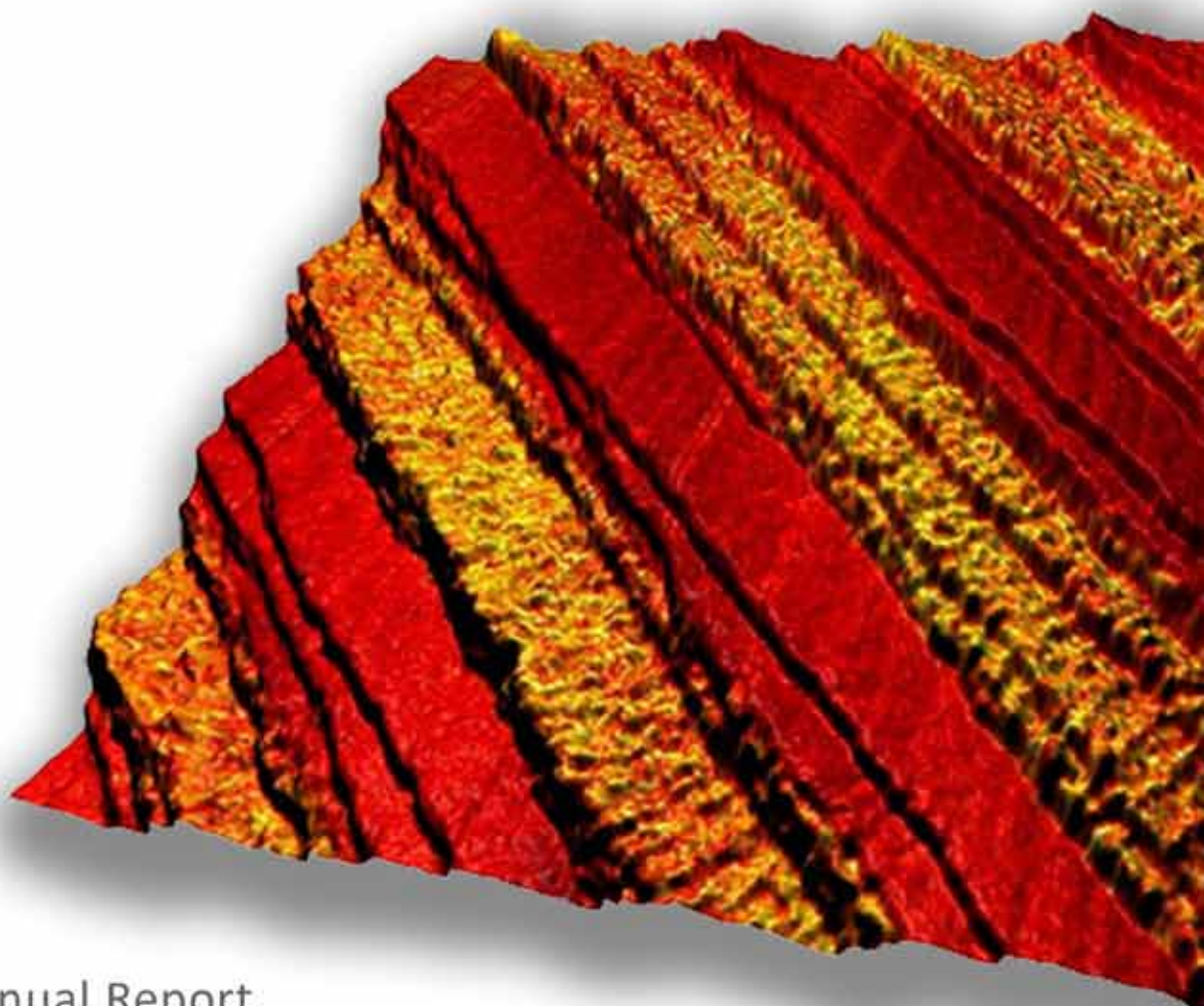


LDRD

Laboratory Directed Research and Development Program Activities

OFFICE OF THE DIRECTOR

March 2010



FY2009 Annual Report

ANL-10/08

A scanning tunneling micrograph (STM) showing a striped pattern. The stripes are diagonal, running from the top-left towards the bottom-right. They vary in intensity, with some appearing darker and some lighter, creating a textured, almost wood-grain-like appearance. The background is a light, grainy grey.

ON THE COVER

This scanning tunneling micrograph shows the striped pattern that results from fracturing a strontium titanate crystal along one of its crystallographic planes. The stripes reflect the difference between regions where a strontium oxide versus a titanium oxide layer is the last one at the surface. For details, see the project report of Freeland and Guisinger (2009-083-N0) on page 37.

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.

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I am pleased to submit Argonne National Laboratory's Annual Report on its Laboratory Directed Research and Development (LDRD) activities for fiscal year 2009. Fiscal year 2009 saw a heightened focus by DOE and the nation on the need to develop new sources of energy. Argonne scientists are investigating many different sources of energy, including nuclear, solar, and biofuels, as well as ways to store, use, and transmit energy more safely, cleanly, and efficiently. DOE selected Argonne as the site for two new Energy Frontier Research Centers (EFRCs) — the Institute for Atom-Efficient Chemical Transformations and the Center for Electrical Energy Storage — and funded two other EFRCs to which Argonne is a major partner. The award of at least two of the EFRCs can be directly linked to early LDRD-funded efforts. LDRD has historically seeded important programs and facilities at the lab. Two of these facilities, the Advanced Photon Source and the Center for Nanoscale Materials, are now vital contributors to today's LDRD Program. New and enhanced capabilities, many of which relied on LDRD in their early stages, now help the laboratory pursue its evolving strategic goals.

LDRD has, since its inception, been an invaluable resource for positioning the Laboratory to anticipate, and thus be prepared to contribute to, the future science and technology needs of DOE and the nation. During times of change, LDRD becomes all the more vital for facilitating the necessary adjustments while maintaining and enhancing the capabilities of our staff and facilities.

Although I am new to the role of Laboratory Director, my immediate prior service as Deputy Laboratory Director for Programs afforded me continuous involvement in the LDRD program and its management. Therefore, I can attest that Argonne's program adhered closely to the requirements of DOE Order 413.2b and associated guidelines governing LDRD. Our LDRD program management continually strives to be more efficient. In addition to meeting all reporting requirements during fiscal year 2009, our LDRD Office continues to enhance its electronic systems to streamline the LDRD management process.

You will see from the following individual project reports that Argonne's researchers have once again done a superb job pursuing projects at the forefront of their respective fields and have contributed significantly to the advancement of Argonne's strategic thrusts. This work has not only attracted follow-on sponsorship in many cases, but is also proving to be a valuable basis upon which to continue realignment of our strategic portfolio to better match the Laboratory's Strategic Plan.

A handwritten signature in black ink, reading "Eric D. Isaacs". The signature is fluid and cursive, with the first letters of the first and last names being capitalized and prominent.

Eric D. Isaacs
Laboratory Director

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 the Office of Energy Efficiency and Renewable Energy (EERE) and the National Nuclear Security Administration (NNSA), and 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 only be addressed through a sustained, interdisciplinary focus at a national scale. Argonne's eight major initiatives, *Hard X-ray Sciences*, *Leadership Computing*, *Materials and Molecular Design and Discovery*, *Energy Storage*, *Alternative Energy and Efficiency*, *Nuclear Energy*, *Biological and Environmental Systems*, and *National Security*, 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
- ▶ Applied Mathematics
- ▶ Biosciences
- ▶ Computational Science

Applied Sciences and Engineering

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

User Facilities

- ▶ The Advanced Photon Source (APS) provides a high-brightness, high-energy electron beam, a unique source of high-energy X-rays for scattering, spectroscopy, and imaging studies with a timing structure that enables time-resolved experiments from picoseconds to seconds.
- ▶ The Center for Nanoscale Materials (CNM) combines advanced scanning probes (including an X-ray nanoprobe); organic, inorganic, and digital synthesis; and nanofabrication — all coupled with theory and modeling.
- ▶ The Electron Microscopy Center (EMC) provides state-of-the-art chromatic-aberration-corrected electron microscopy 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 for low-energy nuclear research. Based on a superconducting linear accelerator, ATLAS provides heavy ions in the energy domain best suited to study the properties of the nucleus.
- ▶ The Argonne Leadership Computing Facility (ALCF) operates one of the largest open-science supercomputers in the world. ALCF offers user access to petascale computing for research in energy systems, catalysis, life sciences, and environmental and basic sciences.

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by project number and by initiative**

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2007-044-R2	Aligned Carbon Nanotube as Pt-Free Electrode Catalyst for Fuel Cell	5
2007-059-R2	Development of <i>in situ</i> Non-Resonant X-Ray Scattering Technique and its Application to Redox Reactions in Battery Materials.....	6
2007-060-R2	Microporous Filters for Hydrogen Purification.....	7
2007-066-R2	Mesoscale Simulation of Blood Flow Using Kinetic Theory	9
2007-068-R2	Sub-Millisecond Measurements of Structural Changes in Materials under Extreme Conditions	10
2007-071-R2	Design and Synthesis of New Nanocarbon Composites from Carbon Nanotubes and Ultrananocrystalline Diamond	12
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2007-080-R2	Identification and Characterization of Ovarian Cancer Stem Cells toward Ultimate Cancer Treatment.....	16
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Acknowledgments

Argonne's LDRD Program Office comprises Associate Chief Scientist for LDRD, Dr. Elton N. Kaufmann, LDRD Program Manager, Cynthia Sullivan and Administrative Assistant, Rebecca Rank. The Program as a whole reports to the Laboratory Director, Dr. Eric Isaacs, through the Deputy Laboratory Director for Programs, Dr. Mark Peters. Those of us in the Program's management are grateful for the critical support received throughout the year, and particularly while preparing this Annual Report, from the individuals listed below. Special appreciation is, of course, due to the many expert researchers who perform the research and provide their project reports, to the technical and administrative management of Argonne's programmatic divisions within which the R&D is pursued, as well as to the leaders of the Laboratory's LDRD strategic initiative areas, whose vision and understanding of the nation's technological needs help guide and refine the content of Argonne's LDRD portfolio.

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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, to enhance the Laboratory's research and development (R&D) capabilities, and to facilitate the pursuit of the Laboratory's strategic goals. Projects are selected from proposals for creative and innovative R&D studies that require advance exploration before being sufficiently developed for support through normal programmatic channels. Among the aims of the projects supported by the Program are the establishment of engineering proof of principle, the assessment of design feasibility for prospective facilities, the development of instrumentation or computational methods or systems, and the examination of discoveries in fundamental science and exploratory development.

The projects supported by LDRD are distributed across the major mission areas at Argonne, as indicated in the Laboratory's LDRD Plan for FY 2009. 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 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 that correspond 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 multi-program national laboratory and reflects the synergistic manner in which both our LDRD and our programmatic work are pursued.

The FY 2009 DOE-approved funding cap for LDRD was \$30.0 million, or about 5.3% of Argonne's estimated FY 2009 operating plus capital budget. Actual expenditures amounted to \$26.6 million, which includes an overhead levy of approximately 25%. A summary of planned or actual funding profiles for each project active in FY 2009 is provided at the end of this section. Individual brief project reports for FY 2009 comprise the bulk of this document. A list, by title, of new projects begun to date in FY 2010 is provided in the appendix.

LDRD Management Process

Argonne's R&D activities are organized under three Associate Laboratory Directors (ALDs), who oversee the research conducted in some 16 programmatic divisions. At the top of the organization is the Laboratory Director, who is assisted by the Deputy Laboratory Director for Programs and the Deputy Laboratory Director for Operations. This senior management group evaluates the LDRD program annually. 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.

Argonne's FY 2009 LDRD Program consisted of two components: the Strategic Initiatives and the Director's Competitive Grants (DCG) (Figure 1). The Strategic Initiatives component funds 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 between the Strategic Initiatives and DCG components. As part of this allocation process, a fraction of the total allowed expenditure may be temporarily reserved to handle mid-year opportunities, strategic hires for LDRD projects, and LDRD collaborative arrangements.

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 below (Figure 2) illustrates the relationships of the management and review processes for the two components of the FY 2009 program.

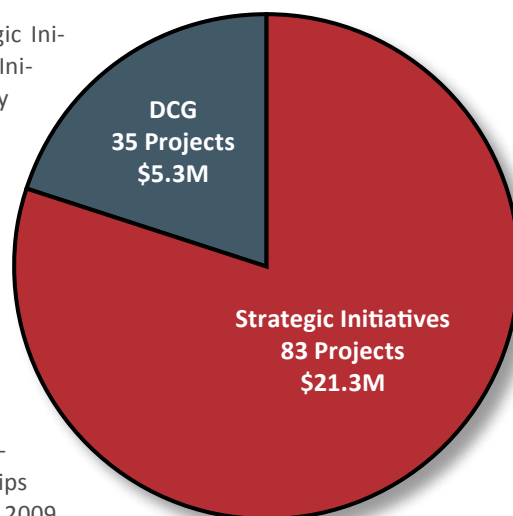


Figure 1. Distribution of FY 2009 LDRD Funds

(Applies to Review and Selection Process for FY 2009 Proposals)



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

The 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 have always been 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. Responsibility for the actual conduct of all Laboratory Directed R&D, including associated environmental safety and health requirements, resides with the ALDs and their line managers.

During FY 2009, all program management requirements were satisfied. Reports required by DOE, including the Annual Report for FY 2008, the LDRD Program Plan for FY 2010, and the project data uploaded to the DOE/CFO database, were submitted in a complete and timely fashion.

Concurrence request forms (also referred to as "data sheets" in relevant guidance documents) were submitted electronically to the DOE Argonne Site Office (ASO) to obtain the DOE site manager's concurrence on a project-by-project basis before proceeding with the FY 2009 LDRD projects.

FY 2009 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 these fields have with existing facilities, capabilities, and staff expertise at Argonne.

The six strategic initiative areas implemented for FY 2009 cover, in part, similar topical areas as in FY 2008, with some changes in terminology and organization, while initiating some new directions as well. The FY 2009 review procedures continued to ensure that all individual proposals identified as strategic in nature are reviewed for scientific quality, innovativeness, and value to each respective mission-related initiative.

The review of proposals to this component relies on a combination of peer and management review 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 a review panel to assist in reviewing the submitted proposals. Results are reported to the Laboratory Director, who makes final selections and approves the content and aggregate budget. In FY 2009, 24 new and 51 continuing projects in the six Strategic Initiative areas listed below were funded, totaling \$19.5M. Also in FY 2009, two new and six continuing projects, totaling \$1.8M, represented the completion of former nanoscience initiative projects and special mid-year starts. The overall FY 2009 funding level for the Strategic Initiative component equaled \$21.3M (Figure 3).

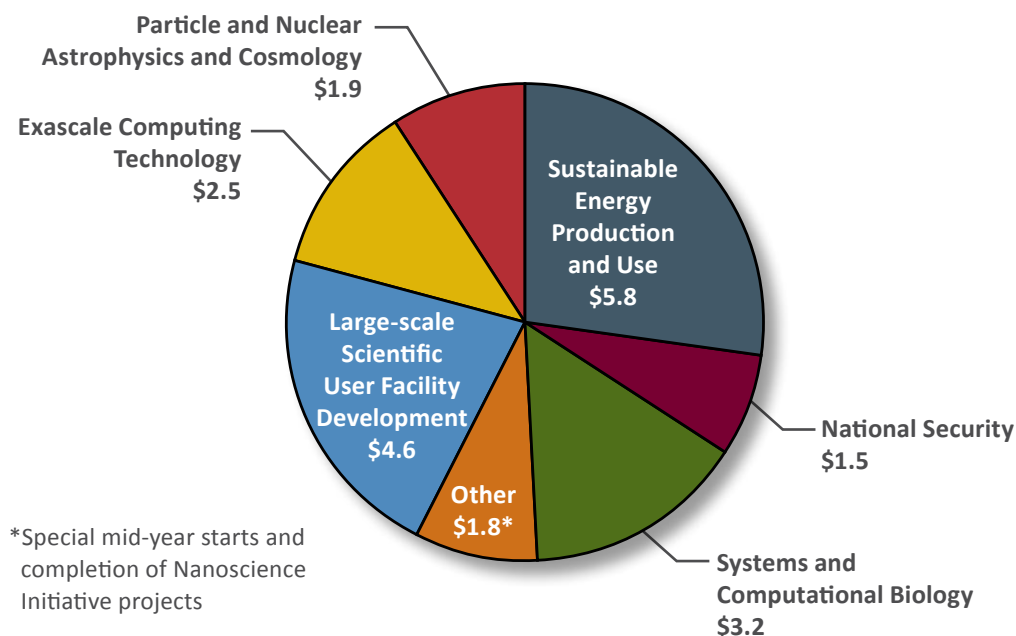


Figure 3. Distribution of Funding vs. Strategic Initiative Areas (\$M)

FY 2009 Strategic Initiative Areas:

Exascale Computing Technology

The key elements of this initiative are covered by the following general areas: programming models, performance tools, and debugging; operating systems, resiliency, and system management; new system architectures; new I/O architectures and software; and extremely scalable algorithms and novel computing methodologies.

Large-scale Science User Facility Development

This initiative focuses on developing new or enhanced science capabilities by developing and expanding existing large-scale scientific user facilities in technical areas, as follows: Accelerator R&D will support forefront accelerator research, including modeling and simulations; Detector Systems projects will focus on novel detector concepts and expertise in detector fabrication to enhance the productivity of existing and future scientific user facilities; and Science Enablers will leverage those programs that will use new or significantly expanded ANL user facilities to develop new or enhanced science capabilities (such as imaging, ultrafast science, and other facility-based science) and to ensure that existing facilities are utilized to the fullest extent.

National Security

The LDRD projects under the national security initiative focus on current and emerging scientific and technological challenges in both homeland security and national defense. Key research areas include sensor research; advanced computational data management and analysis; and the application of complex modeling to infrastructure assurance and social science problems, such as terrorism, and behavioral and decision analysis.

Particle and Nuclear Astrophysics and Cosmology

These projects focus on the following key areas to address some of the basic questions about the universe: (1) fundamental science that addresses the nature and understanding of dark matter and dark energy, (2) fundamental science of nucleosynthesis in stellar explosions and the origin of the heavy elements in nature, (3) use of petascale computing capabilities to address key questions in particle astrophysics and cosmology and nuclear astrophysics, and (4) development of novel detector technologies for future experiments aimed at addressing key questions in particle astrophysics and cosmology and nuclear astrophysics.

Sustainable Energy Production and Use

The key focus areas of projects under this initiative include: systems-level modeling of advanced energy technologies, systems-level modeling and experimental analysis of the environmental consequences of energy production and use, science-based engineering for nuclear energy supply, advanced materials for solar energy supply, sustainable fuels production and catalysis, and efficient fuels utilization.

Systems and Computational Biology

These projects address high-throughput methods for the development and use of massively parallel approaches for genome sequencing, the formulation of computational techniques related to genome analysis and sequencing, protein science and engineering, biofuels and bioenergy research and development, and microbial ecology and ecosystem analysis.

Director's Competitive Grants (DCG)

The DCG component invests in a full spectrum of investigator-initiated proposals across Laboratory and 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 submitted for peer review to the Director's Review Committee to assess the scientific and technical quality. The Committee is comprised of non-managerial scientists and engineers selected by the Laboratory Director. The committee currently comprises 22 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 an invitation of a smaller number of proposals 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 was enhanced this year by the recruitment of members of the laboratory research community who served as volunteer subject matter experts to assist the Director's Review Committee in reviewing proposals. Over 200 researchers volunteered and, with their assistance, made it possible for the Director's Review Committee to recommend the highest quality proposals for funding in FY 2009. These projects comprise about 18% of the Laboratory's LDRD budget. In FY 2009, 13 new and 22 continuing projects were funded at \$5.3M. The distribution of DCG funds across the Laboratory's major technical areas is shown in Figure 4a. The way in which the distribution of funds detailed in Figure 4a contributes to the ultimate purpose of the work is shown in Figure 4b.

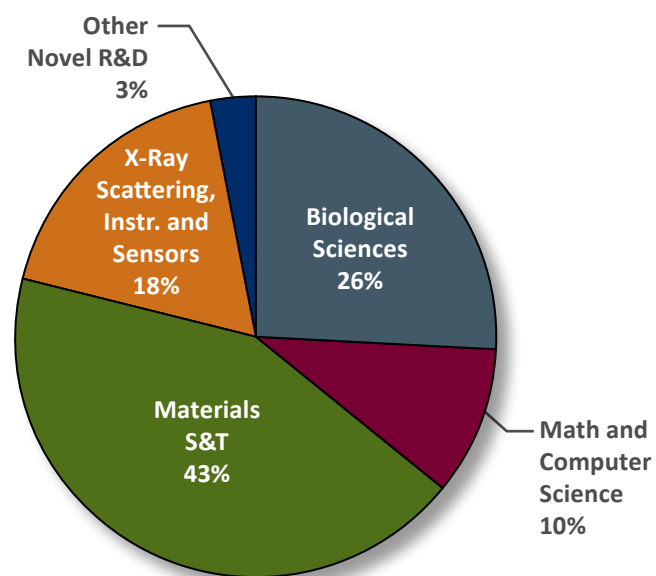


Figure 4a. Distribution of DCG Funds by Technical Area of Work

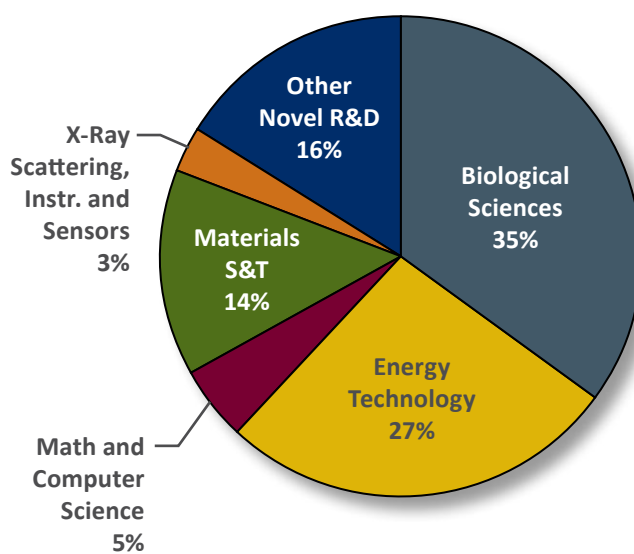


Figure 4b. Distribution of DCG Funds – Ultimate Purpose of Research

FY 2010 Update

DOE approved Argonne's FY 2010 LDRD Plan and program expenditure, not to exceed \$30M. A list, by title, of projects begun in FY 2010 is provided in an appendix to this report.

For FY 2010, we are continuing to refine our use of electronic formats to communicate with investigators and reviewers and to collect and document performance information on LDRD projects. We are improving existing web-based applications and developing a new electronic proposal submission process. A new proposal submission web site is being developed for the FY 2011 proposal submission and review cycle.

A Director's Grand Challenge element of our program has been instituted for FY 2010. It focuses on supporting one highly cooperative innovative project that devotes sufficient talent and resources to a specific technical topic, such that major strides toward its research and development goals can be expected. The topic will be within an area of substantial strategic value to the Laboratory and DOE. Energy Storage is the Grand Challenge topic that will be addressed in FY 2010.

Continued enhancements to the FY 2010 DCG review process include recruiting more members of the laboratory research community to serve as volunteer subject matter experts to assist the Director's Review Committee in reviewing proposals.

Peer Review Experience in FY 2009

The pursuit of LDRD research 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 M&O contractor, UChicago Argonne, LLC. The Laboratory believes that the quality of the science and technology performed under LDRD funding by 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 2009 is provided in Table 1, along with an aggregate accounting of the number of LDRD projects exposed to committee review and their total dollar value. The LDRD Office also requires principal investigators to report all other relevant external reviews of their work. LDRD projects from the Mathematics and Computer Science (MCS) and the Biosciences (BIO) divisions and the Institute for Genomics and Systems Biology (IGSB) were reviewed as part of an overall University of Chicago review of the Computing, Environment, and Life Sciences ALD area.

