haidan Wen, XSD
2013-063	Visualization of Stress-Induced Polarization Switching in Electromechanically Coupled Ferroelectric Polymers	Seungbum Hong, CNM
2013-070	Imaging Ecological Engineers: A Novel Quantum Dots Approach to Map Microbes in Complex Soil Structures with X-rays	Sarah O'Brien, CELS
2013-080	Ultra-Low Loss Superconducting Microstrip for Multi-Chroic Cosmic Microwave Background Detectors	Gensheng Wang, HEP
2013-096	Graphene Windows for Advancing Electron RF Guns	Chun-xi Wang, ASD
2013-100	3-D Compositional Control of Intermediate-Band Solar Cells	Alex Martinson, MSD
2013-111	Feasibility Study of Applying Thin Film High-Temperature Superconducting Films on Copper or Niobium-Sputtered-on-Copper for the Purpose of Achieving Helium-Free Operation with Cryocoolers	Alireza Nassiri, ASD
2013-114	Electromagnetic Variably Polarizing Undulator (EMVPU): Developments of the Test Model	Mark Jaski, ASD
2013-116	Nanolaminate Coatings for Improved Nuclear Fuel Cladding Performance	Michael Pellin, PSE
2013-129	Probing Magnetic Excitations in a Quantum Spin Liquid by Resonant Inelastic X-ray Scattering	Bumjoon Kim, MSD
2013-143	Next-Generation Storage Ring Light Sources	Michael Borland, ASD
2013-148	Development of Predictive Multi-Dimensional Combustion Modeling Capability with Detailed Chemistry	Sibendu Som, ES
2013-152	Nanolaminate Materials for Extreme Environments – A Demonstration of Argonne Capabilities for Design, Synthesis and Accelerated Testing of Radiation Tolerant NE Materials	Michael Pellin, PSE
2013-154	Atomic Layer Deposition System for Continuous, High Speed Thin Film Processing	Joseph Libera, ES

FY 2013 New Start Projects (continued)

LDRD #	Project Title	Lead Investigator
2013-156	Fast High-Efficiency Process to Fabricate Aligned Nanotubes in Nano-Composite Membranes for High-Performance Filtration Applications	Richard Brotzman, ES
2013-165	Integrating Simulation and Observation: Discovery Engines for Big Data	Ian Foster, CELS
2013-168	The Tao of Fusion: Pathways for Big-Data Analysis of Energy Materials at Work	Chris Jacobsen, XSD
2013-171	Unconventional Signatures for Characterizing Culture Conditions	Daniel Schabacker, ES
2013-173	Ratiometric Semiconductor Nanocrystal-Based Sensors for Threat Reduction Applications	Richard Schaller, CNM
2013-177	Identifying Novel Pathways for Anaerobic Microbial Oxidation of Methane	Edward O'Loughlin, BIO
2013-178	Uranium and Plutonium Detection by Plasmonic Graphene-Based Nanosensors	Giselle Sandi-Tapia, CSE
2013-184	Hierarchical Modeling of Self Assembly in Nanostructured Soft Materials at Equilibrium and Far from Equilibrium	Stephen Streiffer, PSE
2013-185	Electrochemical Materials Discovery: from Performance to Stability	Peter Beckman, CELS
2013-194	Annotating, Modeling, and Exploring Enzyme Promiscuity	Christopher Henry, MCS
2013-196	Bridging the RAST Annotation and the Structural Genomics Pipelines at Argonne	Gyorgy Babnigg, BIO
2013-199	MADNESS for Materials	Nichols Romero, LCF
2013-200	Exploring a New Approach for Parallel Programming at Exascale	Peter Beckman, CELS
2013-202	Computational Molecular Science	Gregory Voth, CELS
2013-206	Mathematical Techniques to Model Urban Data	Charlie Catlett, MCS
2013-208	General-Purpose Technical Cloud Platforms	Narayan Desai, MCS
2013-210	Dynamic Data Mirroring for Data-Intensive Science	Ian Foster, CELS
2013-212	Multiscale Materials Modeling Using Accurate *Ab Initio* Approaches (M3A3)	Jeffrey Hammond, LCF

FY 2013 New Start Projects (continued)

LDRD #	Project Title	Lead Investigator
2013-213	X-PECT: Performance Framework to Characterize and Transform Applications and Architectures at Extreme Scales	Kalyanasundaram Kumaran, LCF
2013-214	Computational Mesoscale Materials Modeling	Dieter Wolf, MSD
2013-215	Mesoscale Materials by Design from Assemblies of Ionic Polymers and Nanoparticles	Derrick Mancini, PSE
2013-216	Directed Assembly and Three-Dimensional Characterization of Block Copolymers in Semi-Thick Films	Paul Nealey, MSD