Table 1. Summary of Peer Review History by Organization

Organization	MCS	BIO	IGSB	Totals
Date of Review	9/15/2009	9/15/2009	9/15/2009	
No. of LDRD Projects	2	6	1	9
Dollar Value of Projects	\$1,842.4K	\$2,852.3K	\$165.8K	\$4,860.5K

Performance Metrics

The LDRD Program Office collects statistical data on current and completed LDRD projects. Such data relate, for example, to publications, inventions, follow-on sponsorship, and staff enhancement through post-doctoral appointees and new hires. Although these data are of little value on a project-by-project basis, in the aggregate, they provide a picture of overall program productivity. The management processes employed to collect these data include surveys of current and former investigators; an analysis of project annual reports; and validation against records of the Office of Technology Transfer (OTT), the Legal Department (LEG), and the Publications and Record Services Section of the Technical Services Division (TSD). A summary of the most recently collected data is provided in Tables 2 and 3. Table 2 displays project outcomes realized only during FY 2009 but derived from projects active in any year or years from FY 2006 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 2009 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
2006							
	Competitive Grants	2	0	0	0	0	0
	Strategic Initiative	2	0	0	0	0	1
2007							
	Competitive Grants	0	0	0	0	0	0
	Strategic Initiative	15	0	1	0	1	0
2008							
	Competitive Grants	16	0	3	0	1	0
	Strategic Initiative	8	0	4	0	4	1
2009							
	Competitive Grants	37	57	5	0	4	3
	Strategic Initiative	46	85	9	0	3	3
Grand Totals: 317 Projects		126	142	22	0	13	8

Table 3. Aggregate Outcomes for All Years of Recently Completed and Current Projects (2006 to 2009)

Most Recent Project Year	Number of Projects Receiving Follow-on Funds	Number of Proposals Submitted To Sponsors	Number of External Reviews
2006	24	123	26 DOE 25 Other 18 UoC
			69 Total
2007	23	121	21 DOE 6 Other 10 UoC
			37 Total
2008	27	173	34 DOE 16 Other 9 UoC
			59 Total
2009	29	208	8 DOE 15 Other 2 UoC
			25 Total
Totals: 317 Projects	103	625	89 DOE 62 Other 39 UoC
			190 Total

LDRD Five-Year Funding Summary (in \$K) (For projects active in FY 2009)

Proposal No.	2007	2008	2009	2010 (a)	2011 (b)	Total
2006-268-R3	99.8	97.0	80.3			277.1
2007-007-R2	197.8	207.7	216.2			621.7
2007-008-R2	135.2	114.5	135.0			384.7
2007-027-R2	133.4	133.2	150.1			416.7
2007-044-R2	135.2	128.4	149.6			413.2
2007-059-R2	118.4	114.1	104.3			336.8
2007-060-R2	201.7	182.4	200.4			584.5
2007-066-R2	130.5	124.2	98.4			353.1
2007-068-R2	169.9	119.4	135.3			424.6
2007-071-R2	190.0	187.9	187.6			565.5
2007-075-R2	225.5	223.0	238.4			686.9
2007-080-R2	98.5	98.8	98.2			295.5
2007-088-R2	103.2	104.6	105.5			313.3
2007-100-R2	614.1	794.0	600.1			2,008.2
2007-105-R2	155.8	176.3	157.2			489.3
2007-107-R2	99.1	97.3	99.3			295.7
2007-110-R2	171.8	317.3	299.2			788.3
2007-113-R2	149.1	74.9	74.9			298.9
2007-133-R2	118.7	119.0	97.8			335.5
2007-142-R2	71.5	60.6	54.4			186.5
2007-150-R2	95.7	98.1	98.2			292.0
2007-157-R2	93.6	131.9	113.0			338.5
2007-158-R2	87.8	106.9	61.4			256.1
2007-161-R2	385.7	496.5	461.5			1,343.7
2007-162-R2	512.6	410.9	387.9			1,311.4
2007-164-R2	71.5	112.7	102.7			286.9
2007-165-R2	291.5	105.5	198.5			595.5
2007-166-R2	192.5	188.3	211.6			592.4
2007-180-R2	330.1	202.4	128.9			661.4
2007-186-R2	497.4	524.6	500.9			1,522.9
2007-189-R2	701.3	625.2	577.9			1,904.4
2008-003-R1		99.2	116.3	115.0		330.5
2008-008-R1		123.5	139.2	161.0		423.7
2008-009-R1		178.1	177.2			355.3
2008-020-R1		136.0	155.0	161.0		452.0
2008-026-R1		153.5	152.8	156.0		462.3
2008-027-R1		167.1	199.3			366.4
2008-035-R1		173.1	190.1	230.0		593.2
2008-036-R1		185.2	225.1	235.0		645.3
2008-070-R1		143.0	103.0	75.0		321.0
2008-071-R1		120.6	137.6			258.2
2008-090-R1		129.7	125.4	150.0		405.1
2008-118-R1		296.4	504.4	500.0		1,300.8



LDRD Five-Year Funding Summary (in \$K) continued (For projects active in FY 2009)

Proposal No.	2007	2008	2009	2010 (a)	2011 (b)	Total
2008-119-R1		39.4	80.5	85.0		204.9
2008-120-R1		124.7	101.3			226.0
2008-121-R1		651.4	699.8	450.0		1,801.2
2008-122-R1		124.6	250.4	65.0		440.0
2008-124-R1		449.0	243.7	225.0		917.7
2008-128-R1		183.0	271.9	90.0		544.9
2008-130-R1		191.6	109.6	100.0		401.2
2008-135-R1		60.9	66.6	80.0		207.5
2008-136-R1		281.5	145.7			427.2
2008-138-R1		201.7	149.4	90.0		441.1
2008-140-R1		749.8	524.1	270.0		1,543.9
2008-141-R1		248.0	200.0	200.0		648.0
2008-142-R1		219.0	219.7	200.0		638.7
2008-146-R1		549.0	600.2			1,149.2
2008-147-R1		199.1	259.9	250.0		709.0
2008-150-R1		273.9	376.5	300.0		950.4
2008-152-R1		80.4	91.9	150.0		322.3
2008-154-R1		600.6	601.2	520.0		1,721.8
2008-156-R1		348.2	410.5	350.0		1,108.7
2008-157-R1		99.8	99.3	100.0		299.1
2008-159-R1		311.6	319.5	270.0		901.1
2008-160-R1		724.6	751.4	600.0		2,076.0
2008-161-R1		371.2	474.2	300.0		1,145.4
2008-166-R1		199.1	98.5	90.0		387.6
2008-171-R1		493.4	479.9	440.0		1,413.3
2008-172-R1		199.0	316.4			515.4
2008-177-R1		168.1	151.0	150.0		469.1
2008-178-R1		249.8	217.1			466.9
2008-179-R1		483.7	551.7	580.0		1,615.4
2008-183-R1		183.6	157.0			340.6
2008-188-R1		159.1	204.9	185.0		549.0
2008-190-R1		42.0	180.0			222.0
2008-191-R1		114.7	498.6	152.0		765.3
2008-192-R1		40.7	154.3	120.0		315.0
2008-193-R1		483.3	853.4	365.0		1,701.7
2008-195-R1		163.0	192.2	196.0	201.0	752.2
2009-014-N0			78.0			78.0
2009-017-N0			99.3	70.0		169.3



LDRD Five-Year Funding Summary (in \$K) continued (For projects active in FY 2009)

Proposal No.	2007	2008	2009	2010 (a)	2011 (b)	Total
2009-028-N0			150.2	80.0	150.0	380.2
2009-035-N0			251.8	262.0		513.8
2009-037-N0			112.2	130.0		242.2
2009-047-N0			194.2	200.0	200.0	594.2
2009-050-N0			407.8	300.0		707.8
2009-059-N0			70.7	185.0		255.7
2009-062-N0			165.4			165.4
2009-068-N0			154.9	155.0	175.0	484.9
2009-070-N0			199.0	207.0	215.0	621.0
2009-071-N0			180.0	150.0	200.0	530.0
2009-076-N0			173.9	175.0	200.0	548.9
2009-080-N0			99.2	100.0	150.0	349.2
2009-083-N0			112.2	135.0	135.0	382.2
2009-085-N0			220.4	350.0	350.0	920.4
2009-091-N0			119.6			119.6
2009-097-N0			598.5	550.0	700.0	1,848.5
2009-111-N0			100.5	130.0	130.0	360.5
2009-115-N0			234.1	300.0	350.0	884.1
2009-117-N0			245.1	105.0		350.1
2009-138-N0			153.7	185.0	190.0	528.7
2009-146-N0			119.7	100.0	80.0	299.7
2009-155-N0			221.4	200.0	200.0	621.4
2009-156-N0			173.6	162.0	180.0	515.6
2009-158-N0			243.4	260.0	300.0	803.4
2009-171-N0			132.1	225.0	250.0	607.1
2009-176-N0			316.7			316.7
2009-177-N0			99.6	108.0		207.6
2009-180-N0			320.4	250.0	400.0	970.4
2009-186-N0			165.8	180.0	200.0	545.8
2009-190-N0			144.4	175.0	185.0	504.4
2009-204-N0			125.6	134.0	127.0	386.6
2009-209-N0			205.4	250.0		455.4
2009-212-N0			141.4	165.0		306.4
2009-214-N0			109.7	110.0		219.7
2009-226-N0			323.9	250.0	150.0	723.9
2009-227-N0			99.8			99.8
2009-228-N0			73.7			73.7
Totals	6,578.9	18,445.5	26,589.7	15,094.0	5,418.0	72,126.1

(a) 2010 figures represent estimates and not actual expenditures

(b) 2011 figures represent projections assuming the project is renewed



RESEARCH REPORTS



DIRECTOR'S COMPETITIVE GRANTS

Enzymes for Cellulosic Ethanol Production: Structure-Function Studies

2007-007-R2

Phani Raj Pokkuluri and Marianne Schiffer

Project Description

Although lignocellulosic plant material is abundant, the enzymatic degradation process needed to produce ethanol from such material is expensive. One of the key barriers is the natural recalcitrance of plant cell walls (a complex mesh of cellulose, hemicellulose, and lignin) that prevents their breakdown into fermentable sugars. The microbial enzymes used to degrade the plant materials are slow, and their peak activities are not compatible with conditions encountered during industrial processes. The main objective of this project is to better understand the structure-function relationship of selected enzymes in order to design improved variant enzymes for lignocellulosic biomass degradation. The structural studies of enzymes were undertaken in collaboration with scientists at the U.S. Department of Agriculture (USDA) office in Peoria, Illinois.

Mission Relevance

The project is relevant to DOE's mission in energy. As a result of increased worldwide demand for energy and diminishing fossil fuel supplies, conversion of cheap and abundant plant biomass to fermentable sugars for the production of ethanol or other biofuels is vital. Such studies are at the heart of DOE's energy mission. The goal of this project is to understand and improve the function of some of the enzymes that are used in enzymatic degradation of lignocellulosic material through structure-function correlations.

FY 2009 Results and Accomplishments

In this project, which began in FY07, we crystallized the catalytic domains of three novel hydrolases for which no structural information had been collected to date. Crystallization of these proteins posed a significant challenge because they are fungal proteins and have post-translational attachment of carbohydrate moieties. High-throughput structure determination is also not feasible because selenomethionine-labeled proteins — needed for solving the crystallographic “phase problem” — cannot be easily obtained. Nonetheless, we crystallized the three proteins and collected x-ray diffraction data at the 19BM beamline at Argonne's Advanced Photon Source. Results for two of the proteins are briefly described below.

Cip2S

Structure

We determined the structure of the catalytic domain (Cip2S) of glucuronoyl esterase (Cip2) from *Hypocrea jecorina* (formerly known as *Trichoderma reesei*). This is the first identified

structure of the recently established carbohydrate esterase family 15 (<http://www.cazy.org/fam/CE15.html>), an enzyme that is important in degradation of lignocellulosic material (see Figure 1).

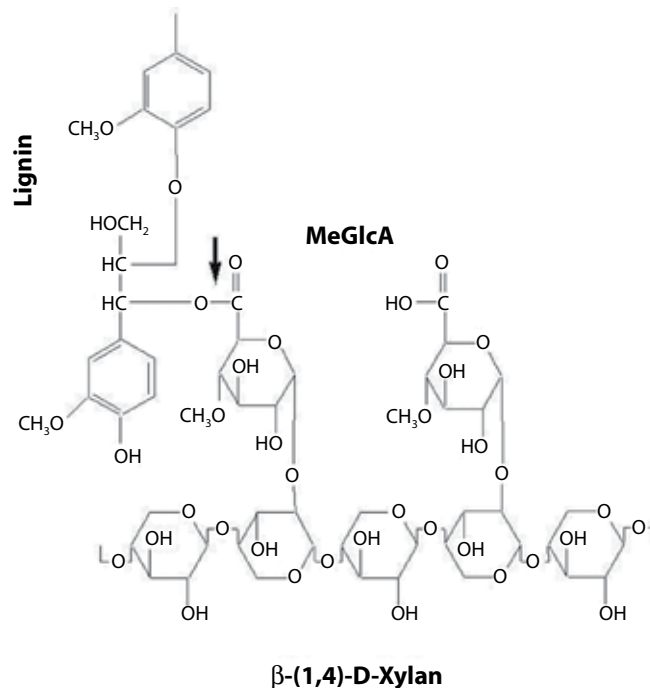


Figure 1. Proposed cross-link between lignin and glucuronoxylan in plant cell walls. The arrow indicates the possible ester bond hydrolyzed by the glucuronoyl esterase. Image is courtesy of Dr. Peter Biely, Institute of Chemistry, Slovak Academy of Sciences, Slovakia.

The crystals of Cip2S have three independent molecules (and a total of 1125 amino acids), as indicated by collection of diffracted x-rays to 1.9-Å resolution. The structure was determined by using the conventional “heavy-atom soaking” method and refined to a crystallographic R-factor of 19.5% and R-free of 23.4%. The Cip2S has α/β hydrolase fold; the catalytic residues were unknown prior to our structure determination. Inspection of the structure revealed a triad arrangement of residues (Ser193 – His326 – Glu216) on the surface of the protein. As expected, a carbohydrate molecule is found in the electron density attached to the side chain of Asn326 for each of the three independent molecules.

Co-Crystallization

To identify the active site and substrate binding site, we obtained crystals of Cip2S in the presence of an active serine inhibitor, phenyl methyl sulfonyl fluoride (PMSF), and a substrate analog, methyl ester of 4-O-methyl-D-glucuronic acid. Interestingly, soaking of preformed Cip2S crystals with these compounds resulted in crystal damage. This observation indirectly supports our predicted active site for Cip2S because this site is only accessible in one of the three independent molecules in the crystal; the equivalent sites of the other two molecules in the crystal are occluded in contacts that make up

the crystal lattice. In all cases described below, the structure was determined by means of rigid-body refinement using the native Cip2S structure as the search model. Examination of the putative active site revealed the presence of “extra” density. In each case, the unexplained density is not identical, suggesting the possibility of complex formation by the compounds studied. The native Cip2S structure contains only water molecules near the active site.

Cip2S + Inhibitor PMSF

To identify the active site in Cip2S, we grew crystals of Cip2S in the presence of the inhibitor, PMSF, and collected diffraction data to a 2.0-Å resolution. Examination of the different electron density maps revealed the presence of “extra” density, which could correspond to the inhibitor near the putative active site Ser293. However, this “extra” electron density did not connect to the hydroxyl group of the serine residue, as expected for an authentic inhibitor complex. (PMSF is known to form a covalent bond with the hydroxyl groups of active serine residues.) Further refinement of the structure did not resolve the “extra” density. Examination of all serine residues present in the protein did not show any other serine to which PMSF could have bound. In summary, it is not clear whether PMSF is bound to the protein in the co-crystals.

Cip2S + Substrate Analog(s)

We completed crystallization trials of Cip2S in the presence of two potential substrate analogs, methyl ester of 4-O-methyl-D-glucuronic acid (compound 1) and methyl ester of 4-O-methyl-D-glucuronic acid (MeGlcA)-linked alpha-1,2 to 4-nitrophenyl-β-D-xylopyranoside (compound 2). Crystals of Cip2S were obtained in the presence of compound 1 and diffraction data were collected to a 2.0-Å resolution. Cip2S did not crystallize in the presence of compound 2.

X-ray diffraction data were collected to a 1.9-Å resolution on co-crystals of Cip2S obtained in the presence of compound 1. The structure was determined by using native Cip2S structure. As in the case of the PMSF co-crystals, “extra” density was present near the active site but did not correspond well to the expected structure of compound 1. Thus, the results of this experiment were also inconclusive.

RfGE

Ruminococcus flavefaciens Glucuronoyl Esterase (RfGE) is the C-terminal domain (418 amino acids) of a cellulosomal acetyl esterase (CesA) of *Ruminococcus flavefaciens* 17 and the first glucuronoyl esterase isolated from bacteria. Native RfGE was crystallized and diffraction data (to a 1.9-Å resolution) were collected, but selenomethionine-substituted RfGE could not be crystallized. Although the sequence identity between RfGE and Cip2S is low (about 30%), our collaborators at USDA

have evidence that the function of the two enzymes is the same — suggesting that their structures could be similar. However, our extensive efforts using the refined structure of Cip2S as a search model to determine the structure of RfGE by molecular replacement method failed.

Proposed Work for FY 2010

The project does not continue into FY10.

Refereed Publications

Wood, S.J., X.-L. Li, M.A. Cotta, P. Biely, N.E.C. Duke, M. Schiffer, and P.R. Pokkuluri, “Crystallization and Preliminary X-Ray Diffraction Analysis of the Glucuronoyl Esterase Catalytic Domain from *Hypocrea Jecorina*,” *Acta Crystallogr. F* **64** (2008), 255–257.

Astrochemical Studies of the Origins of Life Using Circularly Polarized Synchrotron Radiation

2007-008-R2

Richard A. Rosenberg

Project Description

The objectives of this project are to simulate the astrochemical reactions that occur on interstellar grains and apply the results to gain a fundamental understanding of the origins of life. By using the intense x-rays from the Advanced Photon Source (APS), we will be able to induce photochemical reactions in one hour that take one million years in the interstellar medium. Previously, we showed that exposure of such cryogenic ices to low energy spin-polarized electrons induces chirality in the reaction products. Chiral molecules are essential for the origin of life as we know it. We believe that this finding will make a major impact in the field of biogenesis. During the last year of the project, we extended the experiments to more biologically relevant systems, alanine (the simplest chiral amino acid) and DNA, and tested the potential of a new analytical tool that we developed, infrared induced by x-rays (IRIX).

Mission Relevance

This project is tied to DOE’s mission in science, particularly in the fields of biogenesis and interstellar chemistry. This research should also be of interest to the National Aeronautics and Space Administration. The development of IRIX as a diagnostic and microscopic probe will have a broad impact on a variety of disciplines, including biology, medicine, polymers, catalysis, and fuel cells. In the life sciences alone, it could be

used in the study of, for example, peptides, proteins, DNA, cellular activity, neuroscience, and cancer with sub-100-nm spatial resolution, not to mention the possibility of time resolution in the picosecond range. The research should also be applicable to imaging and time-resolved studies of hydrogen, carbon, oxygen bonding relevant to fuel cells, and catalysis, which interest other agencies, such as the National Institutes of Health.

FY 2009 Results and Accomplishments

We hypothesized that a previously unconsidered agent can play a role in chiral-selective chemistry: namely, low-energy spin-polarized secondary electrons, produced by photon, electron, or ion irradiation of a magnetic substrate. To test this premise, we performed detailed measurements of the reaction rate for x-ray induced, secondary electron photolysis of a model chiral compound, (R)- or (S)-2-butanol (Figure 1), adsorbed on a magnetized permalloy ($\text{Fe}_{0.2}\text{Ni}_{0.8}$) substrate. We found that a reversal of the secondary electron spin polarization results in a significant change in the reaction rate for a given chirality. For (S) 2 butanol, this difference $8.9 \pm 3.5\%$, while for (R) 2 butanol, it is $10.9 \pm 3.8\%$. This enhancement is well above that seen in most previous studies. Furthermore, these prior experiments were predicated on mechanisms that were more limited in their scope. The present mechanism is general in that it requires only a magnetic substrate and a source of ionizing radiation. Iron is one of the most common elements and is magnetic in many forms. Ionizing radiation and magnetic fields are ubiquitous throughout the universe. Therefore, this mechanism for inducing chirality should be viable in a wide variety of possible environments.

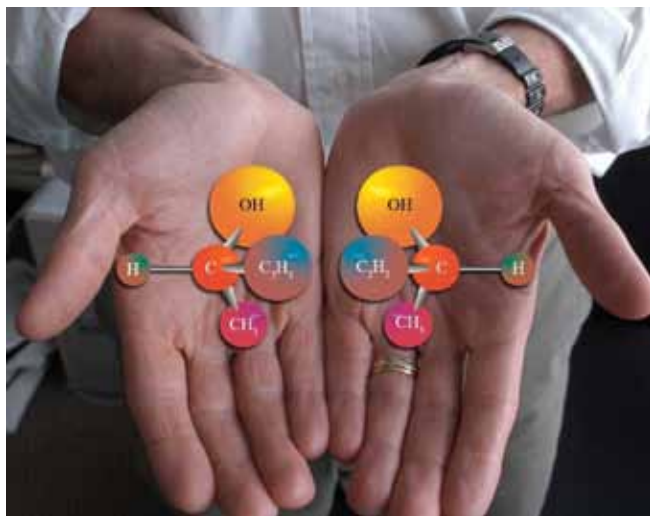


Figure 1. Molecular models illustrating the chirality of (S)-2-butanol (in the right hand) and (R)-2-butanol (in the left hand). Chirality arises when two molecules are mirror images of one another but are not superimposable.

During the past year, we extended the experiments to more biologically relevant systems, alanine and DNA. Initial experiments demonstrated that x-ray/secondary electron-induced reactions were observable in a reasonable time span (1–2 hours). For alanine adsorbed on permalloy, we determined that the NH_3 group bonded to the chiral carbon reacts as a result of x-ray irradiation with a time constant of $\sim 5,600$ second(s). Secondary electron induced modifications of DNA evidenced a time constant of $\sim 4,200$ s. Initial measurements were also made of possible polarized secondary electron selectivity by examining reactions on a magnetic substrate. Analysis is ongoing.

Significant milestones were accomplished by using a new analytical tool that we developed, IRIX. We obtained the first FTIR emission spectrum as a result of synchrotron x-ray and electron irradiation by detecting bandgap (0.415 eV) luminescence from InAs. A paper was published and a patent was filed (*Microscopic Infrared Analysis By X-Ray Or Electron Radiation*).

Refereed Publications

Rosenberg, R.A., M. Abu Haija, and P.J. Ryan, "Chiral-Selective Chemistry Induced by Spin-Polarized Secondary Electrons from a Magnetic Substrate," *Physical Review Letters*, **101**, 178301 (2008).

Rosenberg, R.A., M. Abu Haija, and S.P. Watkins, "X-Ray- and Electron-Induced Infrared Emission Spectroscopy," *Review of Scientific Instruments* **80**, 046104 (2009).

Presentations

Rosenberg, R.A., M. Abu Haija, and P.J. Ryan, "A New Spin on Chirality: Reactions Induced by Polarized Secondary Electrons from a Magnetic Substrate," contributed presentation at the 56th International Symposium of the American Vacuum Society (AVS), November 8–13, 2009, San Jose, CA.

Rosenberg, R.A., "XPS and HAXPES Studies of Interstellar Chemistry," invited presentation at the International Workshop for New Opportunities in Hard X-Ray Photoemission Spectroscopy: HAXPES2009, May 20–22, 2009, Brookhaven National Laboratory, Long Island, NY.

Whole Cell-Based Biosensors and Bioelectronics

2007-027-R2

Millicent A. Firestone, Ralu S. Divan, Kenneth M. Kemner, Sungwon Lee, and Kelly A. Skinner-Nemec

Project Description

The objective of this research is to integrate biological cells with patterned device architectures. The work carried out under this proposal pursues development of composite materials that may serve as the basis of novel hybrid sensors or mesoscale devices for use in heterogeneous catalysis, neuronal-based computation, or prosthetics. The specific goals of this project are to (1) develop materials and approaches for the stable encapsulation of cells while preserving their native activity, (2) integrate cells with patterned device architectures (e.g., semiconductors), and (3) control the cell-semiconductor interface so as to facilitate communication/signal transduction. Specifically, a model for an abiotic-biotic sensor to detect environmental metals, toxins, or pollutants will be targeted.

Mission Relevance

This project supports DOE's missions in environmental monitoring and remediation, information technology, and nanoscience and nanotechnology. The project seeks to address the present-day limitations in materials applicable in the development of information transfer from biological components to artificial or synthetic materials (conventional electronics).

FY 2009 Results and Accomplishments

The research focus this year was two fold: (i) completion of fundamental electronic transport studies and (ii) optimization of amperometric sensing of Arsenate [As (V)]/Arsenite [As (III)] by *S. oneidensis* MR-1 supported on gold (Au) electrodes for biosensing applications. Specifically, our efforts were directed toward the evaluation of operating conditions and analytical metrics (e.g., detection limits) for the detection of As (III)→As (V). Measurements were made by using the experimental design developed during FY08. Briefly, our procedure used a planar, thin (100 nanometer [nm]) film of Au supported (via a chromium adhesion layer of 5 nm) on a float glass electrode employing linear sweep voltammetry (LSV). The signal and response times were optimized on the basis of the redox properties of As (V) and As (III) on the microbial and gold electrode in the rich medium, as based on our fundamental electrochemical studies carried out in 2008. The LSV responses to As (V) and As (III) were collected in rich media at a scan rate of 0.1 volt per second (V/s) via anodic scans of between 0 and 0.5 V. The introduced As (V) in the rich-media electrolyte under-

goes microbe-mediated reduction to As (III) in the presence of *S. oneidensis* MR-1. The As (III) is then electrochemically oxidized to As (V). The anodic peak at 0.2 V is assigned to the As (III)→As (V) oxidation. (Prior work confirmed that As (V) yields no electrochemical activity in the potential range between 0 and 0.5 V.) The calibration experiments were performed with the standard addition of As (III) in the range of 19.2–100.0 millimoles (mM) in rich media at a scan rate of 0.1 V/s (Figure 1). The Figure 1 inset shows the corresponding calibration plot, which was made as a function of As (III) concentration vs. peak area. The concentration range used for this study reveals excellent linearity ($r^2 = 0.9958$).

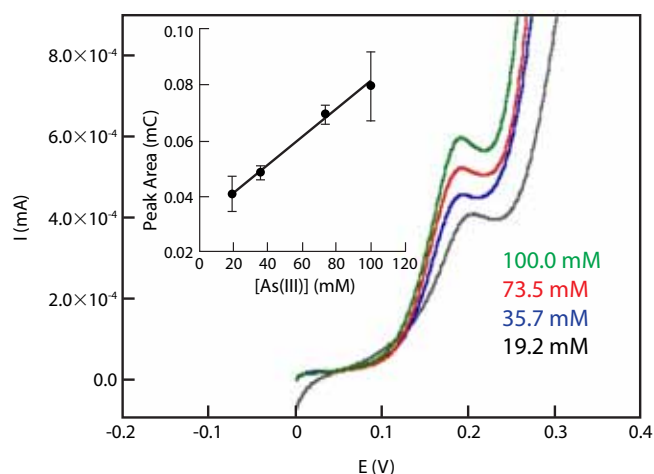


Figure 1. Linear sweep voltammetry of As (III) standard additions to microbes in rich media. Inset: calibration plot derived from LSV data.

In parallel with these studies, the electrochemical response of the bacteria was also examined and calibrated during FY09. LSV was used to determine the redox properties of As (V). Next, a calibration curve using As (V) standard solutions was prepared. In these studies, the As (V) standard solutions were added into the cell suspension, and the electrochemical response in the potential range of 0 to 0.4 V at a scan rate 0.1 V/s was monitored. As expected, a sharp, well-defined peak at 0.18 V was observed, and this peak corresponds to the microbe-mediated oxidation of As (III)→As (V). The calibration plot here also shows good linearity ($r^2 = 0.9898$) in the range of 8–36 mM of As (V). The limit of detection (LOD) for the biosensor device developed under this project was determined to be 1.0 grams/Liter, a value which suggests that, with further optimization, this construct forms a promising bioelectronic device.

Proposed Work for FY 2010

This project does not continue into FY10. The work will be submitted for publication in a peer-review journal during this year.

Aligned Carbon Nanotube as Pt-Free Electrode Catalyst for Fuel Cell

2007-044-R2

Di-Jia Liu, Junbing Yang, and David J. Gosztola

Project Description

Current proton exchange membrane fuel cells (PEMFCs) use platinum (Pt) or platinum group metals (PGMs) as the electrode catalyst. The high price and limited reserves of PGMs pose a significant barrier to commercializing PEMFCs. The goal of this project is to develop a low-cost electrode catalyst with functionalized aligned carbon nanotubes (ACNTs) to replace platinum and PGMs. Functionalized ACNTs represent a promising electrode material with high chemical stability, improved thermal and electronic conductivities, and a unique nanoarchitecture for efficient mass transport. Through this project, we attempted to significantly improve the catalytic activity and stability of functionalized ACNT for the oxygen reduction reaction (ORR). In addition, we explored a variety of new porous framework materials as new approaches to prepare electrode catalysts to replace PGMs.

Mission Relevance

Improving energy efficiency and reducing environmental impacts from fossil fuel consumption represent key DOE energy and environmental missions. The success of our project could facilitate future transportation technology deployment under DOE's Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Program and open up new opportunities for research on non-PGM catalysts.

FY 2009 Results and Accomplishments

Previously, we used a modified chemical vapor deposition (CVD) method to prepare dense, uniformly aligned carbon nanotube layers decorated with transition metals and other elements to create the active catalytic sites. This year, we continued efforts to modify ACNT electrocatalytic activity through CVD process improvements, integrating higher levels of nitrogen into ACNT through modified reaction conditions. The ACNTs prepared by using this method were transferred to a Nafion® membrane, a proton-conducting polymer electrolyte, to form the membrane electrode assembly (MEA). We prepared a single-cell PEMFC, mounted with the MEA, and evaluated the cell under operating conditions. Significant improvements in cell performance were achieved compared with FY08 results. For example, the open voltage potential improved from 0.55 volts to 0.7 volts; the polarization current (0.2 volts) increased from 66 mA/cm² to about 180 mA/cm². This current density is still far below the output from a PEMFC containing a

Pt electrode catalyst primarily because of material limitations involved in incorporating significant high active-site density in ACNT prepared using the CVD process.

To further enhance catalytic activity, we tried a new approach using transition-metal-decorated porous framework materials. Specifically, we evaluated the feasibility of using metal-organic framework (MOF) and porous organic polymer (POP) materials as the precursors for preparing non-PGM electrode catalysts. This approach is rooted in the hypothesis that effective non-PGM catalysts should have high active-site densities with limited volumes and weights in order to compete with the high turnover frequency in Pt-based electrocatalysts. We obtained promising results in terms of electrocatalytic performance for both materials in the preliminary studies. Figure 1 shows the lattice structure of a representative MOF used as the precursor of the electrocatalyst and the oxygen reduction reaction activity measured during a rotating disk electrode (RDE) experiment in which high onset potential — 0.82 volts — was achieved.

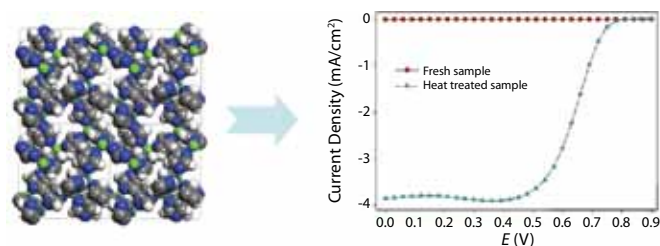


Figure 1. Lattice structure of a representative metal-organic framework material (left) and the electrocatalytic activity of ORR measured by RDE method over the catalyst prepared using this MOF material as the precursor through thermal activation (right). The x-axis represents the polarization potential E with reference to standard hydrogen electrode (SHE) in units of volts.

The following invention disclosure resulted from this project: "Non-Platinum Group Metal Electrocatalysts Using Metal Organic Framework Materials and Method of Preparation," Argonne National Laboratory Invention Disclosure, ANL-IN-09-069

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Liu, D.-J., J. Yang, G. Goenaga, and A. Call, "Polymer Electrolyte Membrane Fuel Cell with Vertically Aligned Carbon Nanotube Electrode," in *Nanotubes, Nanowires, Nanobelts and Nanocoils—Promise, Expectations, and Status*, edited by P. Bandaru, S. Grego, and I. Kinloch (*Proceedings of the Material Research Society Symposium* Vol. 1142, Warrendale, PA, 2009, Paper # 1142-JJ20-08).

Non-Refereed Publications and Presentations

Call, A., G. Goenaga, J. Yang, and D.-J. Liu, "Polymer Electrolyte Membrane Fuel Cell with Vertically Aligned Carbon Nanotube Electrode," American Physical Society Meeting, Pittsburgh, PA, March 16–20, 2009.

Goenaga, G., J. Yang, A. Call, N. Kariuki, and D.-J. Liu, "Aligned Carbon Nanotubes Based Electrocatalyst for Polymer Electrolyte Membrane Fuel Cell," National Society of Black and Hispanic Physicist Conference, Nashville, TN, February 11, 2009.

Goenaga, G., J. Yang, A. Call, and D.-J. Liu, "Parameters Optimization of Aligned Carbon Nanotubes Based MEAs for Proton Exchange Membrane Fuel Cells," Electrochemical Society (ECS) Spring Meeting, San Francisco, CA, May 24–29, 2009.

Goenaga, G., S. Yuan, A. Call, L. Yu, and D.-J. Liu, "New Electrode Catalyst for Oxygen Reduction Reaction Using Porous Polymer Approach," Chicago Catalysis Club Spring Symposium, Naperville, IL, May 18, 2009.

Liu, D.-J., "Advanced Materials and Characterizations for Energy Storage and Fuel Cell Applications," Graduate Colloquium, Northern Illinois University, DeKalb, IL, September 28, 2009.

Liu, D.-J., J. Yang, G. Goenaga, and A. Call, "Material Advantages of Vertically Aligned Carbon Nanotubes as Electrocatalyst Support for PEMFC," 2008 Materials Research Society (MRS) Fall Meeting, Boston, MA, November 30 to December 5, 2008.

Liu, D.-J., J. Yang, N. Kariuki, G. Goenaga, A. Call, and D. Myers, "Performance Improvement in PEMFC Using Aligned Carbon Nanotubes as Electrode Catalyst Support," 214th Electrochemical Society Meeting, Honolulu, HI, October 12–17, 2008.

Yang, J., N. Kariuki, G. Goenaga, A. Call, S. Niyogi, M. Ferrandon, D. Myers, and D.-J. Liu, "Novel PEMFC Using Aligned Carbon Nanotubes as Electrodes in MEA," 2008 Alternative Energy Symposium, Chicago, IL, October 3, 2008.

Development of *in situ* Non-Resonant X-Ray Scattering Technique and its Application to Redox Reactions in Battery Materials

2007-059-R2

Mahalingam Balasubramanian and Christopher S. Johnson

Project Description

Lithium-ion (Li-ion) batteries have cornered the lion's share of today's market for rechargeable batteries in consumer electronics and power tool applications. They are also poised for use in hybrid and/or plug-in hybrid vehicles. However, to minimize our dependence on fossil fuels and help mitigate climate change, it is imperative that improved battery technologies — that can be used in all-electric vehicles and provide a useful range — be developed in the near future. It is likely that storage of electricity generated from other renewable energy sources (such as solar or wind) will be an important component of the nation's future energy portfolio. Any new energy storage technologies should provide energy and power densities comparable to those of gasoline engines, yet be inexpensive, inherently safe, green, and allow for large-scale deployment. Development of such transformational battery technologies requires tailoring of novel materials and incorporation of new chemical processes. A fundamental understanding of the changes in local electronic structure that accompany insertion and removal of lithium is vital for a rational design of improved battery electrodes. This project is focused on the development and use of hard x-ray non-resonant inelastic scattering (NRIXS) to understand the core-shell electronic properties of the constituent elements of an "operating" Li-ion battery. NRIXS measurements have the potential to provide definitive characterization of the redox chemistry for the elements at both electrodes of a Li-ion battery.

Mission Relevance

This project directly addresses DOE's missions in energy storage and energy efficiency. An improved understanding of the redox chemistry underlying charge transfer in Li-ion batteries is important to conservation of fossil fuels and reduction of greenhouse gases through potential improvements in the efficiency and/or cost of plug-in hybrid electric vehicles and electric vehicles. The recent DOE Office of Basic Energy Sciences (BES) report on energy storage characterized the technique being developed in this project as an emerging technique for characterization of working batteries. Our project addresses the important characterization need articulated in the BES report.

FY 2009 Results and Accomplishments

As expected, this final year of the project has been highly rewarding. We completed studies of momentum-transfer (q)-dependent NRIXS at the low-energy loss excitations of titanium (Ti)-based oxides. As an example, Figure 1 shows the electronic excitations of TiO_2 (anatase) in the low-energy loss region. This region covers the Ti 3*p* and Ti 3*s* semi-core-initial electron states of the Ti atom. The presence of large q -dependence in the Ti 3*p* and 3*s* NRIXS spectra is clearly evident. For sufficiently high q , NRIXS is sensitive to dipole-forbidden transitions, providing additional information about the electronic structure.

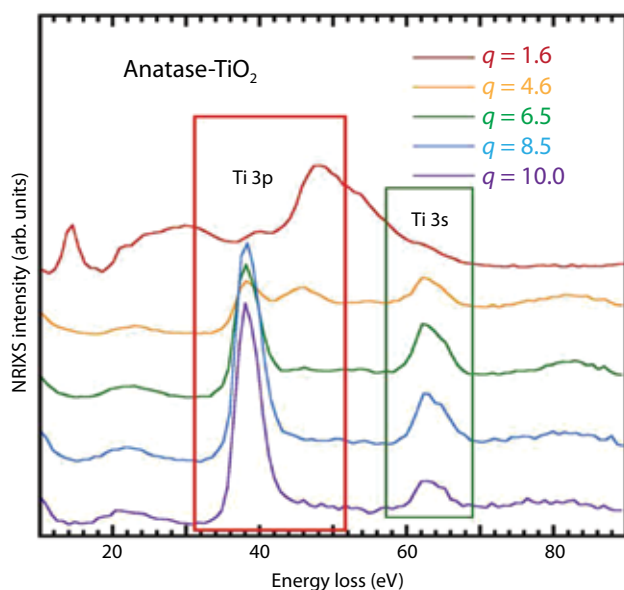


Figure 1. Momentum-transfer-dependent contributions to NRIXS in the low-energy-loss region for anatase TiO_2 . The contributions from Ti 3*p* and Ti 3*s* initial states are shown in the boxed regions. Note the large momentum-transfer dependence arising from non-dipole contributions for both the Ti 3*p* and 3*s* initial states.

We developed an *in situ* NRIXS technique and applied it to understanding the redox reactions of battery electrodes. We performed NRIXS studies from the 2*p*, 3*p*, and 3*s* initial states in cobalt (Co) and the 1*s* initial state in oxygen (O) from operating half cells with a LiCoO_2 cathode. We believe these measurements are the first successful NRIXS studies of operating batteries; they clearly illustrate the ability of NRIXS to combine the power of soft x-ray absorption spectroscopy (XAS) with the *in situ* capabilities of hard x rays. As another example, Figure 2 shows measurements from the O 1*s* initial state of LiCoO_2 compared with CoO_2 prepared by chemical deintercalation. These spectra are similar to those from O K-edge soft XAS or electron energy loss spectroscopy (EELS) measurements, but with true bulk sensitivity.

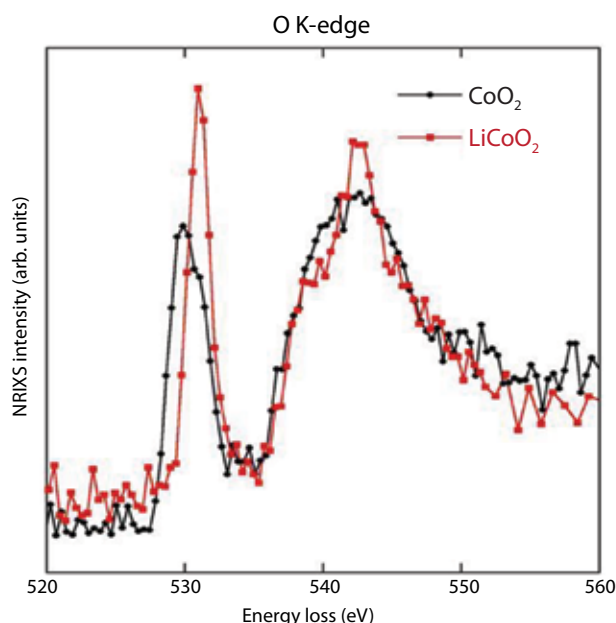


Figure 2. Comparison of the oxygen 1*s* NRIXS of chemically de-lithiated CoO_2 with pristine LiCoO_2 .

Proposed Work for FY 2010

This project does not continue into FY10.

Microporous Filters for Hydrogen Purification

2007-060-R2

John A. Schluter, Larry A. Curtiss, Urs W. Geiser, Christopher L. Marshall, and Michael J. Pellin

Project Description

With the push toward the hydrogen economy, new materials that can separate and purify gases are needed for the efficient operation of fuel cell systems. Membrane separation processes are attractive alternatives to mature, energy-intensive technologies, such as pressure swing adsorption and cryogenic distillation. Ultramicroporous molecular framework materials (UMFMs) represent a promising unexplored membrane component. UMFMs have the potential to be tuned to discriminate precisely among various gases on the basis of two key parameters: kinetic size and interaction energy. Kinetic size can be used to discriminate between gas molecules of significantly different diameters, while interaction energy provides a parameter for distinguishing between gases of similar kinetic size. Discrimination of gases with the use of UMFMs is an exciting new prospect with potential for the delicate tuning of separation behavior by adjusting the nanoscale architecture.

The synthesis and characterization of metal-organic frameworks (MOFs) with intricate structures and various functionalities continues to receive major attention, linking various disciplines of chemistry with materials science. The versatility of these materials, from the perspectives of both design and function, has given rise to materials with a diverse range of physical and chemical properties (e.g., porosity, chirality, magnetic ordering, electronic switching, and anomalous thermal expansion behavior), with potential application areas that are both industrially and environmentally important, such as molecular sensing and gas storage/separation. Typically, MOFs have been fabricated from transition metal ions and bridging ligands with carboxyl, pyridyl, or carbonitrile donor groups. However, the sustained exponential growth in MOF discovery has led to the use of an increasingly diverse range of bridging ligands that often have specifically targeted chemical or geometric properties. In particular, ligands based on five-membered heterocycles, such as imidazole and tetrazole, have recently been shown to be highly effective at generating porous MOFs with network structures that mimic those of zeolites. For example, a series of zeolite-like MOFs (ZMOFs) fabricated from bis(bidentate) imidazoledicarboxylic acid ligands with various metal ions have been reported that represent a molecular extension of traditional zeolite structural topologies, exhibiting large cavities and high chemical stabilities.

Mission Relevance

The project is relevant to DOE's mission in energy. DOE seeks to promote America's energy security through reliable, clean, and affordable energy. The development of a hydrogen economy will require an efficient means to produce high-purity gas at low cost. Our project focuses on the development of a new class of materials for purification of these gas streams to help enable this revolution. The development of UMFM-based membranes for purification of small gas molecules will also be of interest to the U.S. Army and National Aeronautics and Space Administration, which would use such membranes for the operation of light-weight, fuel-cell power packs and for the purification of breathing gas aboard spacecrafts, respectively.

FY 2009 Results and Accomplishments

MOFs fabricated with the bridging ligand 3-amino-1,2,4-triazole (HAmTAZ). AmTAZ and other simple 1,2,4-triazole-based ligands have the ability to generate polynuclear coordination compounds with diverse and often highly complex structures as a result of the various possible bi- and tridentate coordination modes (Scheme 1). While many binary materials are known to form with univalent metal ions, triazolate-based materials with divalent metal ions typically incorporate additional anionic ligands. Most commonly, these secondary anions are terminal halide ligands or other coordinating anions (e.g.,

nitrate or formate) that result from the metal salt used in the synthetic procedure. In other cases, these secondary anions add further structural complexity by acting as a second bridging unit (e.g., hydroxide, oxalate, or terephthalate). Through this project, we report the synthesis and detailed characterization of two nanoporous MOFs incorporating AmTAZ with either sulfide, $[\text{Zn}_3(\text{AmTAZ})_3\text{S}](\text{NO}_3)(\text{H}_2\text{O})$ (1 (H_2O)), or carbonate and hydroxide anions, $\text{Zn}_7(\text{AmTAZ})_8(\text{CO}_3)_2(\text{OH})_2 \cdot 2(\text{EtOH})$ (2 (EtOH)). The host-guest properties of both materials have been investigated by using a range of techniques, including *in-situ* synchrotron-based powder X-ray diffraction.

In recent years, the focus of MOF-related research efforts has begun to shift from targeted exploratory synthesis approaches to more applied fields that exploit the porous nature of MOFs. As such, the accurate elucidation of their often complex host-guest properties now presents a crucial step in advancing the use of MOFs. This objective necessitates the development of *in-situ* structural techniques, such as X-ray diffraction, to precisely monitor the structural response during guest desorption and sorption processes. These techniques promise an unparalleled insight into not only major structural changes, such as phase transformations, but also many other more subtle structural variants, such as those associated with framework dynamics and the rearrangement of host-guest interactions. In particular, *in-situ* synchrotron-based powder X-ray diffraction has recently provided crucial information in understanding the synergistic magnetic and host-guest properties of nanoporous spin crossover framework materials. Dr. Greg Halder, a post-doctoral appointee who was initially hired to contribute to this project, has developed these techniques at the APS and applied them to this project.

Of the two nanoporous materials identified above, 1 (H_2O) represents a highly unusual example of an MOF containing sulfide-bridging anions, achieved here by the *in-situ* formation of sulfide ions during the solvothermal synthesis. More generally, such a synthetic approach may provide a convenient route to generating novel sulfide-containing frameworks in the future. Although no nitrogen uptake was observed for 1, nanoporosity was confirmed through *in-situ* synchrotron-based X-ray diffraction studies of desorption and resorption of the guest water molecules. The cubic symmetry of the system was maintained throughout these processes, revealing a subtle, concerted 'breathing' of the host framework. The inclusion of three unique types of anionic bridging ligands in 2 (EtOH) has generated an intricate three-dimensional network structure that defines a highly convoluted, and primarily one-dimensional, pore system. Nitrogen sorption studies of the desorbed host material, 2, indicate that the passage of nitrogen through the pore system is significantly hindered, suggesting that this material may be well suited for gas separation.

ration applications, especially as related to hydrogen purification. In dramatic contrast to 1, *in-situ* synchrotron-based X-ray diffraction studies of 2 revealed highly anisotropic structural flexing during the desorption and sorption of both ethanol and water molecules, in part a result of the increased degrees of freedom imparted by its complex, lower-symmetry structure. Interestingly, the uptake of the different guest molecules proceeds *via* subtly different structural flexing mechanisms, which leads to a larger overall lattice volume increase for the sorption of the smaller water molecules. This work further demonstrates the importance of *in-situ* structural studies for the precise elucidation of structure-property relationships in MOFs and other advanced porous materials.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Halder, G.J., H. Park, R.J. Funk, K.W. Chapman, L.K. Engerer, U. Geiser, and J.A. Schlueter, "In-situ X-ray Diffraction Studies of Host-Guest Properties in Nanoporous Zinc-triazolate-based Framework Materials," *Crystal Growth & Design* 9 (2009), 3609–3614.

Mesoscale Simulation of Blood Flow Using Kinetic Theory

2007-066-R2

Zinetula Z. Insepov and Ahmed M. Hassanein

Project Description

This project examines two approaches to mesoscale simulation of blood flow. One involves coupling computational fluid dynamics (CFD) with kinetic theory high-frequency fluctuations of blood elements associated with particle migration. The other involves atomistic simulation by using large-scale molecular dynamics (MD) to calculate important blood characteristics from the microscopic representation of the blood particles.

Mission Relevance

The DOE Office of Biological and Environmental Research identified this research subject as a field of biomedical science with the potential to improve the quality of life. Our successful modeling of blood flow on the mesoscale may also be of interest to the National Institutes of Health (which has specifically identified the significance of CFD in medical research in its Bioengineering Partnership and Innovations in Biomedical Computational Sciences and Technology programs), the National Science Foundation, and the American Heart Association.

FY 2009 Results and Accomplishments

During FY09, we developed several atomistic simulations models for investigating the blood aggregation, structure, and dynamics of the cluster formation. One goal was to simulate bubble formation and aggregation phenomena in liquids and apply this knowledge to blood viscosity simulations. To achieve this goal, we developed an atomistic system containing three different types of particles, and we studied the distribution function of the aggregates over their size ranges. One of the main simulation results was the confirmation that the bimodal distribution function of aggregates can be obtained only in the case when the small aggregates were allowed to migrate. This result correlates with experimental and theoretical studies of bubbles and precipitation. We also explored how two or more bubbles can merge and create a large bubble; this information provides insight into the mechanism of blood clogging.

We developed a method to calculate the viscosity of a multiphase fluid. Specifically, atomistic models of three-phase dynamics were developed based on an MD LAMMPS code and on our in-house MD model. We used a three-phase system consisting of liquid (solvent) modeled by a Lennard-Jones (LJ) particle, as well as two phases simulated by using two different-sized aggregates or clusters. These clusters interacted via a model potential consisting of LJ and Coulomb pair-additive interaction potentials. This model was used to calculate the viscosity of the model system and to study nanobubbles. The viscosity was calculated by using a reverse non-equilibrium molecular dynamics (NEMD) method that uses the Norton algorithm; in this method, the simulated system is divided by a number of bins and the variables are averaged within these bins (see Figure 1). The viscosity obtained by atomistic simulation will be used as a boundary condition for CFD simulation of interactions of red blood cells and leukocytes with vascular walls (Figures 2 and 3).

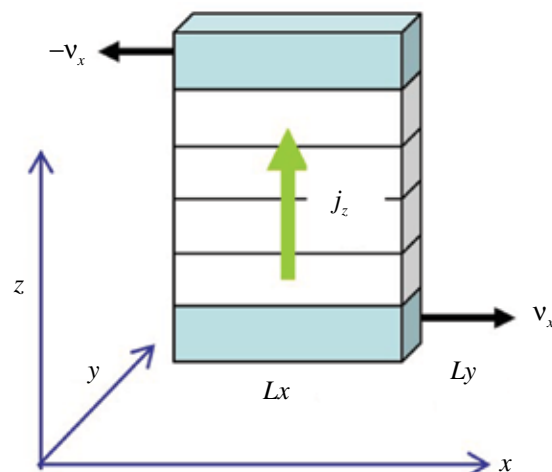


Figure 1. The studied system divided into thin horizontal layers normal to the momentum flux in z -direction. The viscosity was calculated by using a reverse non-equilibrium molecular dynamics (NEMD) method.

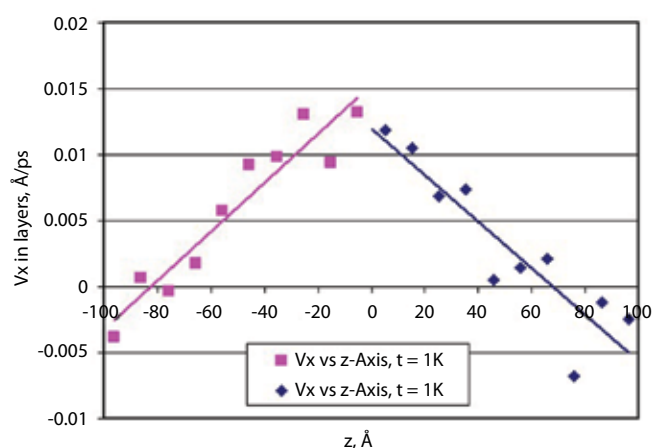


Figure 2. Viscosity simulation of a system containing three phases — a liquid and two types of clusters — via a reverse NEMD method. The size of the system was $200 \times 200 \times 200 \text{ Å}^3$, with 500,000 particles. The number of bins was 20.

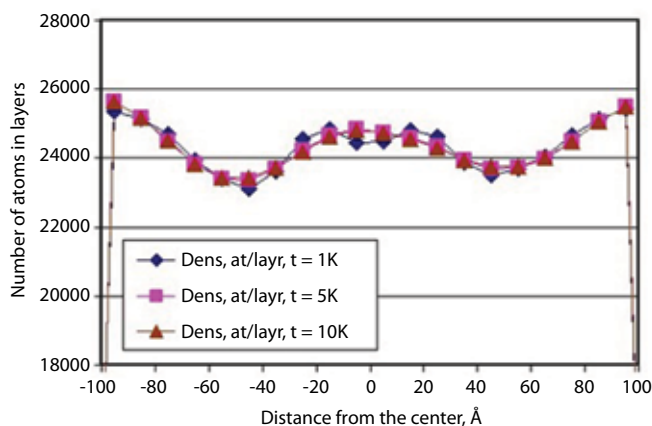


Figure 3. Density of a liquid and two types of clusters. The layer with a lower number of particles contains clusters. The results are shown for the time instant $t = 1,000$ time steps.

Figure 2 shows a typical linear dependence of the velocity component, v_x , that is transmitted in the direction of the momentum flow (z -axis). To generate the shear viscosity, scientists typically swap two particles with different momentums. For example, a particle with the momentum p_x is swapped with the particle in an opposite bin, thus generating a flux of the momentum component.

Our system contains three kinds of atoms, so that approach proved difficult because of the stability of the system and conservation of the energy, total momentum, and cluster concentration. Therefore, we performed the swapping of the momentum between the same kinds of atoms. Our simulations were conducted at various temperatures to determine the dependence of the viscosity on temperature. We obtained good comparisons of our calculations with the available viscosity data in the literature. We also simulated the effect of acoustic waves on fluid properties in a confined volume. We plan to publish these results in the near future.

Proposed Work for FY 2010

This project does not continue into FY 2010.

Non-Refereed Publications and Presentations

Insepov, Z., "New Nanopumping Effects with Carbon Nanotubes," book chapter in *Recent Developments in Modeling and Applications of Carbon Nanotubes*, edited by Q. Wang, B.I. Yakobson, and K.M. Liew, Transworld Research Network, Kerala, India, in press.

Sub-Millisecond Measurements of Structural Changes in Materials under Extreme Conditions

2007-068-R2

Zahirul Islam and Jonathan C. Lang

Project Description

The primary objective of this project was to develop high-field (30-Tesla), pulsed magnet instruments and x-ray techniques for structural and magnetic studies of materials at the Advanced Photon Source (APS). By combining a pulsed field with the natural timing structure of synchrotron radiation, we can detect structural and magnetic changes on the sub-millisecond level. During the final year (2009) of this project, we enhanced the capabilities of the technique by incorporating a fast one-dimensional (1D) detector for quick data acquisition and developing a new longer-pulse solenoid magnet.

Mission Relevance

This project is tied to DOE's mission in science. Our high-field pulsed magnet will be a key instrument for the study of structural responses caused by magnetic fields in such systems as multi-ferroic nanocomposites and in functional materials based on magneto-caloric (change of temperature), magneto-electric (change of electrical polarization), and shape-memory (change of shape) effects, all of which are relevant to DOE's programs in materials science and high-temperature superconductors. The National Institutes of Health may also find our magnet's capabilities of interest; its successful demonstration will help make the case for developing instrumentation to study biological systems subjected to high magnetic fields using synchrotron x-rays.

FY 2009 Results and Accomplishments

Our accomplishments this year include (1) time-resolved data collection using a 1D strip detector; (2) continued studies of field-induced structural effects in a frustrated magnet, $\text{Tb}_2\text{Ti}_2\text{O}_7$; and (3) design of a long-pulse magnet cryostat.

We procured, tested, and used a fast 1D Si microstrip detector for scattering measurements. While a point-by-point collection of time-resolved data using a fast-point (e.g., avalanche photodiode [APD]) detector works well and is necessary when very high-resolution measurements are called for, it is intrinsically inefficient. More efficient data collection can be achieved by employing fast-linear-array micro-strip detectors along an arc in the reciprocal lattice. By recording time-resolved arcs for different orientations of a crystal, we can determine the field dependence of an entire two-dimensional (2D) swath of reciprocal lattice in a few field pulses. Figure 1 shows how the intensity of an (8, 0, 0) Bragg peak in $\text{Tb}_2\text{Ti}_2\text{O}_7$ varies as a function of field, as monitored along an arc in reciprocal space during a single pulse. Note that measurements of the integrated intensity require collection of a set of time-resolved data as the crystal is “rocked” through a Bragg peak — as in the point-by-point method.

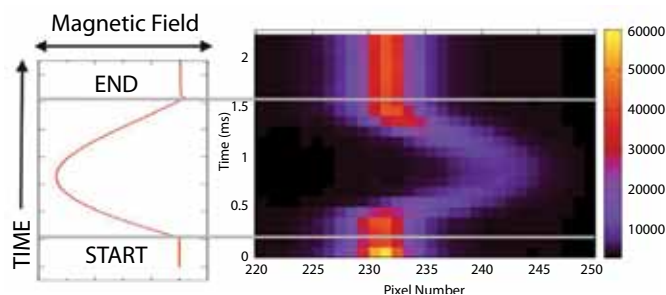


Figure 1. Left: Typical pulsed field profile. Right: 2D time-intensity map of diffracted signal captured by using a 1D strip detector for a peak field of 20 Tesla. Using the known individual strip width and detector-to-sample distance, we can determine angular shifts of Bragg peaks as a function of field.

We also developed a second pulsed magnet with a large-bore (~18-mm) cryogenically cooled solenoid (Figure 2). This magnet can use the existing capacitor bank with full energy of 40 kilojoule (kJ) to generate fields of ~30 Tesla. The pulse shape is half-sine with an extended decay, and FWHM (full width at half maximum) is ~4 ms. A liquid nitrogen cryostat is used for magnet cooling and a cryogen-free 1.4 K cryostat (not shown) is used for the sample. A special sample mount allows a single crystal to be held in the center of the magnet without interfering with the incoming beam, providing as much as 25° of scattering angle. This new instrument will enable both powder and Laue diffraction measurements. Importantly, the design facilitates single-crystal diffraction experiments with the capability to apply magnetic fields parallel to the scattering plane — a feature not available in any other pulsed magnet instruments. This geometry is ideal for applying fields along a unique axis (e.g., c-axis of cuprates and spin-gap compounds)

of a thin crystal plate and, at the same time, having substantial optical access (in transmission) to reciprocal-lattice points orthogonal to that axis for symmetry determination.