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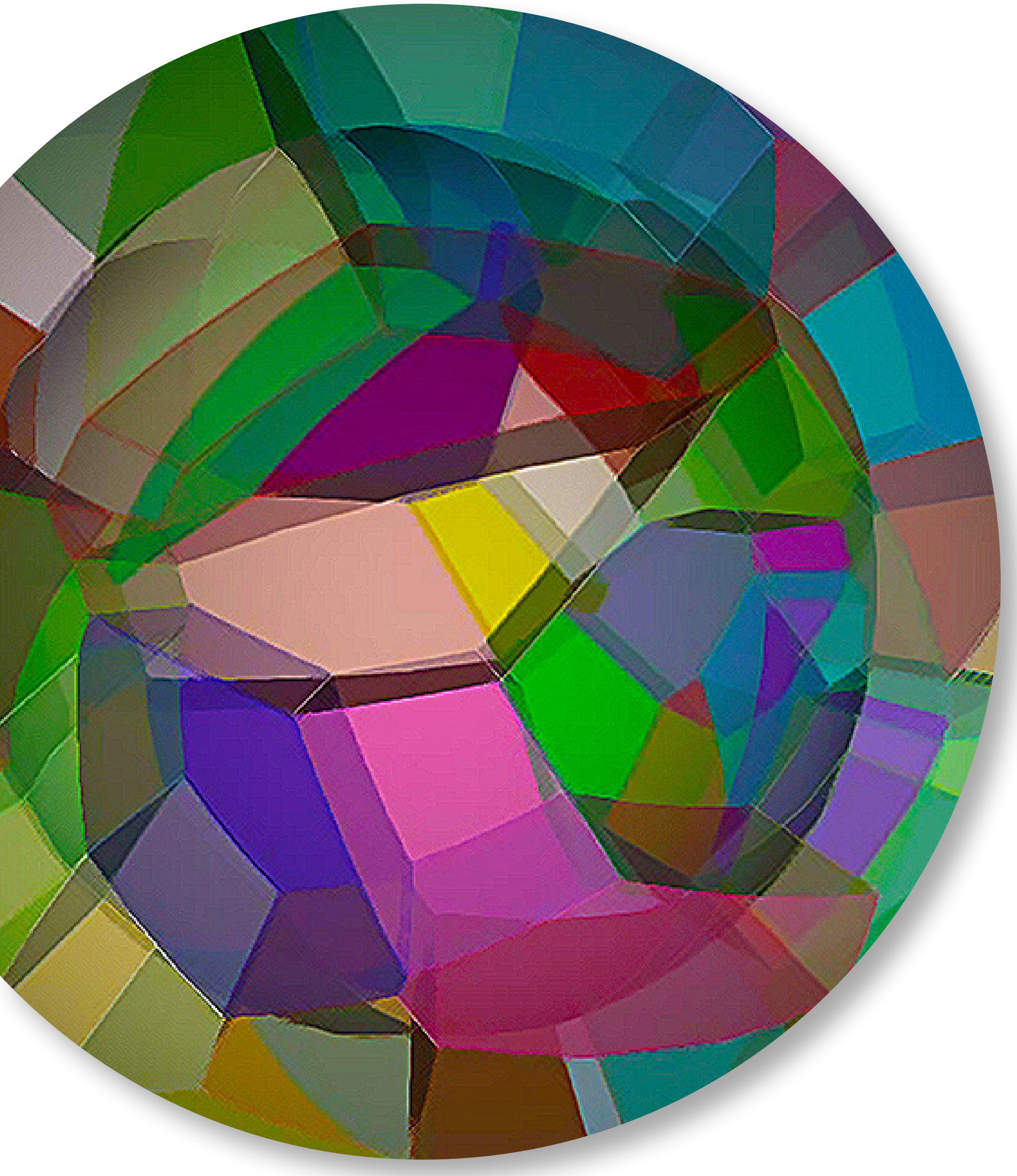
ARGONNE ORGANIZATIONS – ABBREVIATIONS



Argonne Organizations – Abbreviations

ASD	APS Accelerator Systems
BIO	Biosciences
CLS	Computing, Environment, and Life Sciences
NST	Nanoscience and Technology
CSE	Chemical Sciences and Engineering
ES	Energy Systems
HEP	High Energy Physics
LCF	Leadership Computing Facility
MCS	Mathematics and Computing Science
MSD	Materials Science
PSE	Physical Sciences and Engineering
XSD	APS X-Ray Science

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