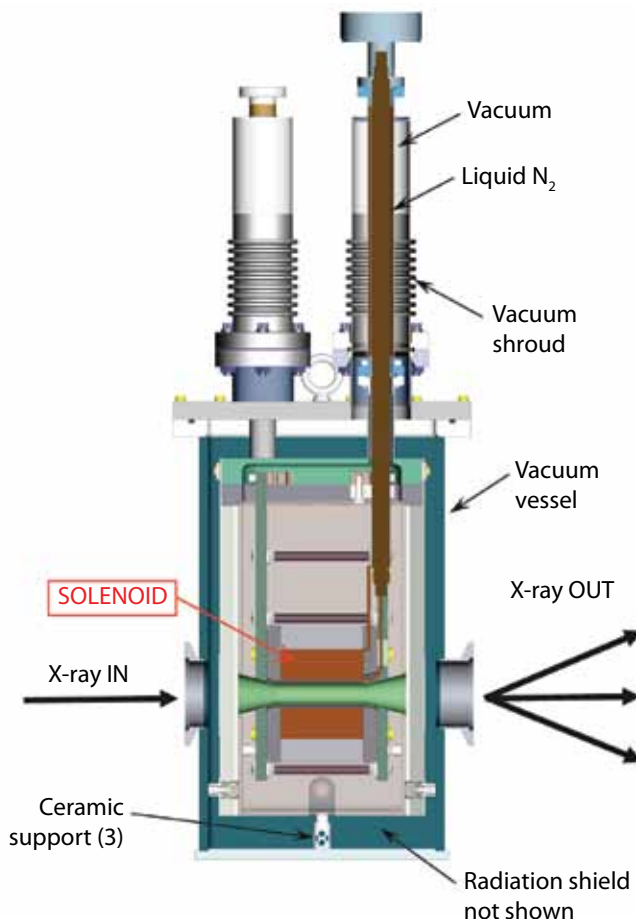


Figure 2. A ~30-Tesla large-bore solenoid instrument with up to 25° of scattering angle. Sample cryostat is not shown in the figure. Note that the magnetic field is in the scattering plane.

Proposed Work for FY 2010

This project does not continue into FY 2010.

Refereed Publications

Islam, Z., J.P.C. Ruff, H. Nojiri, Y.H. Matsuda, K.A. Ross, B.D. Gaulin, Z. Qu, and J.C. Lang, “A Portable High-Field Pulsed-Magnet System for Single-Crystal X-Ray Scattering Studies,” *Review of Scientific Instruments* **80**, 113902 (2009).

Non-Refereed Publications and Presentations

Islam, Z., J.P.C. Ruff, Y.H. Matsuda, H. Nojiri, K.A. Ross, J.P. Clancy, Z. Qu, B.D. Gaulin, Y. Narumi, S. Yoshii, Z. Mao, and J.C. Lang, "A High-Field (30-Tesla), Pulsed Magnet System for X-Ray Studies at the Advanced Photon Source," Poster Presentation, Gordon Research Conference, X-Ray Science, Colby College, Waterville MN, August 2–7, 2009.

Islam, Z., J.P.C. Ruff, Y.H. Matsuda, Z. Qu, H. Nojiri, S. Yoshii, B.D. Gaulin, Z. Mao, and J.C. Lang, "A High-Field (30–45 Tesla) Pulsed Magnet Instrument for X-Ray Studies of Materials at the Advanced Photon Source," Contributed Presentation, American Physical Society, Pittsburgh, PA, March 16–20, 2009.

Islam, Z., "High-Field Science at a Synchrotron: A Novel Methodology Using Pulsed Field Magnets," Invited Presentation, Colloquium, Physics Department, University of Houston, Houston, TX, February 2009.

Islam, Z., "High-Field, Pulsed Magnet System for X-Ray Studies of Materials at the APS," Invited Talk, 4th Japan Atomic Energy Agency (JAEA) Synchrotron Radiation Research Symposium: X-Ray and High Magnetic Field, SPring8, Hyogo, Japan, March 2009.

Design and Synthesis of New Nanocarbon Composites from Carbon Nanotubes and Ultrananocrystalline Diamond

2007-071-R2

Larry A. Curtiss, Dieter M. Gruen, Michael J. Pellin, Michael G. Sternberg, and Peter Zapol

Project Description

The synthesis of composites of diamond and carbon nanotubes (CNTs), as well as other forms of carbon, can provide an entirely new class of nanocarbons that have unique materials properties beyond those of diamond and carbon nanotubes. The composites would have an abundance of structures, and the synthesis parameters could be used to tune the electronic properties of these new materials. The key to attaining these composites is to find ways to form covalently bonded interfaces between CNTs and diamond and then to tailor the properties of the resulting material for applications. This project focuses on development of new nanocarbon architectures based on carbon nanotube and ultrananocrystalline diamond (UNCD). The goal of this project is to combine them into a composite material with covalent interfaces and then to tailor the electronic properties for applications. The work involves

an integrated experimental/theoretical approach that utilizes our expertise in nanocarbon synthesis and characterization coupled with state-of-the-art computational methods.

Mission Relevance

This project is tied to DOE's mission in science, specifically the Materials Science (Basic Energy Sciences) program and the DOE Solar Energy Initiative. The project results may be of interest to the Office of Naval Research (ONR) and DOE's Office of Energy Efficiency and Renewable Energy (EERE). The successful synthesis of diamond-nanotube composites with covalent attachment would establish a new type of carbon nanomaterial that can potentially create an entirely new field of research because of the many possible architectures that could be made and properties that could be built into them. Composites of carbon nanotubes and nanodiamond are of great interest both in terms of fundamental science and of technology because they can combine the unique electronic, mechanical, and structural properties of both components. In addition, because of the very strong covalent bonding of the components, the composites would have very high diffusion barriers making them stable at high temperatures. By learning how to control the properties of the composites such as electron density of states near the Fermi level, electrical and thermal conductivities, these new materials will have potential applications for thermoelectrics, field electron emission devices, thermionic emitters, and catalytic supports.

FY 2009 Result and Accomplishments

Our activities and accomplishments are concentrated around two main efforts:

(1) *Thermoelectric properties of nanocarbon ensembles*

Nanocarbon ensembles composed of mixtures of nanographite or dispersed ultrananocrystalline diamond with boron carbide were found to form mechanically rigid bulk compacts by reaction at high temperatures with methane gas. These ensembles were subsequently annealed in an argon atmosphere at temperatures of up to 2,500 K. The ensembles were characterized by various techniques, including scanning electron microscopy, Raman spectroscopy, x-ray diffraction, and high-resolution transmission electron microscopy. The compacts retain their nanostructural characteristics up to the highest annealing temperatures but display complex structural transformations, changing from a complex mixture of fullerenes, nano-onions, and nanotubes to hollow nanopolyhedra as the temperature is increased. The thermoelectric power factors of nanocarbon ensembles were investigated as a function of temperature. The measured power factors were found to increase strongly both as a function of annealing temperature and of the temperature at which the measurements are carried out, reaching 1 mW/K²cm at 1,200 K without showing evidence of a plateau. The unusual thermoelectric properties are believed to be attributable to the enhancement of elec-

tronic configurational entropy resulting from the large number of boron configurations in the graphite lattice. There is some theoretical evidence to support this finding (see below).

(2) Density functional calculations of nanocarbon composites based on diamond and sp^2 carbon materials

We have completed our quantum chemical studies of composites of a (5,5) single-walled carbon nanotube with a clean (100) diamond surface. Numerous stable structures with covalent bonds at the interface were found for the carbon nanotube that were parallel and perpendicular to the dimer rows on the (100) surface. Figure 1 shows the eight optimized structures for the interaction of the (5,5) nanotube with the diamond (100) surface. The binding energy of the most stable structure is 1.7 eV/Å and results from the formation of a strong covalent bond between the carbon nanotube and the diamond surface. The structure of the nanotube is distorted by adsorption on the surface, such that it forms a nanotunnel-like structure. In molecular dynamics simulations, the nanotunnels are found to be stable at high temperatures, and the addition of the nanotube to the surface occurs at high temperatures without a barrier. In the most stable structure, the interaction between the nanotube and the diamond surface produces a decrease in the density of states near the Fermi level, but the metallic character of the nanotube is maintained in two other less strongly bound nanotunnel-like structures. We have also investigated the interactions of (7,7), (9,9) carbon nanotubes with diamond (100) surfaces.

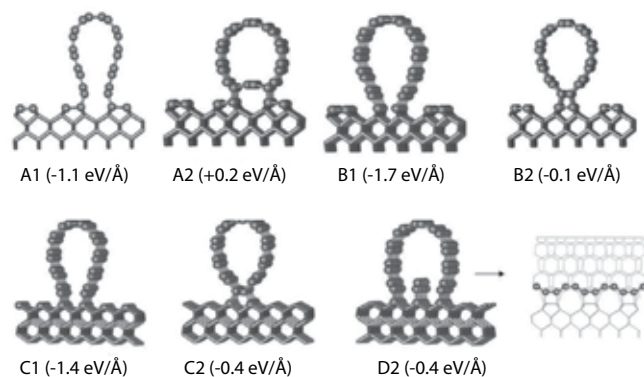


Figure 1. Eight optimized structures investigated for the interaction of the (5,5) nanotube with the diamond (100) surface.

Density functional calculations were carried out on pristine and boron-substituted nanographene sheets containing up to 36 rings to model the electronic structure of the nanocarbon ensembles that were studied experimentally. The results indicate that increasing the size of the sheet stabilizes high-spin states relative to low-spin states. Also, high-spin states are more favorable for non-Kekule structures of nanographene. Boron substitution in the nanographene sheets is found to stabilize low-spin ground states over high-spin states. The electronic structures of the nanographene sheets are used to

help explain recent results on the thermoelectric properties of boron-substituted nanographite ensembles. In the carbon ensembles studied experimentally, the number of possible boron geometric configurations is in the many thousands, each one associated with a distinct nanographite structure. Thus, in principle, the creation of “holes” at the top of the valence band by the electron-deficient borons creates a vast number of empty, perhaps nearly degenerate electronic states. Our model suggests that boron substitution lowers the Fermi level of graphene sheets by about 0.1 eV. A large number of empty states can therefore be populated thermally, creating a highly unusual capacity for the augmentation of electronic entropy. This type of situation has often been described as desirable for promoting the occurrence of good thermoelectric properties.

Proposed Work for FY 2010

This project does not continue into FY 2010.

Refereed Publications

Gruen, D.M., P. Bruno, R. Arenal, J. Routbort, D. Sing, and M. Xie, “Thermoelectric Power Factors of Nanocarbon Ensembles as a Function of Temperature,” *J. Applied Physics* **105** (2009), 073710.

Redfern, P.C., D.M. Gruen, and L.A. Curtiss, “Effect of Boron Substitution on the Electronic Structure of Nanographene and its Relevance to the Thermoelectric Transport Properties in Nanocarbon Ensembles,” *Chem. Phys. Lett.* **471** (2009), 264.

Magnetically Targeted Thermal Tumor Therapy Using Designer Nanospheres

2007-075-R2

Valentyn Novosad, Frank Fradin, Dong-Hyun Kim, John E. Pearson, Elena A. Rozhkova

Project Description

Temperature elevation is a natural and powerful defense mechanism of the body and is successful in fighting off various diseases. Current hyperthermia treatment options make use of different energy sources to achieve elevated temperatures within tissues; among these approaches are externally induced electromagnetic waves (e.g., radio frequency or microwave-hyperthermia), ultrasound (externally or internally applied), current-flow between two or more electrodes, electrical or magnetic fields between implanted antennas, and electrical or magnetically induced thermo seeds or tubes. Major unsolved problems of clinically applied hyperthermia include mitigating its invasiveness; restricting the hyperthermic effect to a specific area of interest within the body (i.e., targeting); and achieving on-demand, homogenous, and

temperature-controlled heat distributions within the target organ (i.e., controlled delivery). In contrast to currently investigated hyperthermia treatment modalities, we propose that designer nanospheres encapsulated with magneto-thermal responsive materials will provide — in conjunction with a precisely regulated, magnetically based temperature-induction device — well-defined treatment parameters to overcome current disadvantages in targeted hyperthermia.

Mission Relevance

This project is relevant to DOE's mission in science. The effort contributes to the scientific underpinnings of nanomagnetic particles and to their biomedical applications. The project activities are related to DOE's basic science mission to understand the properties and behavior of advanced materials and to identify methods that enable materials to perform better at acceptable costs through innovative design, synthesis, and processing. Success in the proposed work will also be of interest to the National Institutes of Health (NIH) (through their recently established "nanomedicine" programmatic area and NIH R21 Exploratory and Developmental and R21/R33 Phased Innovation awards on "Application of Emerging Technologies for Cancer Research" supervised by the National Cancer Institute), the National Science Foundation (NSF), and other national and private programs.

FY 2009 Results and Accomplishments

Magnetic nanoparticles (MNPs) have a wide range of biomedical applications, including magnetic resonance imaging (MRI), gene therapy, drug delivery, and magnetic hyperthermia. With the development of MNPs, diagnostic and therapeutic tools for cancer treatment can be integrated into a single multifunctional MNP. On the other hand, gold nanoparticles (AuNPs) also have been used extensively in biological applications, such as protein and DNA detection, optical imaging, photo-induced hyperthermia, and drug delivery. AuNPs display electromagnetic resonance because of collective oscillations of their free electrons known as plasmons. For particles that are small compared to the wavelength of the incident light, plasmons are excited when light with an appropriate wavelength is shone on them. This results in a strong absorption at that wavelength. Because of plasmon behavior, these particles act as novel contrast agents for optical detection to visualize a specific region, as well as a photo-thermal therapy and DNA/protein sensing. Thus, hybrid AuNPs/MNPs, which combine the advantages of both magnetic and photonic materials, have undoubtedly many gains for biomedical applications. This has been achieved by synthesis of gold/iron oxide binary nanoparticles. However, synthesis and surface modification of core-shell Au-MNP structures can be challenging, and the magnetic properties of these binary particles may be altered. Our approach is to combine both kinds of particles, AuNPs and MNPs, in thermosensitive polymeric micelles for imaging, simultaneous magnetic hyperthermia, and drug delivery.

Hybrid AuNP/MNP inside micelles can offer heating for hyperthermia and an optical imaging tool for diagnostic application. Thermoresponsive polymeric micelles were employed as a carrier for triggered drug release by heating AuNP/MNPs under an alternating current (ac) magnetic field. The micelle structure provides considerable advantages, such as significant enhancement of the water solubility and bioavailability of hydrophobic drugs and AuNP/MNP; minimizes aggregation; and improves stability in aqueous environments because of the hydrophilic shells. In addition, AuNP/MNP nanocomposites can be easily prepared by self-assembly of these particles in micellar capsules. Herein, the micelles are made of an amphiphilic block copolymer of poly(N-isopropylacrylamide-co-acrylamide)-block-poly(caprolactone), P(NIPAAm-co-AAm)-b-PCL, combined with binary AuNP/MNP, which are positioned with various weight ratios at the hydrophobic core. An optimized hybridization ratio and amount of Au/MNP in polymeric micelles are important for stable and effective drug delivery and hyperthermia. The synthesized thermoresponsive AuNP/MNP-micelles were characterized and evaluated in various synthetic conditions for the optical imaging and the combined therapy of simultaneous hyperthermia and drug delivery.

To develop functional hybrid thermoresponsive AuNP/MNP micelles, we first synthesized 8-nanometer (nm) magnetite nanoparticles by using established wet chemistry methods. Briefly, $\text{Fe}(\text{acac})_3$ was mixed in benzyl ether with 1,2 hexadecanediol, oleic acid, and oleylamine under nitrogen to synthesize the 6-nm magnetite nanoparticles. Then, the 6-nm magnetite nanoparticles were used as seeds or nucleation centers for further growth. Next, 10-nm gold nanoparticles were synthesized by a thermal decomposition. Gold trichloride acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and oleylamine were added to phenyl ether, followed by the addition of 1,2 hexadecanediol. Finally, gold and magnetite particles were loaded into thermosensitive micelles through self-assembling by using a solvent-evaporation method. Figure 1 shows a representative transmission electron microscope (TEM) image of the sample.

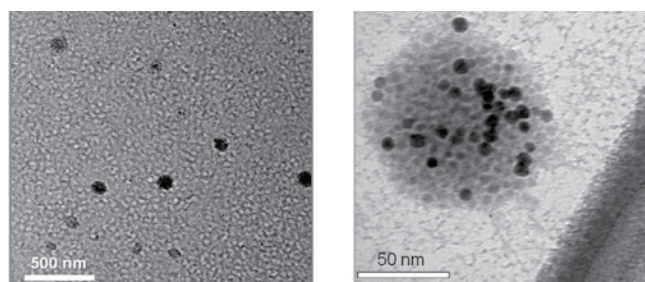


Figure 1. TEM images of hybrid gold-magnetite loaded micelles. Dark particles are gold; grey particles are magnetic nanoparticles.

The hydrodynamic micelle size was measured by dynamic light scattering in the hydrated state at 25°C and 45°C. The size was reversibly changed from approximately 104 nm at 25°C to 71 nm at 45°C (Figure 2). The calculated reversible volume change of the micelles was approximately 68.2% between 25°C and 45°C.

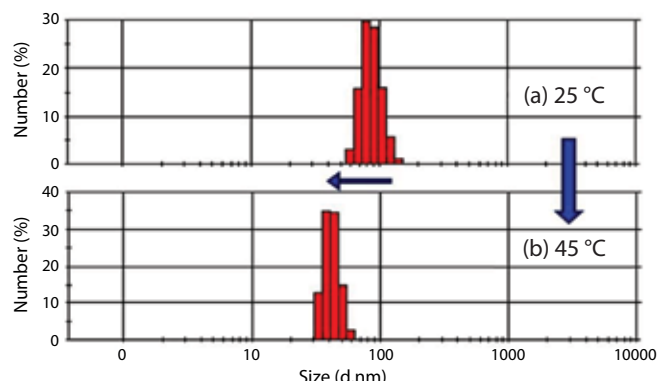


Figure 2. Size distribution of hybrid nanoparticles-loaded micelles at temperatures of (a) 25°C and (b) 45°C.

Both magnetic hyperthermia and drug delivery benefit from the high magnetic moment. Therefore, the magnetization curves of the samples were separately measured by using conventional magnetometry. Self-assembly of the magnetic particles into micelles resulted (in some) of up to a 20% reduction of the magnetization of MNP-micelles. In the case of hybrid AuNP/MNP-loaded micelles, increasing the gold content leads to a gradual reduction of the saturation magnetization, as a result of a decrease in magnetic particles content (Figure 3). Nevertheless, the magnetization of micelles with a high concentration of gold (AuNP/MNP 1:1) was sufficient to magnetically separate the AuNP/MNP micelles from the solution. In addition, the presence of gold in the micelle can be used for photo-induced heating in order to enhance magnetic hyperthermia. Moreover, gold particles are known to have a good contrast for biological imaging. The hybrid AuNP/MNP-micelles solutions gradually change color from red through pink to light brown by increasing the gold content due to excitation of a surface plasmon resonance (SPR) (Figure 4 inset). The characteristic SPR absorption of AuNP/MNP-micelles can be a beneficial contrast agent for optical detection of specific regions through magnetic or bimolecular targeting.

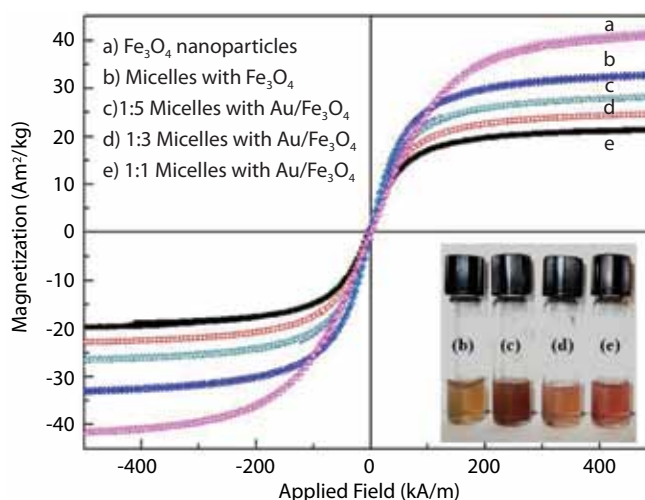


Figure 3. Magnetization curves of nanoparticles-loaded micelles with various weight ratios of AuNP/MNP at room temperature. A. MNP; B. MNP in micelles; C. AuNP/MNP (1:7) in micelles; D. AuNP/MNP (1:5) in micelles; E. AuNP/MNP (1:3) in micelles; F. AuNP/MNP (1:1) in micelles.

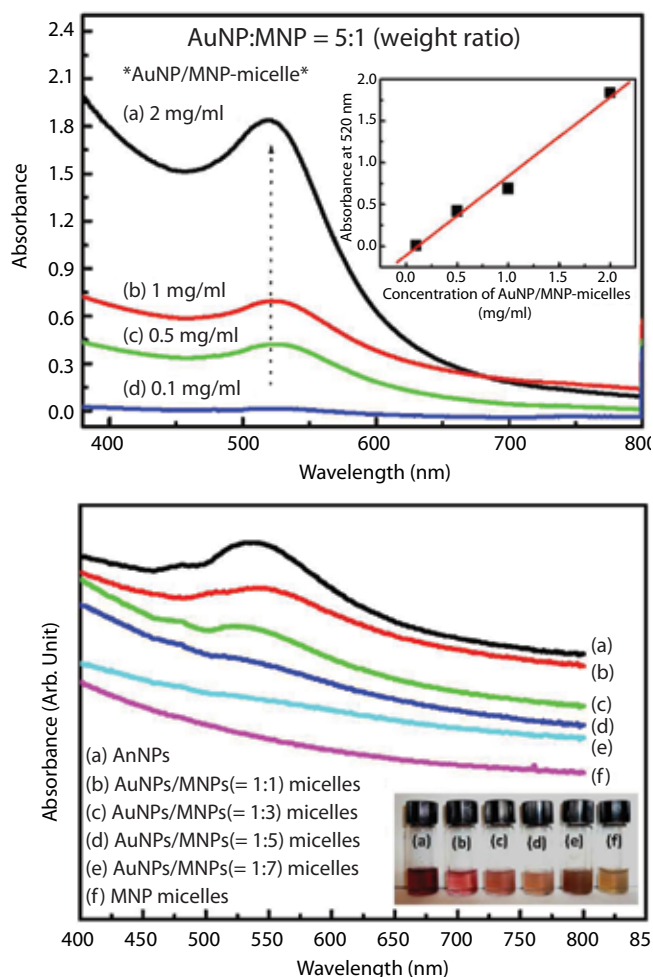


Figure 4. UV/vis absorption spectra of (top) AuNP/MNP-micelles (5:1 wt ratio) at various concentration, (inset) absorbance dependent on micelles concentration at 520 nm, and (bottom) hybrid AuNP/MNP-micelles prepared with various weight ratios of AuNP/MNP and (inset) corresponding color changes in micelle solutions.

In conclusion, thermosensitive hybrid AuNP/MNP-micelles applicable for combined hyperthermia and chemotherapy with optical imaging were successfully synthesized. A stable reversible volume change of AuNP/MNP-micelle that can trigger a drug release was approximately 68.2% between 25°C and 45°C. An optimal weight ratio of nonmagnetic and magnetic particles self-assembled into the micelles with high-saturation magnetization comparable to that of MNP-only micelles has been found to be 1:7 (AuNP:MNP). The characteristic SPR spectra of AuNP/MNP-micelles, which can act as contrast agent for optical detection to visualize a specific region through magnetic or bimolecular targeting, were represented with various weight ratios of AuNP and MNP. The synthesized hybrid AuNP/MNP-micelles will provide great opportunities as a cancer therapy tool for the combined hyperthermia and chemotherapy with optical imaging.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Kim, D.-H., E.A. Rozhkova, T. Rajh, S.D. Bader, and V. Novosad, "Synthesis of Hybrid Gold/Iron Oxide Nanoparticles in Block Copolymer Micelles for Imaging, Drug Delivery, and Magnetic Hyperthermia," *IEEE (Institute of Electrical and Electronics Engineers) Trans. Magn.* **45** (2009), 4821–24.

Rozhkova, E., V. Novosad, D.-H. Kim, J. Pearson, R. Divan, T. Rajh, and S.D. Bader, "Ferromagnetic Microdisks as Carriers for Biomedical Applications," *J. Appl. Phys.* **105** (2009), 07B306.

Non-Refereed Publications and Presentations

Kim, D.-H., E.A. Rozhkova, T. Rajh, S.D. Bader, and V. Novosad, "Multifunctional Magnetic Micelles for Cancer Treatment," presented at the Engineering Conference International (Advances in Magnetic Nanostructures), Vail, CO, October 4–9, 2009.

Kim, D.-H., E.A. Rozhkova, T. Rajh, S.D. Bader, and V. Novosad, "Thermoresponsive Magnetic Micelles for Simultaneous Magnetic Hyperthermia and Drug Delivery," presented at the 2009 Nanotechnology Conference and Trade Show, Houston, TX, May 3–7, 2009.

Kim, D.-H., E.A. Rozhkova, T. Rajh, S.D. Bader, and V. Novosad, "Multifunctional Magnetic Polymeric Micelles for Dual Anti-Cancer Treatment and Imaging," presented at the 1st CRS (Controlled Release Society) Illinois Student Chapter Symposium, Chicago, IL, May 29, 2009.

Rozhkova, E., V. Novosad, D.-H. Kim, R. Divan, T. Rajh, and S.D. Bader, "Ferromagnetic Microdisks as Magnetic Carriers for Biomedical Applications," presented at the 53rd Annual Conference on Magnetism and Magnetic Materials, Austin, TX, November 10–14, 2008.

Identification and Characterization of Ovarian Cancer Stem Cells toward Ultimate Cancer Treatment

2007-080-R2

Qiaoling Jin and Liaohai Chen

Project Description

Ovarian cancer is an extremely aggressive disease associated with a lack of early symptoms, rapid progression to peritoneal metastases, and poor prognosis for patients. Almost 60% of women with the most deadly type of ovarian carcinomas die within five years of the first diagnosis. This poor prognosis is due to the ineffectiveness of chemotherapy and the incomplete removal of the cancer source, presumably due to the escape of cancer stem cells (CSCs). The objective of this research is to identify and characterize ovarian CSCs and to reveal the mechanisms of their proliferation and differentiation at the molecular level. The outcome of the research will lead to the identification of potential targets for eliminating CSCs responsible for epithelial ovarian carcinoma.

Mission Relevance

This project is tied to DOE's mission in improving the quality of life through innovations in science and technology. According to the American Cancer Society, ovarian cancer accounts for 6% of all cancers among women and ranks fourth as a cause of their deaths from cancer. Therefore, our project has the potential to benefit millions of women who are suffering from this disease or at high risk of contracting this disease.

FY 2009 Results and Accomplishments

Since CSCs are a side population of cells surrounded by a majority of normal tumor cells (niches), it is critical to develop a tool that can perform broad-range gene analysis on single cells under *in situ* and *in vivo* conditions. In FY 2009, we focused on developing such a capability. We first used the house-keeping gene β -actin to establish a protocol to perform gene analysis from single cells without affecting cell vitality. The experiment was carried out by coupling an atomic force microscope (AFM) with a fluorescence microscope. The AFM tip was premodified by a fluorescent-dye-labeled oligonucleotide (5'-thiol labeled oligo-dT) via the gold-thiol chemistry. Since the apex of an AFM tip is ~ 15 nm in radius, the tip can be selectively positioned at the center of a cell. Also, because the tip ($10\text{--}15\ \mu\text{m}$ in length) has a high aspect ratio, it can penetrate the membrane surface when a high loading force (~ 2 nN) is applied after the tip engagement. The tip was kept at the center position for 90 seconds to allow sufficient binding of messenger ribonucleic acid (mRNA) with the oligo-dT. Upon tip retraction, the mRNA was extracted via the binding between the oligo-dT and the polyadenylated tail of mRNA.

The tip was subsequently incubated in a buffer containing all of the components required to perform a single-step reverse transcription-polymerase chain reaction (RT-PCR). As shown in Figure 1, the amplification of β -actin from multiple cells (lane 1) or a single cell (lane 2) obtained directly from a human ovarian cancer cell line (SKOV3 cell suspension) was used as positive controls for the single-step RT-PCR. An equivalent β -actin band was successfully amplified from mRNA extracted by a modified AFM tip (lane 3), while no band was detectable when a bare tip was incubated (lane 4). This experiment was conducted at least six times with consistent observation of β -actin amplification, implying that the modified AFM tip successfully and reproducibly retrieved mRNA from single cells.

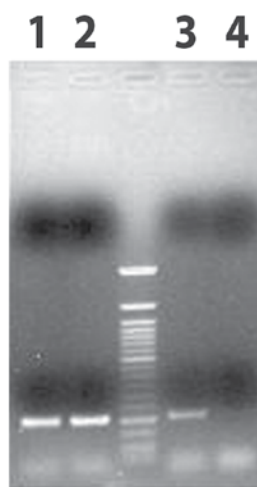


Figure 1. Single-step RT-PCR of β -actin by using mRNA retrieved by oligo-dT modified AFM tip from single SKOV3 cell. Lanes 1 and 2 were used as positive controls, showing the amplification of β -actin from mRNA extracted from cultured multiple or single cells. Lanes 3 and 4 reflect the amplification from mRNA retrieved by the oligo-dT modified AFM tip or bare tip.

After the establishment of the single-cell protocol, we used the modified AFM tip to analyze multiple potential ovarian CSCs or universal CSC marker genes, such as the hyaluronate receptor (CD44), epithelial cell adhesion molecule (EpCAM), and aldehyde

dehydrogenase isofom1 (ALDH1) at the single-cell level. As shown in Figure 2, the amplification of CD44 (lanes 1 and 2) and EpCAM (lanes 3 and 4) has been successfully detected under the current protocol. ALDH1 has so far remained undetectable (lanes 5 and 6), indicating that modification of the current protocol might be necessary, or the expression level is too low to be used as a marker gene. The successful detection of the current marker genes has laid the foundation for us to conduct single-cell broad-range gene analysis of clinical tumor tissues. If combined with stem cell marker immunofluorescence staining, we can not only pinpoint the existence of CSCs and extract their mRNA to conduct broad-range gene analysis, but also analyze the surrounding tumor niche cells *in situ* and *in vivo*. Such *in situ* and *in vivo* analysis should greatly aid the understanding of the origin and treatment of ovarian cancer.

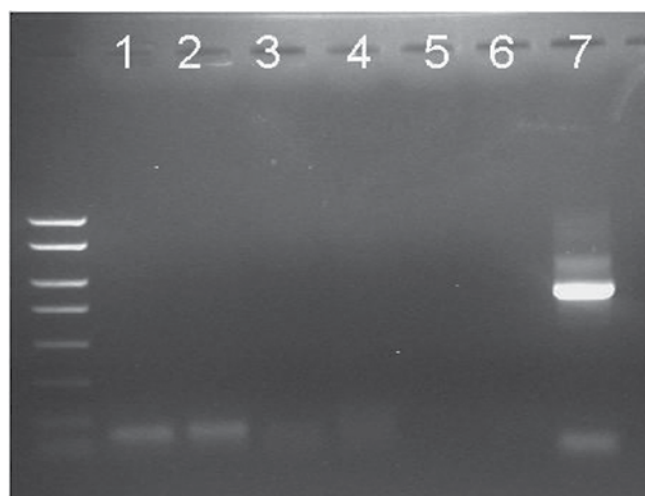


Figure 2. Single-step RT-PCR of cancer stem cell marker genes by using mRNA retrieved by oligo-dT modified AFM tip from single SKOV3 cell. Lanes 1 and 2 reflect the amplification from two individual cells by using CD44 specific primers; lanes 3 and 4, the amplification from two individual cells by using EpCam specific primers; lanes 5 and 6, the amplification from two individual cells by using ALDH1 specific primers; and lane 7 (used as control), the amplification of β -actin.

Solar Thermoelectric Energy Conversion in Nanocomposites

2007-088-R2

Ulrich Welp, Wai-Kwong Kwok, Zhili Xiao, and Tao Xu

Project Description

The grand challenge for improving solar thermoelectric energy conversion efficiency is to increase the temperature on the hot end (T_h) and the thermoelectric figure of merit (ZT) of the thermoelectric materials. Two types of materials are therefore exceptionally desirable for solar thermoelectric energy conversion: (1) a solar-absorbing material that can absorb almost all of the incident solar radiation and build up high temperature inside the material without losing its thermal energy through re-radiation from the heated surface and (2) thermoelectric materials with high ZT values. Semiconducting bismuth telluride (Bi_2Te_3) and its alloys are the best thermoelectric materials currently available, because they have the highest figure of merit (about 1). Given this ZT value of 1 and a temperature at the hot end of 300°C above room temperature, the theoretical thermoelectric energy conversion in these alloys can reach about 11%, much higher than the reported inorganic nanowire-based photovoltaic solar cell (~3%). Currently, there are no proposals that combine the benefits of efficient solar energy absorption and confinement effects in thermoelectric materials that are grown on nanoporous templates. Theoretical analysis predicts that finite-size effects in the thermal conductivity and electronic transport can lead to substantial increases in the thermoelectric figure of merit. Our design for

the integration of photothermal nanowires and thermoelectric nanowires uses the porous surface of a nanoporous anodized aluminum oxide (AAO) membrane as the template to synthesize porous black metal solar absorbers and thermoelectric nanowires. When metal surfaces are properly patterned, they absorb essentially 100% of the incoming light, a prerequisite for efficient solar energy conversion. Furthermore, in samples with nanoscale dimensions, the phonon transport can be suppressed more effectively, thus allowing us to enhance the figure of merit.

Mission Relevance

The critical importance of solar energy conversion for securing our long-term energy supply is being recognized. In addition to photovoltaics and solar fuel, another promising approach to solar energy conversion for mid-range power installations is thermoelectric conversion. Converter efficiencies of 25% to 35% appear possible. The primary challenge to achieving these efficiencies is the development of new and highly efficient materials. This project addresses this challenge and is therefore directly related to DOE's energy mission.

FY 2009 Results and Accomplishments

In the past year, we extended our approach of using one-dimensional (1-D) wires in solar energy conversion to dye sensitized cells and have achieved efficiencies of 1.4% and open-circuit voltages of about 0.8 V, which are among the highest ever reported for a single cell. One-dimensional, thermoelectric semiconducting nanowires are the important building block for solar thermoelectric energy conversion because of the suppressed phonon transfer. Many efforts have been directed toward the enhancement of electron harvest from these 1-D semiconductors. However, we have realized that the improvement resulting from these ordered 1-D nanostructured electrodes is often offset or diminished by the deterioration in other device parameters intrinsically associated with the use of these 1-D nanostructures, such as the two-sided effect of the length of the nanowires impacting the series resistance and roughness factor. We mitigate this problem by allocating part of the roughness factor to the collecting anode instead of imparting all the roughness factors onto the semiconductor layer attached to the anode. We have developed a procedure to grow microscopically rough zinc (Zn) microtip arrays for use as an electron-collecting anode on which zinc oxide (ZnO) nanotips are grown to serve as the semiconductor component (Figure 1). For the same surface roughness factor, our Zn-microtip|ZnO-nanotip cell exhibits an enhanced fill factor compared with cells that have ZnO nanowires supported by a planar anode. In addition, the open-circuit voltage of the Zn-microtip|ZnO-nanotip cell is also improved as a result of a favorable band shift at the Zn-ZnO interface, which raises the Fermi level of the semiconductor and consequently enlarges the energy gap between the quasi-Fermi level of ZnO and the redox species.

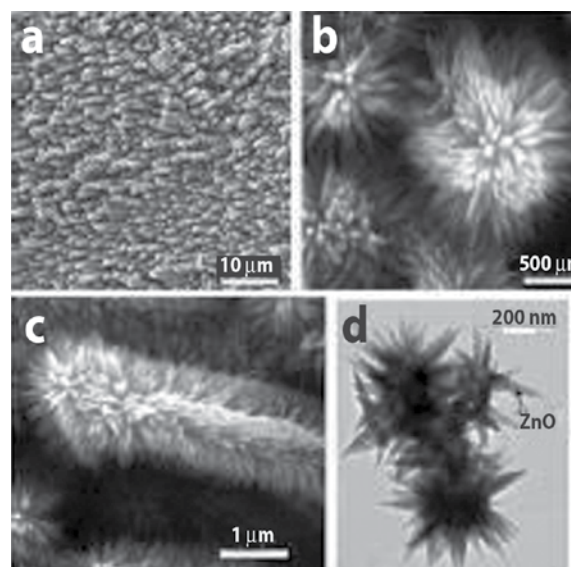


Figure 1. Electron-microscopy images of the Zn-microtip|ZnO-nanotip structures: (a) large area view of an array of Zn-microtips and (b)–(d) high-resolution images of ZnO-nanotips grown onto the Zn microtips.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Yang, Z., T. Xu, Y. Ito, U. Welp, and W.K. Kwok, "Enhanced Electron Transport in Dye-Sensitized Solar Cells Using Short ZnO Nanotips on a Rough Metal Anode," *Journal of Physical Chemistry C* **113** (2009), 20521–20526.

Hybrid Block Copolymer-Nanocrystal Material for Efficient Photovoltaics

2008-003-R1

Seth B. Darling

Project Description

The opportunities and potential payoff of using organic materials for photovoltaics (OPVs) are considerable and could lead to flexible, large-area solar cells that are low cost, lightweight, easy to process, and with ultrafast optoelectronic response. The principal reason the use of OPV and hybrid devices has not yet been widely adopted is that they have low efficiency levels. This project aims to tackle some of the fundamental obstacles to enhanced efficiency that have limited OPV and hybrid devices to date.

In OPVs, unlike in conventional inorganic solar cells, absorbed photons create tightly bound pairs of charges called excitons. To be useful, the excitons must diffuse to the donor/acceptor (D/A) interface where charge separation can occur. The active region of a device is roughly the D/A interface plus the sum of the exciton diffusion length within the donor and acceptor regions — on the order of 10 nm. A diblock copolymer naturally self-assembles two dissimilar polymeric blocks into a morphology with alternating domains on the length scale of the molecule — again on the order of 10 nm. Therefore, diblock copolymers permit the entire volume of the material to be within the active region, so the device can be made sufficiently thick to absorb most of the incident photons — a few hundred nanometers. In this project, the diblock copolymer Poly(3-hexylthiophene)-*block*-polylactide (P3HT-*b*-PLLA) is designed with molecular weights of the two blocks that encourage lamellar morphology — a structure consisting of alternating nanoscale layers (Figure 1). The PLLA block is removed after it facilitates the self-assembly of the nanoscale phase-separated structure. Once the PLLA block is selectively removed, the resulting nanostructured P3HT will be used as a scaffold for the self-organization of electron acceptors.

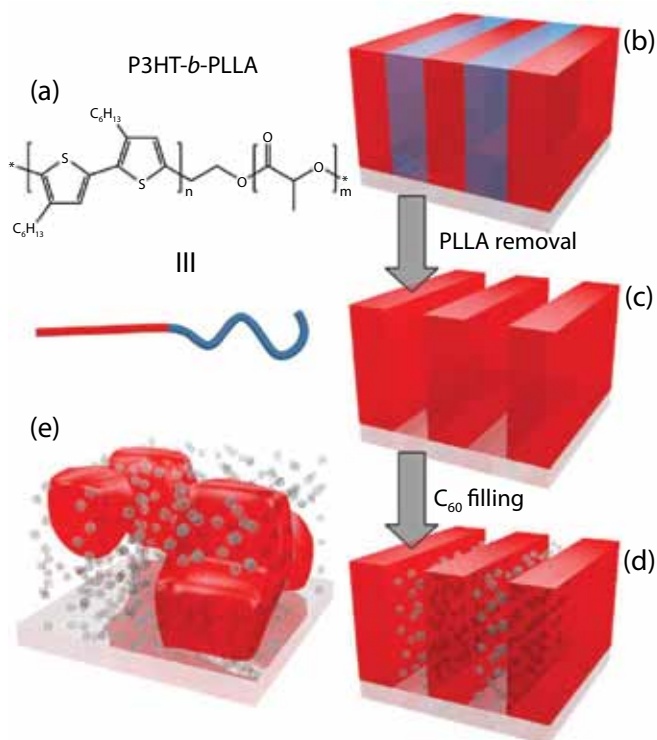


Figure 1. Schematic of block copolymer approach to create nanostructured organic photovoltaic devices. (a) Chemical structure of P3HT-*b*-PLLA polymer. (b) Schematic of lamellar phase domains formed by self-assembly of the block copolymer. (c) Structure following selective removal of the PLLA blocks. (d) Domains previously occupied by PLLA are infiltrated with electron accepting materials, such as C₆₀, to form an idealized morphology. (e) Schematic of disordered bulk heterojunction obtained by depositing a blend of P3HT and C₆₀.

Mission Relevance

This project is tied to DOE's missions in energy and environment. The commitment to developing novel approaches to sustainable, renewable energy sources — such as solar energy — represents a cornerstone of the DOE missions in energy and the environment. Additional benefits from advances in this area include energy independence, which is intimately tied to national security, and new fundamental insights into the structure-property relationships in nanostructured optoelectronics.

FY 2009 Results and Accomplishments

Thin films of P3HT-*b*-PLLA have been prepared on various substrates, and the self-assembled lamellar domains have precisely the orientation and spacing desirable for PV applications. PLLA has been selectively removed from these films by using chemical degradation. With the nanostructured electron donor system prepared, the next step is to introduce electron acceptors into the matrix. This step is challenging because organic solvents that solvate the acceptor species will tend also to solvate the P3HT, thereby destroying the carefully constructed morphology. We have, therefore, turned to aqueous preparations. C₆₀-hydroxide electron acceptors have been incorporated into the patterned P3HT film. Photoluminescence spectroscopy provides a useful tool for quantifying the degree of charge transfer from the P3HT to the C₆₀. These data (Figure 2) indicate that by nanostructuring the films using the block copolymer methodology, we have doubled the degree of exciton separation (electron transfer) with respect to a simple bilayer structure.

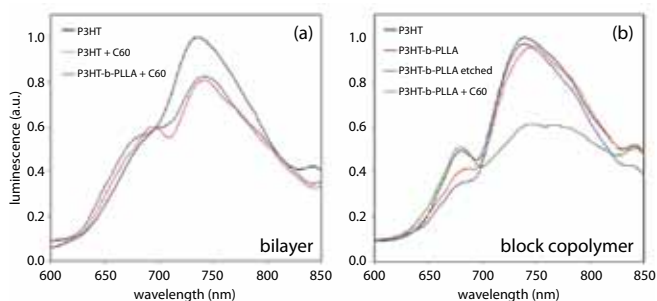


Figure 2. Photoluminescence spectra of (a) thin films of P3HT homopolymer and bilayers composed of P3HT + C₆₀ hydroxide and P3HT-*b*-PLLA + C₆₀ hydroxide; (b) thin films of P3HT homopolymer, P3HT-*b*-PLLA before and after sodium hydroxide (NaOH) etching, and etched P3HT-*b*-PLLA filled with C₆₀ hydroxide. Quenching with the block copolymer material is approximately 100% larger than with the simple bilayer construction.

Another issue we have explored relates to the structural integrity of the P3HT domains following PLLA removal. We have shown that the remaining nanostructured thiophene domains tend to collapse laterally, compromising the idealized morphology. By controlling the surface tension forces associated with the drying process, we find that domain collapse can be minimized, and desirable photophysical properties can be preserved as a result.

Proposed Work for FY 2010

To decipher the influence of the nanoscale morphology on internal photophysical processes, transient absorption spectroscopy and mobility measurements of space-charge-limited current will be performed. In addition, test solar cell devices will be fabricated and compared with traditional organic photovoltaic material systems.

Refereed Publications

Botiz, I., and S.B. Darling, "Self-Assembly of Poly(3-hexylthiophene)-Block-Polylactide *Block* Copolymer and Subsequent Incorporation of Electron Acceptor Material," *Macromolecules* (2009) DOI: 10.1021/ma901420h.

Darling, S.B., "Block Copolymers for Photovoltaics," *Energy and Environmental Science* (2009) DOI: 10.1039/b912086f.

Botiz, I., and S.B. Darling, "Rational Design of Nanostructured Hybrid Materials for Photovoltaics," in *Active Polymers*, edited by A. Lendlein, V. Prasad Shastri, K. Gall (Mater. Res. Soc. Symp. Proc. Volume **1190** (2009), 1190-NN03-20, Warrendale, PA).

Non-Refereed Publications and Presentations

Darling, S.B., "Rational Design of Nanostructured Hybrid Materials for Photovoltaics," presented at Brookhaven National Laboratory, Upton, NY, May 18, 2009.

Darling, S.B., "Coaxing Nanomaterials to Build Themselves," presented at South Dakota State University, Brookings, SD, April 25, 2008.

Automated Theoretical Chemical Kinetics

2008-008-R1

Stephen J. Klippenstein and Lawrence B. Harding

Project Description

The field of gas-phase theoretical chemical kinetics has recently undergone an important paradigm shift. Until about 10 years ago, theory in this area was primarily used as an empirical tool for correlating sets of data and representing the temperature and pressure dependence of experimental observations. Numerous advances in quantum chemical methodologies and software, coupled with ever-increasing computational power, have now made it feasible to obtain "chemically accurate" electronic energies for "interesting" systems. At the same time, the procedures for converting the electronic energies into rate estimates have also been undergoing major improvements in both their accuracy and their efficiency. As a result, it is now feasible to make reliable rate predictions *a priori* for many important reactions.

This paradigm shift for theoretical chemical kinetics, from an empirical to a predictive science, presents tremendous opportunities that are yet to be realized. Currently, the limiting step in application studies is simply the human time involved in gathering, correlating, preparing, and analyzing the input and output from various programs employed in the theoretical analysis. The focus of this project is the automation of the theoretical analysis in a variety of ways, with the goal of reducing the need for human intervention and data manipulation as much as possible.

Mission Relevance

This project contributes to the Grand Challenge arising from DOE's Office of Basic Energy Science's Basic Research Needs workshop on Clean and Efficient Combustion of 21st Century Transportation Fuels, which is to develop "a validated, predictive, multi-scale, combustion modeling capability to optimize the design and operation of evolving fuels in advanced engines for transportation applications." Such a predictive modeling capability will necessarily involve several aspects; one of the central components is the generation of accurate chemical mechanisms. The automated chemical kinetics approach will provide a means for obtaining quantitative predictions of the rate constants comprising the chemical mechanism. An automated chemical kinetics approach is also relevant to many other areas of gas-phase kinetics. As such, the project is also of relevance to such agencies as the National Aeronautic and Space Administration (Planetary Atmospheres, Laboratory Astrophysics, and Interstellar Chemistry), U.S. Department of Defense (DoD) (Air Force Office of Scientific Research, Office of Naval Research, and Army Research Office for atmospheric chemistry and signatures, kinetics of energetic materials, and novel fuels, among others), the U.S. Environmental Protection Agency, and the National Science Foundation.

FY 2009 Results and Accomplishments

Progress continues on producing a preliminary version of a fully automated kinetics package that functions well for many cases; further revisions are needed before it is completely satisfactory. In particular, we have written a code for generating the location of the radical from a given set of Cartesian coordinates for an arbitrary radical. This code has now been tested for a variety of radicals representative of combustion chemistry, including propyl, heptyl, $i\text{-C}_4\text{H}_9$, and hydroperoxypropyl radicals ($\text{C}_3\text{H}_6\text{OOH}$). A code for enumerating all possible beta-bond fissions from a given radical site has also been written and tested.

We have recently developed a universal representation for representing and sampling all torsional modes from within a single framework. This representation allows us to determine the thermochemical properties of the stationary point structures via a random sampling of the configuration space for

all torsional modes. The code also determines the symmetry of the species and the presence or absence of enantiomers, which is required for transition-state, theory-based kinetics evaluations.

Finally, this structure interpretation code has been coupled to the Molpro quantum chemistry package, which is the package that we most commonly employ in our analyses. Importantly, this coupling has been implemented in a parallel computing framework so that we may make the necessary multiple calls to the quantum chemistry code simultaneously.

Proposed Work for FY 2010

The final stage of code development will involve the more difficult task of determining the properties of the saddlepoint connecting a given pair of molecular complexes. This automation will involve the implementation of a number of standard procedures from the literature, where success will be determined via trial and error. Once a set of connected isomers is found, the code will consider the possible importance of each isomer to the overall kinetics via solutions to the master equation. The complete solution of the kinetics then involves the iteration of this process of finding connected isomers with significant flux.

Superslick Anti-Fog Transparent Coating for a Bronchoscope

2008-009-R1

Millicent A. Firestone, Ali Erdemir, Osman L. Eryilmaz, Jacqueline A. Johnson, and Hermona K. Pandya

Project Description

Tailored coatings that maintain transparency under extreme or unusual environmental conditions may find use in a variety of optical devices, such as those used in remote sensing. In medicine, for example, laparoscopic instruments (such as bronchoscopes) could benefit from such coatings. Camera lenses on laparoscopic instruments are prone to fogging and biofouling, thereby limiting their usefulness and operational lifetime. Furthermore, traditional methods to prevent fogging have the side effect of trapping (and potentially spreading) bacteria among patients. Therefore, there is a significant need to develop coatings to be applied over a camera lens to address these problems. Thus, the goal of this project has been to develop optically transparent, self-cleaning, and super-hydrophilic coatings that are also slick and compatible with biologically active environments. Argonne's diamond-like carbon coating or "near-frictionless" carbon (NFC) has formed the foundation of this work. These coatings would be made transparent by modification of the deposition chemistry and

would be non-biofouling and anti-bacterial by chemical modification with selected peptides, enabling high-quality imaging and the sterilization of devices.

Mission Relevance

This work supports DOE's mission in developing revolutionary new materials (e.g., coatings) that withstand demanding environmental conditions. Many optical devices, such as those used for remote sensing, would benefit from tailored coatings. In this project, we are specifically addressing coatings that will function under conditions of high humidity and potential biofouling.

FY 2009 Results and Accomplishments

Solid-phase peptide synthesis was used to prepare the phage-display-determined, NFC6-binding peptide containing the binding sequence, FPSWARS. In prior work, this sequence showed strong, selective binding to an NFC film formed from a plasma composition of 75% hydrogen gas and 25% methane gas (NFC6). Preparation of the nonvirus-bound peptide was carried out to determine whether removal of the associated virus (phage) altered NFC film binding affinity. During FY09, the sequence was synthesized, purified, and characterized by mass spectrometry. The purified product was then dye (fluorophore) -labeled in order to monitor both spectrophotometrically and with fluorescence microscopy its binding to various carbon films.

In parallel with the peptide chemistry, various modifications in carbon thin-film deposition procedures were performed to improve the adhesion of the carbon film on glass substrates without sacrificing optical transparency. Good adhesion on glass is a requirement for being able to transfer this chemistry as a coating material onto medical devices. Work in FY08 had shown that the NFC6 deposition was quite variable and was not directly transferable to glass substrates. To address this issue, the composition of the coating and the deposition procedure were varied. These approaches did not yield, however, an identical film composition as was found in the original NFC6. Because of the very selective binding of the peptide, little to no association was observed. This component of the work was important, demonstrating how selective the phage-determined peptides are to subtle changes in the carbon film composition. The results required us to resort to the introduction of a silane coupling layer that served as an adhesion layer between the carbon and glass substrate. While this approach significantly improved adhesion, it was detrimental to optical transparency. In addition, fluorescence microscopy on the dye-labeled peptide revealed heterogeneous binding, indicating that the carbon thin films are not uniform (Figure 1). The poor film uniformity is an additional factor that must be corrected for the project to proceed.

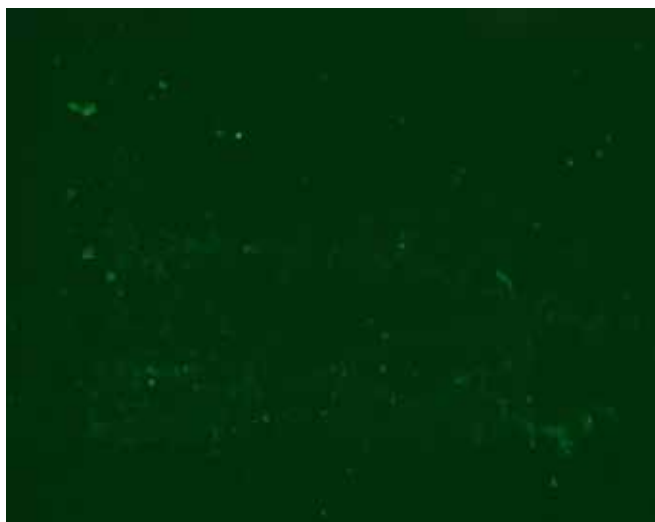


Figure 1. Fluorescence micrograph of dye-labeled NFC68 peptide on NFC6 carbon-coated glass slide. The image shows heterogeneous peptide coverage over the surface of the carbon film, indicating that the carbon coating of the glass is not uniform.

Proposed Work for FY 2010

This project does not continue into FY10

A Cell-Free Approach toward Membrane Protein Production

2008-020-R1

Philip D. Laible and Deborah K. Hanson

Project Description

Membrane proteins represent an extremely important class of hydrophobic biomolecules, the functions of which are vital to normal cells. As such, they represent the vast majority of drug targets pursued at present. In contrast to soluble proteins, we know little about them primarily because producing sizeable quantities of membrane proteins in natively folded, functional, and pure form is an arduous task. Paradigm-shifting technologies are being sought in order to approach and study these molecules with greater efficiency and, as a result, with improved success at reduced cost. Paramount among these technological pursuits is obtaining a means for overexpression of membrane proteins to increase their abundance as source material for biochemical studies. The cell-free membrane protein expression system that we seek to develop would fill this need.

Mission Relevance

This project is relevant to DOE's mission in science. The inability to produce membrane proteins frustrates any efforts to understand their functions. The restructured Genomes-to-Life Program in DOE's Office of Biological and Environmental Research has vested future interests in such functional studies.

FY 2009 Results and Accomplishments

Our initial efforts clearly established that the membrane proteins we produced in cell-free reactions can be incorporated into membrane vesicles added concurrently. We are now proceeding to larger-scale reaction volumes (5–20 mL), knowing that cell-free synthesis reactions can tolerate the addition of large quantities of *Rhodobacter* intracytoplasmic membranes (ICMs). The amount of target membrane protein that is associated with the membrane fraction increases with the addition of ICMs and appears to plateau at higher membrane levels, but not before capturing more than 85% of the target protein produced in the reaction. Our ability to compare and contrast cell-free expression by using *Rhodobacter* extracts with extracts derived from other organisms (some commercial) will be critical for the optimization of our *Rhodobacter*-based technology. These efforts include new research with H. Hellinga of Duke University. Additional optimization efforts involve the evaluation of different types of DNA templates in the synthesis reactions. Circular plasmid templates work well but require a cloning step before their use in cell-free reactions. The use of linear templates derived from polymerase chain reactions (PCR) would circumvent the need for a cloning step; however, the half-life of linear molecules is very short because they are subjects for the digestion for endogenous exonucleases. A strategy to protect and use linear templates is being tested.

Recent experiments show that the addition of *Rhodobacter* ICMs dramatically increases expression yields — by 300–500% — for four target membrane proteins that were studied. We observe that the addition of *Rhodobacter* membranes decreases the proportion of protein that remains in the soluble fraction. We are very excited about these recent results since they indicate that *Rhodobacter* ICMs could be used to complement cell-free extracts derived from other organisms for use in the production of membrane protein samples. A model reactor has been designed for continuous exchange, cell-free reactions using *Rhodobacter* extracts (Figure 1). These systems overcome the limitation of closed-batch reactions in which precursors are depleted rapidly and inhibitory breakdown products accumulate.

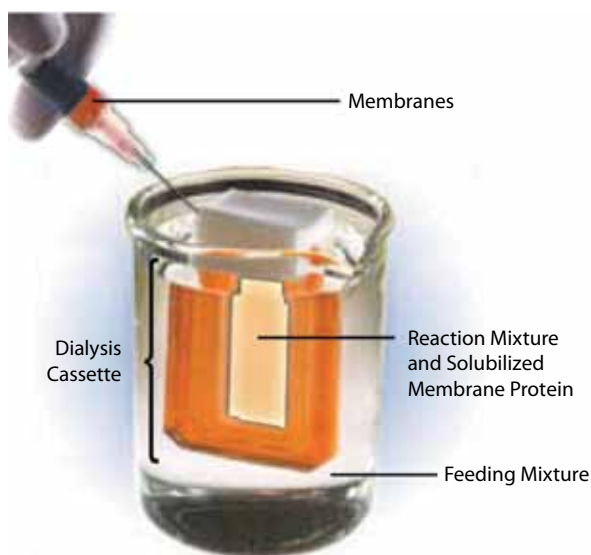


Figure 1. Proposed model for a larger-scale, continuous-exchange cell-free reaction chamber. The reaction is contained within the cassette and is separated from the surrounding solution by a dialysis membrane that retains biosynthetic machinery and the newly synthesized proteins

Proposed Work for FY 2010

On the basis of results obtained recently with cell-based expression of targets of increasing complexity and that have a high value to the pharmaceutical industry, we plan to expand significantly the target range for the cell-free synthesis reactions. We will include genes encoding human G-protein coupled receptors and ion channels in the experimental target set.

Several types of membrane fractions can be produced from *Rhodobacter*. A notable difference between these subpopulations is their “sidedness,” and this feature can be exploited in the design of functional assays. We are perfecting protocols for separation of these membrane subpopulations from *Rhodobacter* host strains that vary in the complement of membrane proteins that are present in their ICMs, and we will evaluate their use in *Rhodobacter*-based, *E. coli*-based, and commercial extracts.

Use of membrane proteins produced in cell-free reactions for NMR (nuclear magnetic resonance) structure determination strategies depends upon the ability to label them uniformly with stable isotopes. The open nature of cell-free synthesis reactions allows for the substitution of common building blocks with labeled amino acids for incorporation into the nascent polypeptide chain. We will produce ^{15}N -labeled forms of five proteins and will provide them to S. Koide of the University of Chicago for NMR evaluation of structural integrity and sample uniformity.

The Use of the Hedvall Effect to Control Catalytic Properties of Subnanometer-Size Magnetic Clusters

2008-026-R1

Jeffrey P. Greeley, Stefan Vajda, Seth B. Darling, and Daniel Torres Rangel

Project Description

The main goal of the project is to understand and exploit the Hedvall Effect (HE), a phenomenon wherein changes in the magnetic state of a nanoparticle lead to measurable changes in the particle’s catalytic activity on size-selected subnanometer clusters. These clusters are known to possess both very high catalytic activities for certain reactions and much higher per-atom magnetic moments than larger nanoparticles; both of these characteristics suggest that these materials would be ideal for HE studies. We are pursuing this initiative on two fronts, both by developing detailed electronic structure-based catalytic models of the clusters and by synthesizing/testing the clusters with our unique, size-selected cluster deposition apparatus. By developing a comprehensive understanding of the HE on subnanometer metal particles, we will ultimately be able to use magnetic effects to manipulate the catalytic activity of these particles and thereby introduce a new “tuning parameter” for catalytic processes.

Mission Relevance

This project will benefit the science and energy missions of the DOE Office of Basic Energy Sciences. Catalysis is an extremely important component of many energy and chemical production processes in the United States, and the need to develop improved catalysts for devices ranging from fuel cells to petrochemical refineries is great. DOE recognizes this national need and has focused on it in several recent DOE reports. By developing a new “tuning knob” for the catalytic properties of subnanometer metal clusters, our project will provide an important contribution to the development of future catalysts, with subsequent direct impacts on these national priorities.

FY 2009 Results and Accomplishments

We have studied the HE on subnanometer Ni, Co, and Fe clusters (these magnetic materials are particularly susceptible to the HE), focusing on the catalytic properties of these clusters for both the methanation reaction, wherein CO and hydrogen are converted to methane and water, and the decomposition of methyl nitrite (CH_3ONO), a simplified “probe reaction” that occurs at very low temperatures. The work is continuing along combined theoretical and experimental fronts.

Theoretical modeling. We have been working on computational models of the methanation and CH_3ONO decomposition reactions; we have made significant progress in understanding the catalytic and magnetic properties of these reactions on different clusters, including Ni_4 , Co_4 , and Fe_4 . A full potential energy surface for the methanation reaction on nickel clusters, in both spin-polarized (ferromagnetic [FM]) and nonspin-polarized (paramagnetic [NM]) states, is shown in Figure 1. In Figure 2, results from both Co and Fe clusters are also shown. In that figure, we show the energetics for the two kinetically significant steps on each metal in both the spin-polarized and nonspin-polarized states; the other steps have been calculated but are not shown for clarity. Although they are chemically similar, the different metals clearly have different free energy profiles for methanation, implying that there could be some flexibility to tune the magnetocatalytic properties of transition metal clusters by appropriate selection of the clusters' composition.

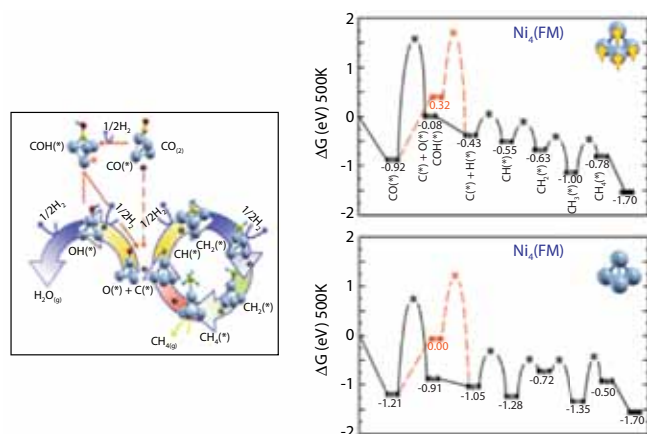


Figure 1. Schematic depiction of the methanation reaction network. Detailed free energy profiles for the reaction on both spin-polarized (FM) and nonspin-polarized (NM) Ni_4 clusters.

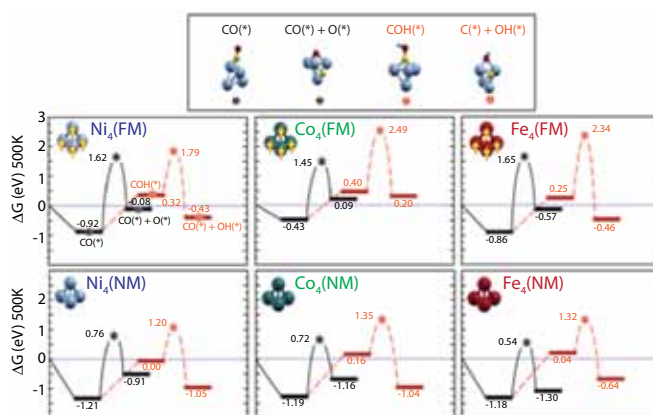


Figure 2. Free energy profiles for the initial (rate-determining) steps in methanation on Ni, Co, and Fe clusters in their spin-polarized (FM) and nonspin-polarized (NM) states.

Results for the methyl nitrite decomposition reaction have also been obtained on Ni_4 clusters. This reaction could be thought of as a model reaction that may occur at low temperatures (near room temperature), in contrast to the methanation reaction, which occurs at significantly higher temperatures. This chemistry also shows significant sensitivity to the magnetic state of the Ni clusters, with the reaction energetics being modified by ~ 0.5 eV in going from nonmagnetized to magnetized states.

The results described above demonstrate a computational prediction of a magnetocatalytic effect for two very different types of catalytic reactions. These consistent predictions increase the likelihood that our continuing experimental efforts will, ultimately, succeed in observing this effect.

Size-selected nanocatalyst fabrication and test of catalytic performance. This year marked the successful synthesis of size-selected Ni_4 , Co_4 , and larger clusters; the testing of the stability of the clusters under reaction conditions; and preliminary reactivity measurements for the methanation and Fischer-Tropsch (FT) reactions on these clusters. By using a combination of grazing incidence small-angle X-ray scattering (GISAXS) to monitor the cluster shapes under reaction conditions and x-ray absorption (GIXANES) to probe their oxidation states, we have confirmed that the clusters are partially oxidized in CO/H_2 atmospheres and that they do not sinter up to $\sim 300^\circ\text{C}$; these are essential properties for methanation catalysts.

Figure 3 shows the reactivity of size-selected clusters with a mixture of CO and H_2 (methanation and FT reactions) as a function of cluster size, composition, and support. The data shown are mass peak intensities of the C1, C4–C8, and C6–C8 fractions, normalized to the intensity of the C1 intensity obtained for Ni_4 . Calibration to standards, also for the reactivity of cluster sizes not shown here, is in progress to yield absolute reactivity data. The results show that the catalysts produce a substantial amount of methane from CO/H_2 (the goal of the methanation reaction) and that there are significant changes in activity as a result of changes in the catalyst composition (nickel vs. cobalt), size, and support. To the best of our knowledge, these are the first X-ray absorption experiments on size-selected subnanometer clusters and the first methanation and FT reactions performed on such particles.

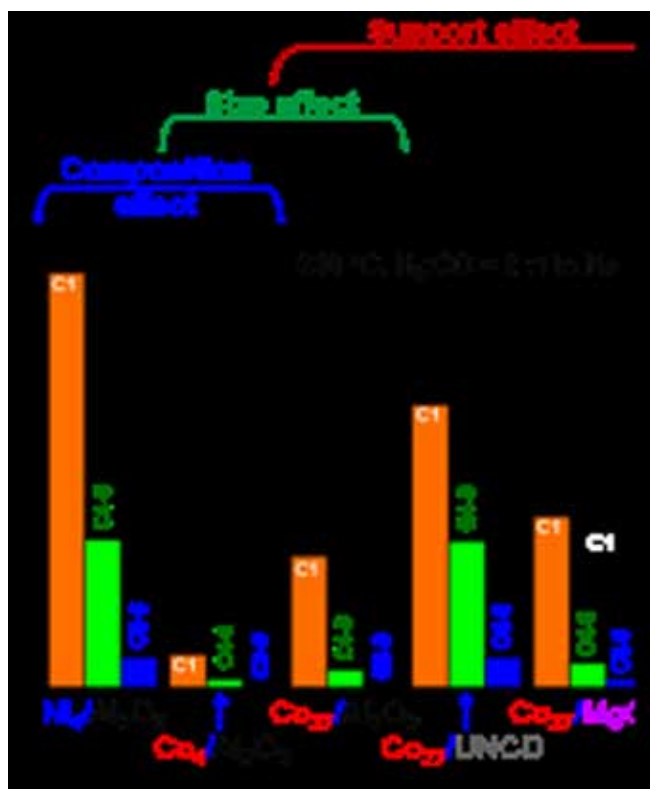


Figure 3. Reactivity of size-selected clusters with a mixture of CO and H₂.

Magneto-tunnel junction (MTJ) sensor installation. Because the transition metal catalytic clusters in this study are likely to undergo significant oxidation upon exposure to ambient conditions, it is critical to probe their magnetic character under synthetically relevant ultra-high vacuum (UHV) conditions. Moreover, the minuscule mass of the deposited subnanometer clusters demands extraordinary instrumental sensitivity for magnetic measurements. We are assembling a UHV-compatible MTJ sensor apparatus on a support rig that will enable it to be mated with the cluster deposition tool for *in situ* characterization; the tool can also accommodate the presence of gaseous reactants, if desired. The sensor is mounted on a linear manipulator and positioned downstream from a series of ion-focusing optics for alignment with the incident cluster beam. Electromagnets are situated to provide external fields in three independent dimensions. Our installation will be the first ever to make use of an MTJ sensor to study magnetic nanoclusters, and it will provide the only method available to obtain magnetic information on such systems. To ensure that our sensor reliably reproduces known magnetic results, we have measured the Curie temperature of bulk gadolinium; the results are fully consistent with known literature standards.

Proposed Work for FY 2010

We will continue the excellent progress that we have made in both the computational and experimental portions of this project. We will continue to enhance our computational modeling of the methanation reaction by adding theta alumina supports to the calculations and by incorporating more detailed adsorbate coverage effects; we will also complete the modeling of the methyl nitrite decomposition reaction to provide a theoretical demonstration of the generality of the Hedvall effect over multiple temperature regimes; to provide experimental insight into these theoretical results, we will extend our subnanometer cluster reactivity measurements to this system. We will complete the MTJ installation and will measure the detailed magnetic states and Curie temperatures of the subnanometer Ni, Co, and Fe clusters. By comparing these results to our theoretical work and to our methanation reactivity measurements, we will be able to provide a definitive demonstration of the Hedvall magnetocatalytic effect on size-selected clusters, which is essential to our continued scientific analyses.

Refereed Publications

Mehmood, F., J. Greeley, and L. Curtiss, "Trends in Catalytic Properties of Methanol Decomposition on Co, Pd, and Cu clusters," submitted to Journal of Physical Chemistry C.

Non-Refereed Publications and Presentations

Greeley, J., "Subnanometer Catalysis and Electrochemistry," presented at the Notre Dame University chemical engineering department seminar, October 29, 2009.

Optimal Active Thermochemical Tables

2008-027-R1

Zhen Xie, Branko Ruscic, and Sven Leyffer

Project Description

Active thermochemical tables (ATcT) is a novel paradigm that provides scientists with internally consistent thermochemistry at an unprecedented scale of reliability and accuracy. Thermochemical tables are tabulations of thermochemical properties. Their quality ranges from fully documented critical properties to lists providing multiple values without any explanation. Thermochemical properties are derived from basic determinations that fall into two categories: species-specific and species-interrelating. The latter leads to a complex network linking all chemical species and their properties together (see Figure 1). The dependencies in this complex network have traditionally been resolved by a sequential approach. In contrast, ATcT views the complete thermochemical network all at once and treats the calculation of property values as a data-fitting

problem over the whole network. The thermochemical network approach has been used in small networks in NIST-JANAF (National Institute of Standards and Technology-Joint Army, Navy, Air Force) thermochemical tables. However, the full potential of this all-at-once approach has not been exploited until recently (Ruscic et al. 2006).

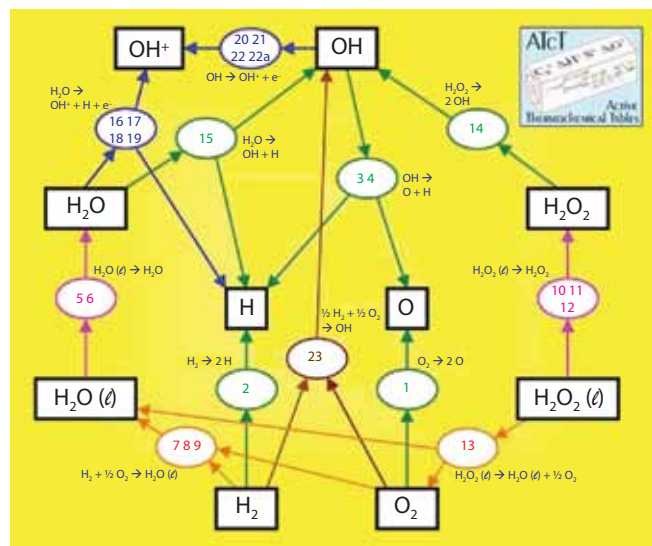


Figure 1. Thermochemical network for OH.

A key challenge in the derivation of thermochemical tables is the robust and fast solution of the underlying data-fitting problem over the thermochemical network. Unfortunately, the current approach lacks robustness and speed-of-solution performance to obtain optimal ATcT.

Mission Relevance

The project is relevant to DOE's mission in science. The availability of reliable, accurate, and consistent thermochemical values for a broad range of species plays a central role within chemistry and has many industrial applications, ranging from the interpretation of controlled laboratory chemical kinetics measurements to predictive large-scale modeling of complex chemical environments, such as flames or the atmosphere. Research into active tables is supported by the DOE Office of Basic Energy Sciences (BES), Division of Chemical Sciences, Geosciences, and Biosciences. Thermochemistry is an important part of the DOE's Chemical Physics Research. The removal of one of the most important bottlenecks in the ATcT processing of the thermochemical network leading to thermochemistry of unprecedented accuracy and reliability directly benefits the Chemical Physics Research Program of DOE BES. It will also benefit other DOE BES missions, such as those relevant to the Separations and Analysis Program and the Heavy Element Chemistry Program.

FY 2009 Results and Accomplishments

In this project, we are devising new models for the data-fitting problem and developing optimal and robust solvers for this crucial component of ATcT. In addition, we are reducing the solution times by orders of magnitude through the implementation of a sparse linear algebra solver. We also developed a new model for ATcT in outliers' detection and correction.

The underlying mathematical problem of ATcT is a modified weighted least squares (WLS) problem. The difference between standard WLS and the problem in ATcT lies in the weights. In a typical WLS problem, the weights are given as constants, while in ATcT, because there are outliers, the weights of the outliers need to be adjusted if, under some criteria, the uncertainty of those measurements is considered to be "inappropriate."

Worst-Offender Approach

We have implemented the classical worst-offender approach by using both FORTRAN 90 and C++ with a sparse solver for the WLS system. The worst-offender approach was applied to a typical real example for active thermochemical tables (the dimension of the matrix is 11705×870 , and there are 31795 nonzero elements). While the original solver needed a few days to apply the worst-offender approach, the current solver needs less than 2 minutes on a Linux desktop machine with Intel Core2 DUO CPU 6300 at 1.86 GHz with 1 GB RAM. This increase in speed is significant, as we can now solve the problem almost instantaneously. Figure 2 shows that values for the coefficients changed after the worst-offender approach, which is expected. More significantly, the variance of x reduced almost entirely, which is one the goals of the problem.

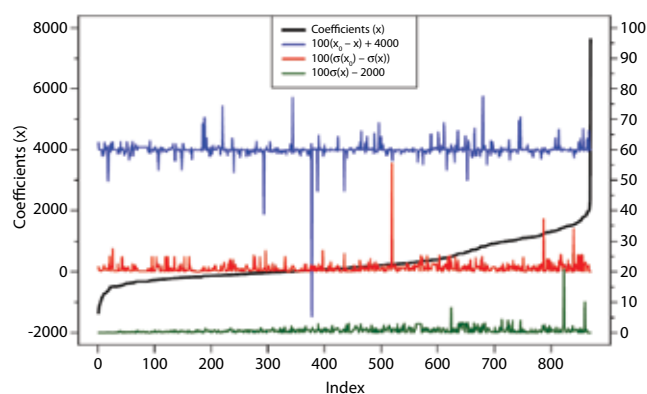


Figure 2. The coefficients vector x , its value change after the worst-offender approach, along with its variance change.

From the results, it is obvious that the worst-offender approach works. It reduced the weighted residuals, lessens the variance of the coefficients to estimate, and keeps most of the original weights (or measurement variance) unchanged. One important improvement of the current solver cut the original run-

ning time of the worst-offender approach to its current value, a small fraction (or negligible amount) of what it had been.

Taking the results from the worst-offender approach as the benchmark results, we tried some other approaches to tackle the ATcT problem.

Maximum Likelihood Estimation

In an ideal situation, if all of the observations have the right measurement uncertainty, so do the correct weights. It is reasonable to assume that the weighted residuals should have a normal distribution with its center at 0. We estimated the variance by using the so-called maximum likelihood estimation (MLE) and used this criterion to select outliers in an approach that improves on the worst-offender approach.

We compared the two approaches on a range of test problems that have between 200 and 11,000 unknowns. We observed that the new MLE approach generates more similar estimates than does the worst offender approach while using far fewer iterations. In addition, the new approach provides a better approximation of a normal distribution, as illustrated in Figures 3 and 4.

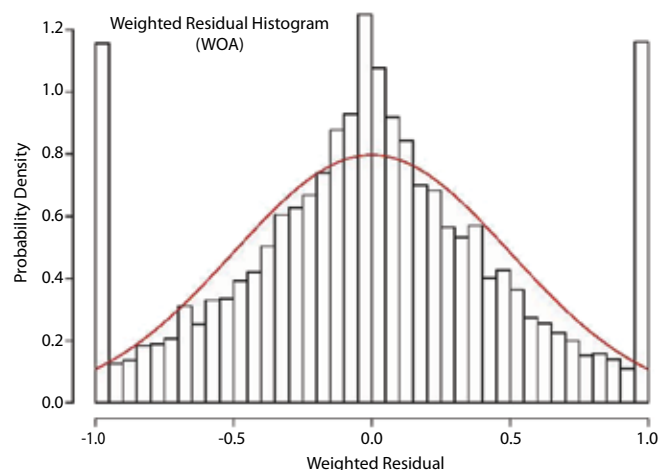


Figure 3. Distribution of worst-offender residuals. Note the existence of outliers.

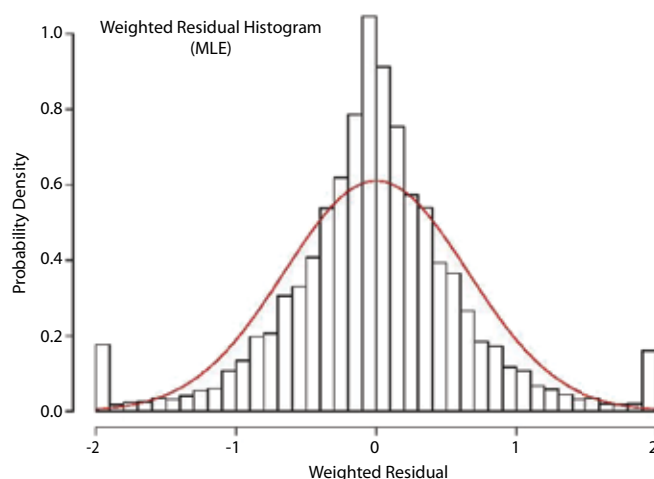


Figure 4. Residuals from MLE approach with smaller outliers.

Proposed Work for FY 2010

This project does not continue in FY10.

Refereed Publications

Ruscic, B., R.E. Pinzon, M.L. Morton, N.K. Srinivasan, M.-C. Su, J.W. Sutherland, and J.V. Michael, "Active Thermochemical Tables: Accurate Enthalpy of Formation of Hydroperoxyl Radical, HO_2 ", *J. Phys. Chem. A*, 2006, 110(21), pp. 6592–6601.

Rapid XRF Elemental Imaging for High-Throughput Identification of Metal-Binding Proteins Critical to Life, Disease, and Bioremediation

2008-035-R1

Lydia A. Finney and Stefan Vogt

Project Description

An estimated one-third of all proteins bind metal ions (such as calcium, manganese, iron, zinc, and copper), and many of these proteins have regulatory or catalytic functions. However, no practical resources exist to identify and measure the levels of metals bound to proteins in complex mixtures. We seek to enable routine scanning and analysis of an entire two-dimensional (2-D) gel by micro x ray fluorescence (XRF) and develop methods to preserve intact metalloproteins during electrophoresis. This capability will enable the high-throughput, systematic identification of metal-binding proteins that act as switches for numerous physiological functions, as well as provide a new way to track the biological fates of metallic environmental contaminants.

Mission Relevance

This project is tied to DOE's missions in science and environment, particularly the Office of Science Environmental Remediation Science Program. Metalloproteins are key to the electron transport mechanisms of bacteria that are endogenous to numerous DOE waste sites. The methods developed and preliminary data produced by the project thus will provide a unique avenue of investigation pertinent to DOE's environmental remediation mission. At the same time, both the development of new tools for visualizing post-translational regulation of cellular activity and the study of metals in biology are areas of active interest at the National Institutes of Health (NIH).

FY 2009 Results and Accomplishments

We developed and optimized gel preparation techniques by using known, purified proteins. By employing a test XRF system installed at beamline 2-ID-E of the Advanced Photon Source (APS), we identified and minimized factors limiting sensitivity, both in terms of the sample environment and of the sample itself. Metalloproteins are essentially metal ion coordination complexes and are subject to varying degrees of kinetic and thermodynamic instability that can be further influenced by environmental factors, including the buffers and voltages of electrophoresis. During FY09, we further refined our biochemical techniques, identifying and eliminating potential sources of contamination and working with Millipore R&D to identify the best sample substrates available. This effort allowed us to improve our overall sensitivity from 200 ng to 60 ng in the case of urease, nearly a four-fold improvement.

We have also begun to assemble instrumentation at a bending magnet beamline dedicated to high-throughput X-ray fluorescence techniques. At this beamline, the design is optimized specifically for these experiments. Many factors, such as a helium sample environment, promise further improvements in our sensitivity. We expect to begin experiments there in the near future.

In the past year, we have continued to functionally verify our ability to identify metalloproteins in complex mixtures. In 1-D analyses, we were able to demonstrate that our technique can be extended to the identification of metalloproteins in many systems. These included the study of chromium's binding to human proteins, identification of metalloproteins expressed by a *C. elegans* model of Alzheimer's disease, and the study of metalloproteins secreted by biofilm-forming bacteria. Also in FY09, we demonstrated that we can successfully extend our studies from 1-D to 2-D electrophoretic separations (see Figure 1).

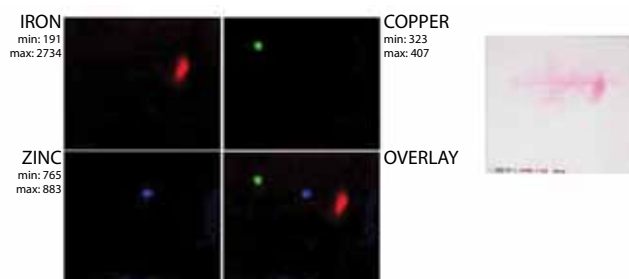


Figure 1. Extension of Metalloproteomics to 2D Electrophoresis. The presence of iron (top left), copper (top middle), and zinc (bottom left) can all be seen in the three-element overlay (bottom middle) image of a 2D electrophoretic separation of ceruloplasmin, hemoglobin, and carbonic anhydrase. By comparing these images to the Ponceau-stained image (upper right), which stains for all proteins, we are clearly able to identify the metal-binding proteins in the context of a complex 2D separation. Extending our studies on natural samples to this level will enable us to use mass spectrometry to determine their identity, potentially discovering new metalloproteins.

Proposed Work for FY 2010

In FY10, we will continue work to improve the sensitivity of our approach by utilizing our dedicated instrumentation. We will complete assembly of our optimized instrument, develop a user-friendly software interface, and modify our image analysis software for display of protein and x-ray image overlays. We will also extend our analyses of 2-D systems, which will enable us to use mass spectrometry to identify metalloproteins. This work will culminate in important preliminary data for future work.

Refereed Publications

Finney, L., Y. Chishti, T. Khare, C. Giometti, A. Levina, P. Lay, and S. Vogt, "Imaging Metals in Proteins by Combining Electrophoresis with Rapid X-ray Fluorescence Mapping" *ACS Chemical Biology*, submitted.

Non-Refereed Publications and Presentations

Finney, L., "Unleashing the Potential of X-ray Fluorescence Microscopy" poster presented at the Gordon Research Conference: Cell Biology of Metals, Newport, RI, August 9–14, 2009.

Finney, L., "High throughput Metalloproteomics: X-ray Fluorescence Imaging Paired with Electrophoresis," presented at the Annual Meeting of the American Electrophoresis Society, Philadelphia, PA, November 17–19, 2008.

Finney, L., "High-throughput Metalloproteomics: X-ray Fluorescence Imaging Paired with Electrophoresis," presented at the 6th International Copper Meeting: Copper 08, Alghero, Italy, October 11–15, 2008.

Systematic Analysis of the Role of Zinc in Stem Cell Plasticity and Pluripotency

2008-036-R1

Lydia A. Finney, Liaohai Chen, and Qiaoling Jin

Project Description

Human embryonic stem cells (hESCs) are capable of unlimited self-renewal and retain pluripotency (i.e., the ability to differentiate into all cell lineages in the body). The current challenge is that stem cells only retain their pluripotency when they grow slowly in monolayer colonies. We have found evidence that a direct correlation exists between the differentiation of hESCs and their levels of endogenous zinc. As a result of this finding, we characterized the way in which this highly detectable aspect can serve as both a biomarker and an intervention point for the entire cellular system. This project resulted in a better understanding of the role of zinc in the balance between stem cell proliferation and differentiation.

Mission Relevance

This project will benefit DOE's mission in science by improving the quality of life through innovations in bioscience and biotechnology. Achieving research goals at the forefront of stem cell pluripotency will establish new lines of hypothesis-driven research.

FY 2009 Results and Accomplishments

We interrogated the relationship that we discovered earlier between pluripotency of hESCs and their zinc content. Toward this goal, we used x-ray fluorescence microscopy to determine the zinc content in stem cell colonies induced to differentiate and those that are as pluripotent as can be maintained. In FY09, we expanded our studies to obtain statistically significant quantitation of this relationship. We verified the correlation, finding nearly twice as much zinc to be present in differentiated cells as compared to pluripotent cells.

We also began to test whether zinc provides a unique intervention point for the control of differentiation by establishing the functional relationship between zinc and hESC differentiation. We found that as little as 1 μ M of the cell-permeable, zinc-specific chelator, tetrakis-(2-pyridylmethyl)-ethylenediamine, TPEN for short, resulted in loss of >90% of cells. This level is 15 times lower than the sensitivity of other progenitor cells to zinc depletion, indicating a critical role for zinc in hESC maintenance. This response was completely rescued by replacing zinc, indicating that the hESC response is due to the specific action of TPEN in chelating zinc, and not any other side effect

of TPEN itself. We also investigated the use of a gentler, extracellular zinc chelator, diethylenetriaminepentacetate (DTPA), to find a window of culture conditions, between 1 nM and 1 μ M, within which cells appear healthy despite depletion of zinc. We have collected both immunofluorescent and x-ray data on these samples and are currently analyzing our data.

We earlier set out to identify the macromolecular partners of this metal specific to stem cell differentiation. In FY08, we established our ability to identify zinc-binding proteins by using our proteomics approach. In FY09, by comparing differentiated and undifferentiated cell lysates, we found that the difference in cellular zinc does not appear to correspond to the presence of additional zinc proteins. We are currently expanding our studies to identify the macromolecular partners of zinc in stem cells.

Proposed Work for FY 2010

In FY10, we will repeat our imaging experiments in another stem cell line (H1), as well as with an alternative form of differentiation induced (to an endothelial cell type) to determine any specificity that may exist relative to type of hESC or specialization. We will also work to identify the macromolecules interacting with the zinc by using fractionation techniques to isolate different components of the cell and spectrometry to determine the zinc levels. By comparison of the set of identified macromolecular partners of zinc in differentiating hESCs with those of undifferentiated hESCs, we will identify pathways and macromolecules with potential to serve as specific targets for the intervention and control of hESC differentiation.

Non-Refereed Publications and Presentations

Finney, L., "Visualizing a Dynamic Role for Metals in Cell Biology by X-ray Fluorescence Microscopy," invited presentation at University of Illinois at Chicago, Pharmacology Department Seminar, Chicago, IL, September 18, 2009.

Finney, L., "Unleashing the Potential of X-ray Fluorescence Microscopy," poster presented at Gordon Research Conference: Cell Biology of Metals, Newport, RI, August 9–14, 2009.

Development of a Total Absorption Spectrometer (TAS) for Advanced Fuel Cycle Applications

2008-071-R1

*Christopher .J. (Kim) Lister, Filip G. Kondev,
Christopher J. Chiara, and Elizabeth Ricard-McCutchan*

Project Description

The aim of our project is to measure the decay schemes of specific isotopes that are produced when “minor actinides,” like americium and thorium, are burned as reactor fuel as part of the advanced fuel cycle (AFC) concept. The decay scheme studies will involve (a) discrete line decay studies (for structure and decay strength investigation), (b) decay heat calorimetry, and (c) measuring delayed neutron branches. We had identified a few selected isotopes from the International Atomic Energy Agency (IAEA) list and intended to investigate them as soon as the ATLAS/CARIBU (Argonne Tandem Linac Accelerator System/Californium Rare Isotope Breeder Upgrade) fission source became operational, which was scheduled for early 2009. However, because the ion-source upgrade was delayed by more than a year, we directed our efforts toward such steps as developing new equipment to enable continued progress on this project.

Mission Relevance

The proposed research is closely tied to DOE’s missions in energy and national security. Nationally, there is a re-examination of nuclear power as a key component of energy generation in the future, both as it can impact global warming issues, and it could reduce U.S. dependency on foreign oil. The Department of Energy is responding to this need by seeking innovative “end-to-end” solutions to energy generation and waste management on a scale that would significantly impact the total profile of national energy generation. This is the origin of the Advanced Fuel Cycles concept. In addition to advancing DOE’s missions, the results from this work would be of interest to a variety of private, federal, and international organizations concerned with development of advanced fuel cycles research and development.

FY 2009 Results and Accomplishments

In 2006, DOE focused basic academic research resources back toward applied reactor science. Argonne’s Nuclear Engineering Division and extensive experimental research resources at the Physics Division’s ATLAS accelerator — including a unique fission source, CARIBU, which was then in the process of being built — have been strengths in supporting this LDRD project. We hoped to make the first measurements during the LDRD timeline, which would serve to jumpstart other related DOE-funded research.

In practice, the research has progressed more slowly than anticipated. Because of delays related to regulation, funding, and component delivery, the CARIBU ion-source is only now being completed and will not have research beams until mid-2010. Consequently, although we had to considerably revise what we could achieve in the LDRD context, other favorable developments have succeeded in moving this research project in the direction it was originally intended. Some highlights of our progress are noted below.

During the LDRD cycle, we have been interacting with and learning from groups from around the world that are engaged in similar activities as follows. The University of Massachusetts, Lowell, led by Professor Partha Chowdhury, has a long history of reactor-related research; in fact, it has a 1-MW reactor at the Lowell campus. The Australian National University (ANU) sent a nuclear engineering graduate student to work at Argonne in 2009 who will return for a 9-month study period in 2010. In addition, ANU scientists, led by Professor George Dracoulis, will come to Argonne to participate in the first CARIBU experiments.

Professor Berta Rubio of the University of Valencia has put together a European team consisting of Valencia (Spain), University of Surrey (UK), University of Orsay (France), and the University of Jyväskylä (Finland), which has been making decay heat measurements. We (Kondev) participated in their most recent experiments in decay heat and β -delayed neutrons in Jyväskylä.

In terms of equipment development, a new tape transport system, which we expect to be faster and more efficient than other systems, is being fabricated to carry activity into the spectrometer and to carry it away after a counting period of two half-lives. We are developing a scheme to permit its use at CARIBU, Gammasphere, and at the focal plane of the Fragment Mass Analyzer (FMA). Drawings from other laboratories worldwide were obtained to learn from previous experience. We have a new design, and assembly (at Argonne) of the first system will be completed in January 2010 with follow-on funding support.

We designed a “Super-Clover” detector that is presently being assembled and will complete the “X-Array,” which is vital for this (and many other projects) at ATLAS. The detector will be delivered in June 2010 in time for the first research campaign. The rest of the X-Array infrastructure is undergoing assembly to be ready for experiments in 2010.

In addition, we have started collecting data with the NaI(Tl) TAS (thallium-doped sodium iodide total absorption spectrometer) sum spectrometer, which we received from Idaho National Laboratory. Initial tests with a charge-to-digital converter (QDC) charge-integrating system were disappointing; as

a result, we will use a more conventional preamplifier-shaping amplifier system. We are investigating the resolution as a function of source position and eliminating small “satellite” peaks from signal reflections arising from impedance mismatches. We have acquired a substantial amount of borated polyethylene from the Intense Pulsed Neutron Source group. This material is used as part of the shielding to suppress neutrons and enhance the sensitivity of the spectrometer.

Finally, we acquired some large neutron counters from a U.S. Department of Homeland Security “portal” model. This portal was designed to detect sensitive nuclear materials and contains two 5-foot by 1-foot neutron counters, which will be ideal for detecting weak delayed neutron branches. The neutron counters have been dismantled from the portal and moved to our laboratory for testing.

Proposed Work for FY 2010

This work continues with support from DOE through American Recovery and Reinvestment Act funds.

Selective, Efficient C-H Bond Activation of Alkanes by High-Surface-Area, Size-Selected Noble Metal Clusters

2008-090-R1

Michael J. Pellin, Jeffrey W. Elam, Stefan Vajda, and Randall E. Winans

Project Description

Alkanes, or saturated hydrocarbons, are major constituents of natural gas and petroleum; there are very few practical processes, however, for converting them directly to more valuable products. The reason for this difficulty is alluded to by their other name, “paraffin” (meaning “not enough affinity”): alkanes are relatively inert. This chemical inertness arises from strong, localized C-H and C-C bonds with high reaction activation barriers owing to the lack of empty orbitals of low energy, such as are present in olefins or alkynes. While combustion of alkanes occurs efficiently at high temperature (making them excellent portable fuels), this process has been difficult to control and inevitably leads to CO₂ and H₂O as products. The controlled activation of small, relatively inert molecules has been a ubiquitous theme in transition metal catalysis since its renaissance began in the late 1950s. Recently, significant effort has been directed toward C-H bond activation both by enzymatic and by homogeneous catalytic routes. At present, no industrial catalyst is available for direct C-H bond activation. The difficulty is threefold. First, no catalyst with sufficient activity is available. Second, achieving selective activation of the C-H bond is difficult and complicated by the differential

reactivity of various C-H bonds (i.e., terminal bonds have the lowest activity but the most desirable products). Third, thermodynamics makes limiting the reaction to partial oxidation extremely difficult.

By employing coatings of high-surface-area supports with ultra-small catalytic particles, new noble-metal-based catalysts for highly efficient C-H bond activation can result, leading to efficient olefin, alkyne, and longer-chain alkane synthesis, including a considerably simplified separation of the final product. The new atomic layer deposition (ALD) method described here uses alternating exposures to a metal-containing vapor and a reducing agent to prepare size-selected mono- and bimetallic clusters with independent control over the number density of the particles (particles/cm²), as well as the diameter of the particles. The number density is controlled by the duration of the reactant exposures in the initial cycle. Subsequently, we can increase the size of these clusters by using a controlled number of additional ALD exposures that serve to grow the clusters to a given size but not to initiate or nucleate any new clusters on the Al₂O₃ surface. In addition to the ALD deposition, we apply size-selected cluster deposition from molecular beams, which allows for precision control of cluster size and composition at the atomic level.

Mission Relevance

This project is relevant to DOE’s missions in science and energy. Catalytic research has been described as a “high-pay-off research direction for achieving the revolutionary breakthroughs that would lower the cost and raise the performance and reliability of technologies needed for hydrogen production, storage, and use.” DOE identified catalysis, and specifically nanoscale catalysis, as one of the crosscutting issues in the 2003 BES (Basic Energy Sciences) report on “Basic Research Needs for a Hydrogen Economy” that set forth a road map for achieving the needed fundamental scientific breakthroughs. BES has since revisited catalysis and made it a research priority. In addition, the *Chemical Industry Vision2020 Technology Partnership* has identified oxidative dehydrogenation catalysis as a leading technology for industrial chemical synthesis with the greatest potential to improve feedstock efficiencies, environmental impact, and energy savings. Thus, our research is highly relevant to EERE (Energy Efficiency and Renewable Energy)-based research as well.

FY 2009 Results and Accomplishments

Over the last year, we have developed ALD methods for preparing noble metal alloys. For our first investigation of this process, we selected Pt-Ir mixed metal films. We discovered that the growth of each of these materials is unperturbed by the presence of the other component in the film. This mutual compatibility between the Pt and Ir ALD surface chemistries enables us to control both the thickness and composition of the Pt-Ir mixed metal films with atomic-level control (Figure

1). X-ray diffraction measurements confirmed that the alloy films are composed of single-phase solid solutions. We have extended this method to a number of systems, including Pt-Ru, Ir-Ru, and Pt-Pd. Furthermore, we have prepared catalyst samples composed of mixed noble metal nanoparticles on high-surface-area supports (Figure 2). We are in the process of characterizing and testing these novel materials.

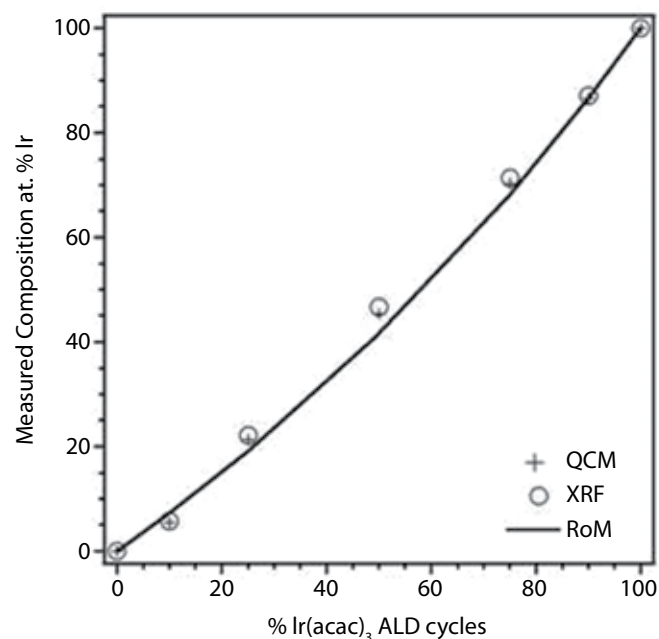


Figure 1. Film composition deduced from quartz crystal microbalance (QCM) and x-ray fluorescence (XRF) measurements as a function of the percentage of Ir(acac)₃ (acac = acetylacetonate) exposure cycles. The data agree well with the rule of mixtures for film composition (solid line).

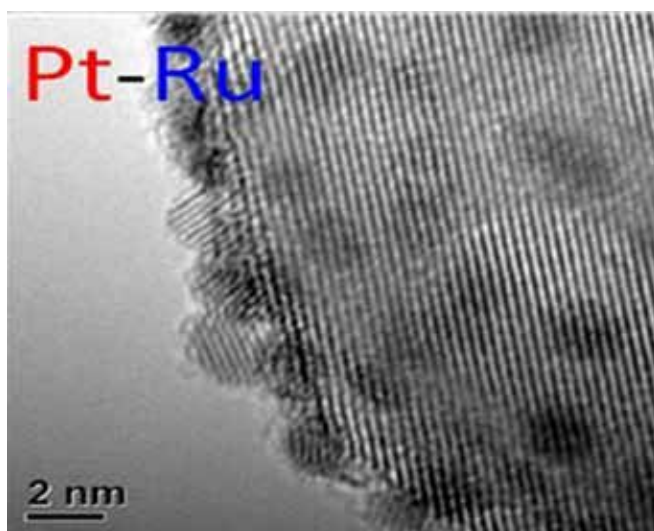


Figure 2. Transmission electron micrograph of ALD Pt-Ru nanoparticles on strontium titanate nanocube support.

We have shown that size-selected Pt₈₋₁₀ clusters that are stabilized on a high-surface-area support of ALD-coated nanoporous membranes are highly active for the oxidative dehydrogenation of propane. The subnanometer clusters are 40–100 times more active than previously studied platinum and vanadia catalysts (Figure 3), and yet, at the same time, maintain selectivity toward formation of propylene over carbon oxide species and cracked by-products. Quantum chemical calculations indicate that the under-coordination of the Pt atoms in the clusters is responsible for the surprisingly high reactivity compared to extended surfaces. We anticipate that these results will form the basis for the development of a new class of catalysts. While challenging, further development of these subnanometer clusters with highly active sites that are stabilized on appropriate supports could result in novel catalysts for a range of industrially relevant chemical reactions by providing a route to bond-specific chemistry. Such developments would have practical implications ranging from more energy-efficient and environmentally friendly strategies for chemical synthesis to the replacement of current petrochemical feedstocks by inexpensive and abundant small alkanes. The combined experimental and theoretical study was published in *Nature Materials* (see reference below).

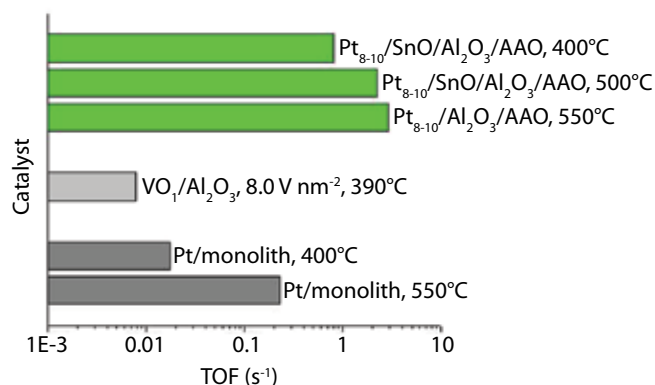


Figure 3. Turn-over frequencies of propene produced on the Pt₈₋₁₀ catalysts (green) and reference ODH (oxidative dehydrogenated) catalysts (gray) expressed as the number of propene molecules formed per metal atom.

Proposed Work for FY 2010

During FY10, the project will focus on the further advancement of the ALD methods for preparing noble metal alloy particles of controlled size and composition. *In situ* tests of catalysts of sub-nanometer to nanometer size will be performed.

Refereed Publications

Christensen, S.T., and J.W. Elam, "Atomic layer deposition of Ir-Pt alloy films," *Chem. Mater.*, Articles ASAP (As Soon As Publishable); Publication Date (Web): March 2, 2010 (Article); DOI: 10.1021/cm9031978

Christensen, S.T., H. Feng, J.L. Libera, N. Guo, J.T. Miller, P.C. Stair, J.W. Elam, "Supported Alloy Nanoparticles Prepared by Atomic Layer Deposition," Submitted Chem Mater. (2010).

Vajda, S., M.J. Pellin, J.P. Greeley, C.L. Marshall, L.A. Curtiss, G.A. Ballentine, J.W. Elam, S. Catillon-Mucherie, P.C. Redfern, F. Mehmood, and P. Zapol, "Subnanometre Platinum Clusters as Highly Active and Selective Catalysts for the Oxidative Dehydrogenation of Propane," *Nat. Mater.* **8** (2009), 213–216.

Non-Refereed Publications and Presentations

Elam, J.W., "Atomic Layer Deposition of Platinum on Strontium Titanate Surfaces," presented at the AVS (American Vacuum Society) 56th International Symposium, San Jose, CA, November 8–13, 2009

Vajda, S., "Highly Selective Oxidative Dehydrogenation of Propane on Sub-Nanometer Platinum Clusters," presented at the 21st North American Catalytic Society Meeting, San Francisco, CA, June 7–12, 2009.

Vajda, S., "Nanocatalysis by Size-Selected Clusters under Realistic Reaction Conditions," invited presentation at the Genesis Research Institute Symposium II on Cluster Science, Nagoya, Japan, February 24–26, 2009.

Vajda, S., "Nanocatalysis Size-Selected Clusters at Work under Realistic Reaction Conditions: Size, Shape, Composition, and Support Effects," presented at the Symposium on Size-Selected Clusters (S3C), Brand, Austria, March 8–13, 2009.

The Development of Neutron Skins

2009-037-N0

Christopher J. Lister, Ivan Brida, Elizabeth Ricard-McCutchan, and Robert B. Wiringa

Project Description

We are making a combined theoretical and experimental investigation of excited states and their decays in light neutron-rich nuclei. These are nuclei such as the beryllium isotopes ^9Be , ^{10}Be , and ^{11}Be that are now amenable to accurate theoretical calculation using quantum Monte Carlo (QMC) methods and the sophisticated two-nucleon (NN) and three-nucleon (3N) potentials that the Argonne theory group has developed over the past decade. Experimental properties, such as lifetimes, of many of the excited states in these nuclei are poorly known, but they are also amenable to newly improved experimental techniques, like the Doppler shift attenuation method (DSAM), which the Argonne low-energy group is developing to ever-greater precision. The new experimental results that are

being obtained are presenting new challenges to the theoretical models, which, in turn, are suggesting possible new experiments. The outcome will be a greatly improved understanding of the structure of light neutron-rich nuclei, particularly in the weakly bound regime where extended neutron skins develop.

Mission Relevance

The project is relevant to DOE's basic science mission. Argonne has played a leading role in the development of *ab initio* theory for light nuclei, and this work has been prominently featured in the last two DOE Nuclear Science Advisory Committee (NSAC) Long-Range Plans. The combination of the Argonne Tandem Linac Accelerator System, the Fragment Mass Analyzer, and Gammasphere allow for the most precise experimental techniques to be applied to the problems under study.

FY 2009 Results and Accomplishments

The theory group calculated $E2$ transitions in ^{10}Be for a number of excited states by using several different Hamiltonians. The experimental group measured two of these transitions with unprecedented accuracy: <5% uncertainty for the decay of the first 2^+ excited state to the ground state and <20% uncertainty for the second 2^+ excited state to the ground state. Our preferred theoretical model predicted a $B(E2)$ transition probability for the first state of $8.8(2) e^2\text{fm}^4$, while the experiment found $9.2(3) e^2\text{fm}^4$, which is in excellent agreement. However, the predicted $B(E2)$ for the second state was too large by an order of magnitude compared to experiment: $1.7(1)$ vs. $0.11(2) e^2\text{fm}^4$. This second 2^+ state is very close to the threshold for breakup, which may require significant improvements in the theoretical modeling to explain.

Theoretical calculations have also been made for transitions in the mirror nucleus ^{10}C , which found varying behavior, depending on the Hamiltonian used. This nucleus also consists of an ^8Be core, but now with two diffuse protons outside, and the charge of the final two protons may or may not significantly alter the $B(E2)$ transitions. Consequently, the experimental group has already made a first experiment looking to measure the transitions in this case.

A newly hired theory postdoc has been learning to use the QMC codes by focusing on states in ^9Be . This nucleus is the smallest to exhibit a full range of low-lying unnatural-parity states for which the single neutron outside the ^8Be core can be promoted from the natural-parity p -shell to the next-higher sd -shell. This is a natural lead-in to studying the unnatural-parity states in ^{10}Be , for which the lowest such states are particle-stable, and in ^{11}Be , for which the ground state is an unnatural-parity $\frac{1}{2}^+$ state.

Proposed Work for FY 2010

We will continue with experiments on ^{10}C and continue developing wave functions for the $A = 9, 10, 11$ nuclei, using the transitions to test and improve the wave functions and Hamiltonians.

Refereed Publications

McCutchan, E.A., C.J. Lister, R.B. Wiringa, S.C. Pieper, D. Seweryniak, J.P. Greene, M.P. Carpenter, C.J. Chiara, R.V.F. Janssens, T.L. Khoo, T. Lauritsen, I. Stefanescu, and S. Zhu, "Precise Electromagnetic Tests of *Ab Initio* Calculations of Light Nuclei: States in ^{10}Be ," *Phys. Rev. Lett.* **103** (2009), 192501.

Non-Refereed Publications and Presentations

Lister, C.J. (Kim), "Precision Measurements of Electromagnetic Matrix Elements in ^{10}Be as a Test of *Ab Initio* Calculations," presented at the KERNZ08 Conference on Nuclei and Reactions, Queenstown, New Zealand, December 1–5, 2008.

Lister, C.J. (Kim), "Nuclear Structure Now, *Proceedings of Frontiers in Gamma Spectroscopy 2009 Conference TIFR*, Mumbai, India, March 1–5, 2009, to be published in 2010.

Lister, C.J. (Kim), "Precision Measurements of Electromagnetic Matrix Elements in ^{10}Be as a Test of *Ab Initio* Calculations," presented at the American Chemical Society Symposium on Nuclear Structure Physics, Salt Lake City, UT, March 24–27, 2009.

Lister, C.J. (Kim), "Atoms, Nuclei, and Neutron Stars," presented at a colloquium at University of Massachusetts, Lowell, MA, April 6, 2009.

McCutchan, E.A., "Testing *Ab Initio* Calculations in $A=10$ Nuclei Using Precision Lifetime Measurements," presented at a seminar at the University of Tennessee, Knoxville, TN, March 23, 2009.

McCutchan, E.A., "Precision Lifetime Measurements in Light Nuclei as a Test of *Ab Initio* Calculations," presented at the 3rd International Conference on Collective Motions in Nuclei under Extreme Conditions (COMEX3), Mackinac Island, Michigan, June 2–5, 2009.

McCutchan, E.A., "Testing *Ab Initio* Calculations in $A=10$ Nuclei through Precision Lifetime Measurements," presented at the Gordon Research Conference, New London, NH, June 21–26, 2009.

Next Generation Sequencing Technology Applied to Genome Annotation

2009-062-N0

Frank R. Collart

Project Description

The emergence of "next-generation" sequencing technology has contributed to an exponential increase in the number of completely sequenced genomes. However, this ability to generate sequences has far outpaced computational and experimental methods to efficiently use the genomic data. A consequence of this imbalance is poor-quality gene models that compromise experimental approaches to defining functional and regulatory characteristics. This problem is most apparent with nonbacterial organisms, such as the fungi and plants. We developed methods that use sequence data derived from RNA (RNA-seq) to improve the structural and functional interpretation of genome sequence data. The method described here can be generalized to any gene set in any species, provided that there is a sequenced genome and a set of gene models.

Mission Relevance

The project is relevant to DOE's basic science and environmental missions. The methods and revised gene models derived from this project assist in the identification of functional characteristics of key microbial and plant proteins that are important for developing a predictive understanding of regulatory and metabolic pathways. Integration of this knowledge of the biological components supports the development of systems-level models that predict the response of organisms and ecosystems that are critical to DOE missions. This increased knowledge of function, regulation, and response could be integrated with other projects to support the goal of the Office of Biological and Environmental Research to achieve a genome-based, dynamic systems-level understanding of organism and community functions.

FY 2009 Results and Accomplishments

The project employed the symbiotic fungus *Laccaria bicolor* and tree *Populus tremuloides* as a mycorrhizal model system. The laboratory model for this system enables characterization of the free-living plant and fungus and the development of ectomycorrhizal symbiosis. We used the transcriptomic sequence to validate existing fungal gene models generated by the current automated process and to correct or extend gene models as appropriate. The 46 base pair (bp) sequence reads were aligned to the genome sequence to generate a frequency profile for expressed sequences relative to chromosomal position (Figure 1). This profile map is characterized by clusters of reads separated by well-defined gaps with little or no transcript sequence coverage. These gaps correspond to

intronic or intragenic regions and provide a starting point for application of additional algorithms to cluster and compare local sequence reads. The intron/exon boundaries are specifically defined by the set of sequences that span segments of chromosomal DNA (red peaks in Figure 1, top). The presence or absence of these bridging sequences is used to validate or correct the gene model. In the absence of a gene model or in regions where the sequence profile indicates the model could be extended (Figure 1, region A), the gaps in transcript frequency are used as starting points in the search for intron spanning segments. The sequence analysis parameters and the alignment process are specifically designed to enable the identification of exons smaller than 46 bp (the length of Illumina Solexa instrument-generated sequence reads used in this study), as these are common in basidiomycetes (Figure 1, region B). Intrinsic to the process is the identification of putative stop-and-start sites that can be used to define the coding region of the gene model.

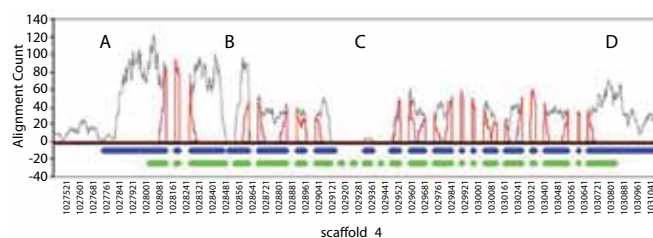


Figure 1. Correction of gene models using transcriptomic data. The position on the chromosome scaffold is on the x-axis and the number of alignments at each bp is on the y-axis. The gray line represents the alignment count for RNA-seq to the genome, and the red line is the alignment count to the gene model, but not to the genome. The original gene model is in blue, and the RNA-seq revised model is in green. At (A) and (D), the gene model is truncated to the first in-frame start codon and stop codon. The corrected green gene model was adjusted to intron-exon splice sites closest to the boundary of genome (grey line). In (C), failure to find gene model alignments that bridged the intron was corrected by the addition of three small exons.

These results indicate that the published gene models require extensive revision and that RNA-seq is an effective tool having the resolution to make these corrections, from small shifts in exon boundaries to major changes in predicted gene structure. The addition of more RNA-seq data and expanding the search to a broader range of gene models can be expected to improve the process of gene structural annotation.

Proposed Work for FY 2010

This project does not continue into FY10.

Non-Refereed Publications and Presentations

Larsen, P.E., V. Lu, and F.R. Collart, "Using Next Generation Sequencing Data for Structural Annotation of *L. bicolor* Mycorrhizal Transcriptome," presented at the Critical Assessment of Massive Data Analysis Conference (CAMDA 2009), Chicago, IL, October 5–6, 2009.

Coherent Diffraction Imaging of Complex Polymeric Networks

2009-068-N0

Lee Makowski

Project Description

The development of coherent diffraction imaging (CDI) for use at today's synchrotron light sources and the next-generation sources that will come on line in the next few years will provide an extraordinary opportunity for studying complex polymeric matrices that constitute a very important but poorly characterized class of biomaterials. This project aims to capitalize on CDI's unique suitability for studying these structures to develop a robust approach to mapping the distributions of a variety of chemical constituents within complex polymeric networks.

Mission Relevance

The project is relevant to DOE's missions in energy and basic science. In particular, understanding the structure of plant cell walls would be of great import to developing strategies for optimal production of biofuels. The project would yield information central to an understanding of the structural principles underlying lignocellulosic structures, thereby contributing substantially to efforts to re-engineer those structures for bio-energy applications. Comparable increases in understanding human extracellular matrices and connective tissues would have profound impact on our ability to treat afflictions associated with aging, which would be of interest to the National Institutes of Health (NIH.) A vast number of materials could be studied by using this technique, including bone, pathogenic protein deposits, silk, and synthetic polymers, among others.

FY 2009 Results and Accomplishments

At the Advanced Photon Source, we scanned isolated microcrystalline cellulose from about 10 different sources (including a variety of cellulose nanocrystals prepared for us by John Simonsen at Oregon State University). We then collected data from vascular bundles of maize. In all, we observed Bragg reflections from numerous cellulose microcrystals, collecting full data sets from more than a dozen of these crystals. On the basis of these data, we have begun reconstructing the shapes of the cellulose crystals. They show similar characteristics, suggesting that many of the features in these preliminary images will prove to be correct. The form of cellulose crystals suggests that cellulose fibrils of similar cross section coalesce into larger crystalline units within plant tissues. These results exceed the progress we anticipated for year one.

Proposed Work for FY 2010

Collecting high quality data from cellulose crystals *in situ* appears to be much easier than anticipated. Furthermore, year-one results included two unexpected and exciting discoveries:

1. Different allomorphs of cellulose appear to form crystals of different shapes.
2. The crystals appear to be made up of cellulose fibrils that are in crystalline registry with the bulk of the crystallite but appear to be physically separated at the ends.

Full characterization and confirmation of these results would yield substantial insight into plant cell wall architecture and provide a highly visible application of the methods we are developing. Consequently, we propose to follow up on these two discoveries in year two.

Non-Refereed Publications and Presentations

Makowski, L., and J. Lal, "Biomedical Applications of Cellular and Molecular Imaging," invited talk at the APS Users Meeting: Workshop on Imaging Structural Hierarchy in Biological Systems, May 6, 2009.

Characterization of Proteins from *Anaeromyxobacter dehalogenans*, a Newly Identified Bacterium of Metabolic and Respiratory Versatility Important for Bioremediation

2009-070-N0

Marianne Schiffer, Deborah K. Hanson,
and Phani Raj Pokkuluri

Project Description

The bacterium *Anaeromyxobacter dehalogenans* has been found in contaminated subsurface environments, such as the DOE Natural and Accelerated Bioremediation Research Program's Field Research Center at Oak Ridge, TN, where *Anaeromyxobacter* species are thought to be key players in metal reduction. The metabolic and respiratory versatility of *A. dehalogenans* is evident in the fact that it grows under a variety of redox conditions and can couple the oxidation of a variety of compounds, such as formate, acetate, and hydrogen, among others, to the reduction of various electron acceptors, such as U(IV), Fe(III), and halogenated phenols. The genome of *A. dehalogenans* was fully sequenced at the DOE Joint Genome Institute and codes for 68 *c*-type cytochromes

and 93 two-component signal transduction proteins. Very few details of the proteins for *A. dehalogenans* are known, providing an excellent opportunity for our laboratory to study important characteristics of some of its key proteins.

Mission Relevance

The project is relevant to DOE's missions in basic science and the environment. Microbial research is especially important for DOE's Office of Biological and Environmental Research because it can provide a basis for the development of innovative biotechnological applications resulting in better and less-expensive ways to clean up contaminated sites. *A. dehalogenans* is well suited for this purpose because of its metabolic and respiratory versatility. It can grow under a variety of redox and pH conditions and can clean up contamination by chlorinated compounds, toxic metals, and radionuclides found at DOE and DOD sites. Harnessing the full potential offered by this bacterium for the development of enhanced bioremediation tools requires research into the details of various proteins present in the organism and characterization of their structures and functions.

FY 2009 Results and Accomplishments

We have chosen to focus on three protein families from *A. dehalogenans* strain 2CP-C for expression and characterization: (1) cytochromes *c*₇, (2) large multiheme cytochromes, and (3) sensor proteins. The results from each are described briefly below.

Cytochromes *c*₇. The cytochromes *c*₇ encoded by the genes Adeh_1696 and Adeh_1697 are small (~10 kDa) three-heme cytochromes. The cytochromes were expressed in *E. coli* strains carrying cytochrome maturation proteins that are necessary for the insertion and covalent attachment of heme cofactors into the newly synthesized *apo* cytochromes. The *A. dehalogenans* cytochromes were engineered at their C-terminal end to carry a polyhistidine tag that enables protein isolation via immobilized metal affinity chromatography. One of the cytochromes (Adeh_1696) was isolated with affinity chromatography. Preparation of the Adeh_1697 cytochrome using the same methodology is in progress. The purified proteins will be used to carry out crystallization trials.

Large multiheme cytochrome Adeh_3077. Sequence analysis of the 40-heme cytochrome Adeh_3077 from *A. dehalogenans* revealed that it has novel pentaheme domains not previously seen in other organisms. These pentaheme domains represent a new structural motif, and cloning two of these domains is in progress.

Sensor domains. Chemotaxis proteins pick up a signal using a “sensor” domain present in the periplasm and transfer the signal to the domains present in the cytoplasm, which, in turn, trigger the downstream regulatory processes that switch on the motility of the organism. There are eight chemotaxis proteins in *A. dehalogenans* that have a sensor domain in the periplasm. On the basis of an analysis of the eight sequences using structure prediction programs, we have chosen sensor domains from four proteins (Adeh_1194, Adeh_1380, Adeh_3718, and Adeh_3897) that represent different folds, two of which occur mostly in *A. dehalogenans* and two with many structural homologs. Genes encoding these four sensor domains have been amplified successfully from *A. dehalogenans* genomic DNA. They have been cloned into a vector that provides a C-terminal polyhistidine tag for expression in *E. coli*; expression experiments are awaiting sequence verification.

Proposed Work for FY 2010

Cytochromes c₇. Purified cytochromes Adeh_1696 and Adeh_1697 will be characterized in solution by ultraviolet-visible (UV-Vis) spectroscopy, and crystallization trials will be carried out to determine conditions for obtaining diffraction-quality crystals. When crystals of data collection quality are available, x-ray diffraction data will be collected at Argonne’s Advanced Photon Source, and the structures will be determined using anomalous dispersion of the heme iron atoms. In addition, we will determine the redox potentials of the cytochromes with help from Prof. Carlos Salgueiro (Universidade Nova de Lisboa, Portugal).

Pentaheme domains from cytochrome Adeh_3077. Large-scale expression of the pentaheme domains from cytochrome Adeh_3077 will be carried out. Proteins will be characterized in solution and will be used for crystallization trials. Diffraction-quality crystals, when available, will be used for structure determination.

Sensor domains of chemotaxis proteins. The sensor domains that express well in *E. coli* will be prepared in large quantities. The purified sensor domains will be characterized in solution with UV-Vis and circular dichroism spectroscopies and will be subjected to crystallization trials. The sensor domains that produce good crystals will be used for structure determination.

Local Probe of Novel Electronic States at Complex Oxide Interfaces

2009-083-N0

John W. Freeland and Nathan P. Guisinger

Project Description

The transistor, which shaped so much of our modern technology and economics, grew out of scientists’ desire to gain a greater understanding of the interfaces between different materials. In the same way, today’s materials scientists seek to expand our understanding of complex oxides by creating new states at the interface of two materials. To understand the spatial variation of these interface states, this project is focused on further developing cross-section scanning tunneling microscopy (STM), which has worked well for the analysis of semiconductor interfaces, but has to date never been applied to oxide heterostructures, which are of interest because of their superconductivity properties.

Mission Relevance

The proposed project is tied to DOE’s mission in science. The DOE, Office of Naval Research, and Air Force Office of Scientific Research are currently funding projects in novel oxide materials leading to new discoveries. By combining the magnetic (spin) component with the superconducting part, we expect to establish the basis for the development of new types of devices that reach beyond the current applications of spin-based electronics (spintronics). As a result of a recent workshop, the Defense Advanced Research Projects Agency (DARPA) is also considering a call in the area of Correlated Oxide Electronics, as part of which local understanding of materials properties at the interface will be a key component.

FY 2009 Results and Accomplishments

During this first year, we developed an *in situ* method for fracturing an oxide heterostructure film in order to gain access to the film in cross section. Since complex oxides films are commonly prepared on SrTiO₃ (STO) substrates, we initially developed methods to fracture SrTiO₃ substrates and create atomically smooth terraces. The perovskite crystal structure, ABO₃, does not possess a natural cleavage plane, so the crystal must be fractured in a controlled fashion in order to create a well-defined surface.

By symmetry, the cleaving of SrTiO₃ to create a (100) surface produces a mixed termination of SrO and TiO₂ surfaces with an unreconstructed surface crystal structure; however, to date no clear images have been obtained of how the mixed termination is manifested in real space. Our STM images revealed that the fractured region of the sample consists of

a periodic arrangement of wide and narrow terraces (see Figure 1). A bigger surprise was revealed when we investigated the electronic properties of the SrTiO_3 by analysis with scanning tunneling spectroscopy (STS) to create a map of the local density of states (LDOS). Since the STS data are acquired concurrently with topography, the LDOS can be overlaid with the topographic image, as shown in Figure 1, to fingerprint the termination. This combined map revealed a strong contrast between different terraces and formed a well-defined nanometer-scale stripe pattern with long-range order consisting of two different surface terminations (SrO and TiO_2). Such a periodic arrangement has never before been observed on the STO surface. These results have been reproduced, demonstrating that we can reproducibly produce atomically flat surfaces by this method.

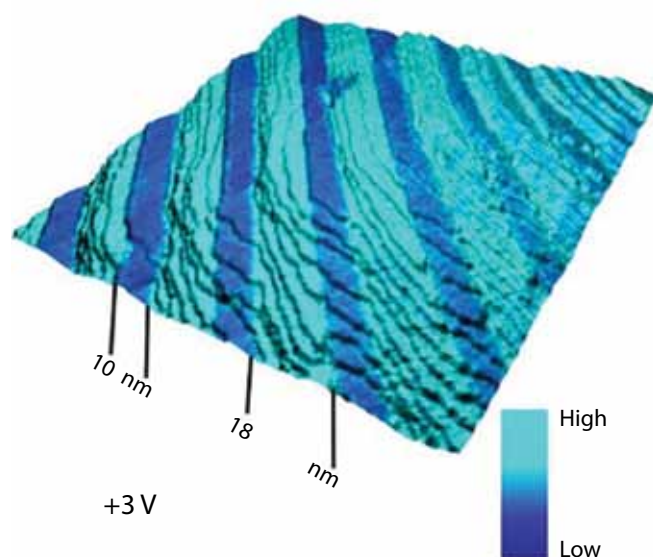


Figure 1. Conductance map of in situ cleaved SrTiO_3 surface overlaid with topography. The tunneling contrast at 3-Volt bias clearly shows the regions of SrO (high conductance) vs. TiO_2 (low conductance) termination.

At the end of FY09, we obtained the first images of the interface between a film and fractured surface, shown in Figure 2. To date, no other groups have succeeded in extending this technique into oxide heterostructures. These initial experiments have shown that this route to understanding interface physics is possible for complex oxide systems.

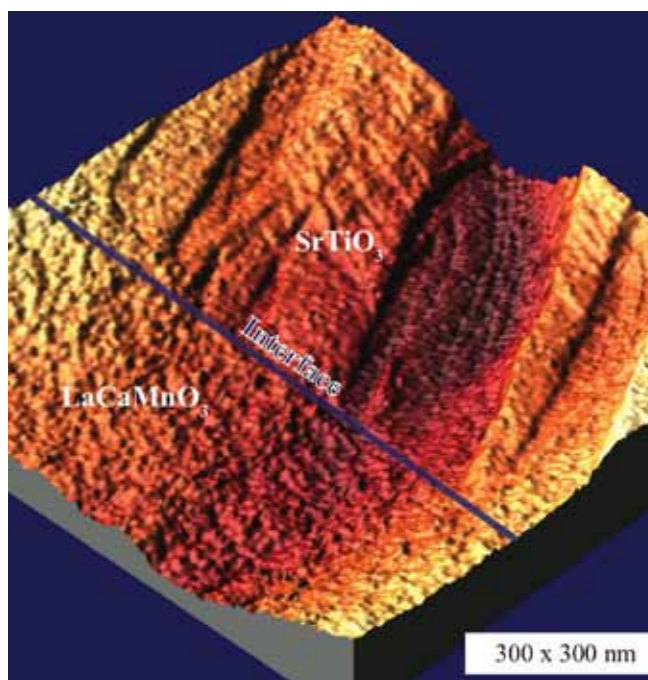


Figure 2. Topography of the fractured surface near the interface between the SrTiO_3 substrate and a 100-nm LaCaMnO_3 film. The color scale refers to the vertical height of the surface. The line marks the location of the interface, which is determined by a local probe of the electronic structure (not shown). These initial results demonstrate the possibility of finding atomically smooth regions close to the interface.

Proposed Work for FY 2010

During FY10, we will refine our initial interface results to explore the details of electronic properties in the interface region. Now that we have succeeded for the case of one interface, during FY10 we will investigate more complex multilayered structures (e.g., $\text{LaCaMnO}_3/\text{YBa}_2\text{Cu}_3\text{O}_7$), where we can track the interface between dissimilar complex oxides.

Refereed Publications

Chien, T.-Y., T.S. Santos, M. Bode, N.P. Guisinger, and J.W. Freeland, "Controllable Local Modification of Fractured Nb-Doped SrTiO_3 Surfaces," *Applied Physics Letters* (2009) **95**, 163107.

Guisinger, N.P., T.S. Santos, J.R. Guest, T.-Y. Chien, A. Bhattacharya, J.W. Freeland, and M. Bode, "Nanometer-Scale Striped Surface Terminations on Fractured SrTiO_3 Surfaces," *ACS Nano* **3**, 4132 (2009).

Non-Refereed Publications and Presentations

Guisinger, N.P., "Current Trends in Scanning Probe Microscopy at Argonne National Laboratory," presented as a colloquium at Purdue University, October 9, 2009.

Solvent Extraction of Colloidal Aluminum Oxide Applicable to High-Level Radioactive Wastes

2009-091-NO

Richard E. Wilson and Lynda Soderholm

Project Description

The legacy of plutonium production for application in nuclear weapons has resulted in the accumulation of several tens of millions of gallons of liquid high-level radioactive wastes currently stored at the Hanford Site in Washington State, as well as at the Savannah River Site in South Carolina. The overwhelming majority of the waste volume exists as non-radioactive aluminum present from the dissolution of fuel-element cladding and as an additive in the separations process to recover the plutonium. Because the waste was treated with caustic, the aluminum in the liquid fraction of the waste exists as colloidal aluminum oxide particles. The current strategy is to vitrify the high-level radioactive portions of the wastes and dispose of the remaining low-level fraction, the majority of which is the non-radioactive aluminum in salt stone waste forms. In this project, we interrogated the solvent extraction behavior of these colloidal aluminum oxide particles with the ultimate goal of reducing the final waste volume requiring disposal. Our approach was to understand the differences in the chemistry between the colloidal aluminum particles and other known metal oxide particles and to investigate the applicability of a solvent extraction method demonstrated to be useful for plutonium oxide colloids. This research was driven by the hypothesis that the surfaces of the colloidal aluminum oxide particles could be functionalized in order to separate them by solubilization in an organic phase suitable for solvent extraction.

Mission Relevance

The research carried out in this project is relevant to several DOE missions. The initial inspiration for this research was the investigation of an alternative method for the management of the high-level radioactive wastes stored at the Hanford and Savannah River sites, which is directly relevant to DOE's mission for environmental remediation and stewardship at these sites. Additionally, the underpinning fundamental science which drives this research is the study of the surface reactivity of colloidal and nanoparticle phases and the fundamental chemical and physical properties of these surfaces and interfaces.

FY 2009 Results and Accomplishments

On the basis of our initial results with plutonium oxide colloids, a similar solvent extraction procedure was employed with commercially available aluminum oxide colloids. Results from these experiments showed that the surface reactivity observed in the case of the plutonium system, as indicated by the successful phase transfer, was not the same in the case of the aluminum oxide system, despite previous reports available in the literature demonstrating that different surfactants could be employed to produce aluminum oxide particles of different sizes and compositions. Several organic-phase solvents were tested: in particular, carboxylate-containing surfactants and organic diluents with varying dielectrics, including alcohols and alkanes, a property previously shown to have a significant impact on the efficacy of the phase transfer between aqueous and organic phases, as well as on the solubility of the colloidal extraction adduct. Additionally, the properties of the aqueous phase were manipulated to determine the effects of different anions (NO_3^- , ClO_4^- , and Cl^-) on the extraction behavior and on the solution pH and ionic strength. In all of these cases, we observed no phase transfer of the aluminum oxide colloids from the aqueous to the organic phase. In fact, only flocculation of the particles and emulsion formation occurred.

Despite the failure of the surface functionalization process and solvent extraction for the aluminum oxide colloids, the process was shown to be effective for nanoparticles and colloids of zirconium oxide, cerium(IV) oxide, and thorium oxide. The inherent differences between these colloids lay in the underlying chemistries of the metal ions. Zirconium, cerium, and thorium are not amphoteric metals, meaning that they do not form anionic complexes at more alkaline pH, rather they form neutral or positively charged species in solution under conditions of relative acidity. Conversely, aluminum is known to be amphoteric, meaning that it may form both soluble cationic and anionic species in solution.

The amphoteric nature of aluminum versus the other metals investigated suggests that the underpinning surface reactivity of the colloidal phases is related to the inherent chemistry of the metal in the metal oxide particle, particularly for surface reactions, such as ligand and ion-exchange-type reactions occurring at the particle surface.

The results obtained in this research project are contributing to our development of a new approach to separating colloids that develop in nuclear waste streams. The work enabled by this funding demonstrates that nanoparticle and colloidal surfaces can be manipulated to achieve a chemical separation without the necessity of destroying the particle, a step that

can be both expensive and time consuming. Moreover, the differences in the reactivity of these surfaces with respect to surfactants and surface reactive molecules indicate that we may use techniques, such as solvent extraction, to investigate and quantify the surface chemical properties of these particles.

Proposed Work for FY 2010

This project does not continue into FY10.

Three-Dimensional Metamaterials with Negative Refractive Index

2009-111-NO

Matthew A. Pelton, Stephen K. Gray, and Xiao-Min Lin

Project Description

The goal of this project is to use the techniques of chemical synthesis and assembly to produce bulk, three-dimensional materials that exhibit a negative refractive index for light. The past several years have seen the development of new “metamaterials” that have optical properties unlike anything occurring in nature. In particular, it is possible to develop negative-index materials (NIMs) that defy all ordinary expectations: light bends in the “wrong” way when entering these materials; light waves move backwards within them; and a thin, flat slab of the material can serve as a near-perfect lens. Achieving a negative index for optical wavelengths requires the fabrication of metallic elements that are fully in the nanometer regime. To date, this has been achieved by top-down fabrication techniques, similar to the methods used to fabricate microelectronic devices. Although such techniques are capable of producing arbitrary nanoscale patterns, they are inherently limited to producing planar structures. Our goal is to use colloidal synthesis to produce metal nanoparticles and then chemically functionalize these particles so that they assemble into configurations that produce a three-dimensional NIM.

Mission Relevance

The proposed project is tied to DOE’s missions in science, national security, and energy. A successful research effort will benefit the extensive scientific community working in the field of optical metamaterials. Development of bulk negative-index materials will be important for the investigation of methods to reduce losses and extend the wavelength range of the materials. In addition, the demonstration of negative refractive index in three dimensions opens up the possibility of many exotic applications, such as invisibility cloaks, perfect lenses, reflectionless interfaces, novel nonlinear-optical effects, negative Doppler shifts, and actively modulated metamaterials. Any

one of these applications will have important potential energy and security implications. We anticipate that defense and intelligence agencies, such as the Defense Advanced Research Projects Agency (DARPA), the Central Intelligence Agency (CIA), and the Defense Intelligence Agency (DIA), which have already demonstrated their interest in metamaterials, would be interested in the research.

FY 2009 Results and Accomplishments

An optical NIM requires subwavelength elements that show strong resonant response, not only to electric fields, but also to magnetic fields at optical frequencies. A pair of gold nanorods arranged side by side has the potential to exhibit such optical magnetic resonances. In the first year of the project, we have developed the necessary techniques to synthesize and assemble these nanorod pairs. As a first crucial step, we synthesized high-quality gold nanorods by using the techniques of colloidal chemistry. We then began developing a strategy to assemble the rods side by side with controlled separation and high yield. We built on a method demonstrated in the literature that is capable of producing a large number of nanorod pairs, but still results in a by-product consisting of single rods and of bundles of three or more rods. We planned to use purification techniques to separate the desired pairs from the by-product, similar to techniques that have been demonstrated for the purification of carbon nanotubes and other nanostructures; however, the pairs produced so far are not stable enough to withstand the purification process. We, therefore, began development of stabilization methods based either on chemically linking the nanorod pairs or on encapsulating the pairs in polymer layers.

In order that the ensemble of nanorod pairs acts as a NIM, it will be crucial to correctly adjust its geometry, including the dimensions of the particles and the spacing between them. To determine the optimal dimensions and arrangements, we have begun to simulate the response of candidate materials by using rigorous computational methods. Because of computational limitations, it is impractical to simulate more than a small number of nanorod pairs at a time. A key element of the theoretical work thus involves identifying the response of an individual structure to electric and magnetic fields and determining how this response relates to the refractive index produced by a large number of these pairs. In the first year, our theoretical work has focused on validating the required computational approach.

Proposed Work for FY 2010

Work in FY10 will involve optimizing the several steps involved in synthesizing, assembling, stabilizing, and purifying gold-nanorod pairs, so that we finally end up with a sample that consists of nearly 100% pairs with controllable size and sepa-

ration. We will also complete the validation of our computational approach and calculate the response of realistic geometries. These calculations will allow us to determine the optimal geometry for realization of a negative refractive index. On the basis of the interaction between synthesis and calculation, we expect to be able to develop a material that demonstrates a negative refractive index at visible wavelengths.

Ultra-Sensitive Protein Biomarker Screening Assay for Early Stage Disease Diagnosis

2009-138-N0

John T. Bahns, Liaohai Chen, and Ralu S. Divan

Project Description

Early stage disease diagnosis requires the detection and characterization of very small quantities of proteins. Ideally, we would like to take a drop of blood (or other bodily fluid) and analyze it for the presence of a particular protein, an array of proteins, or a pattern of the proteins that is only produced when a patient has cancer. That task is extremely difficult because in an early stage of tumor development only one of every 10 billion (or more) proteins in blood plasma may be relevant to disease diagnosis. How can we design a test to reliably identify and detect that protein? And how can we make sure that this test produces no false positives (leading to a false initial diagnosis of the presence of cancer). The way to achieve those ends is to develop a *protein sorting assay* capable of detecting and characterizing extremely low levels (to a single protein molecule) from a bulk specimen sample.

The goal of this project is to build a protein biomarker screening assay via the combination of molecular biology, advanced spectroscopy, and micro/nano fabrication technologies. The proposed assay has high potential for ultimate screening and discrimination against a wide range of biological agents at a high level of confidence and is expected to find immediate use in three major areas: early stage diagnosis of lethal diseases (e.g., cancers, autoimmune deficiency syndrome, and Alzheimer's), national security and public safety (e.g., countering bioterrorism threats and responding to epidemics), and biomedical research (e.g., development of new drugs and treatments).

Mission Relevance

This project is relevant to DOE's mission of improving the quality of life through innovations in science and technology. It is also relevant to many other agencies, including the National Institutes of Health, Department of Homeland Security, Department of Defense, and National Aeronautics and Space Administration, as well as to industrial organizations. In particular, the National Cancer Institute (NCI) in the National Institutes of Health is committed to support nanotechnology for cancer research. Molecular imaging and early detection are key areas in the NCI Cancer Nanotechnology Plan.

FY 2009 Results and Accomplishments

Electron-beam lithography was used to define nano-channel patterns and metal structures, and reactive ion etching was applied to create the channels. Figure 1 shows 3-D atomic force microscopy and optical images of a channel pattern etched into a glass and images of a micro-channel linked with nano-channels. For nano-channel fabrication, we used two approaches: aligning nano-channels between micro-channels on glass and creating long nano-channels on glass, then covering them with polydimethylsiloxane micro-channel structures.

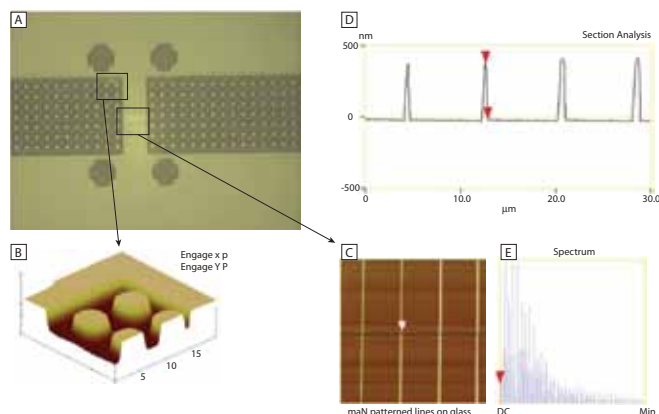


Figure 1. Images of the micro-channel, linked with nano-channels on glass. The completed device is shown in (1A). Figure 1B is a close-up of the filter posts (used to prevent clogging of the analyzer). Figure 1C is a close-up of the analyzer channels (turned 90 degrees) with section analysis in (1D), giving the individual channel dimensions. The roughness spectrum at the micro-channel wall (at the triangle in 1C) is shown in (1E).

Because two-color fluorescence cross-correlation spectroscopy (FCCS) is used to detect biomarkers, we have evaluated the performance of our FCCS system to ensure optimum performance in a micro/nano fluidics channel. This effort involved optimization of channel cross-talk, beam overlap, and system throughput; removal of parasitic oscillations; the determination of flow velocities; and burst height analysis.

To address the issue of cross-talking in the detection channel, we found that because of the finite cross-talk between the red and green detection channels, the correlation function (G) should be expressed as a sum of terms, which we have quantified.

In other efforts, we measured the confocal beam overlap volume and system throughput, establishing that our FCCS system is operating at near optimum. We also developed a new way to eliminate 99.8% of unwanted parasitic oscillations, typically observed for measurements at or near micro-channel interfaces.

We established two-color FCCS signals from flowing beads in transverse flow mode in a micro/nano fluidics channel, then determined accurate flow velocities from fits to the FCCS data by using a standard equation for G_{flow} .

Beam spot/microchannel overlap was studied by inserting negative lenses of varying focal length into the input laser beam and recording the FCCS spectra of flowing dye molecules of known concentration for each lens. Burst size was found to depend on beam spot size. We also determined the optimum spot size by measuring fluorescence records sequentially for the same dye-labeled sample using different beam spot sizes.

Proposed Work for FY 2010

In FY10, we will integrate metal nanoslits on nanofluidic channels and establish near-field illumination in the resulting device. Nanofluidics patterns will be developed, and a new software correlation algorithm will be implemented. The performance of the complete device will be characterized, including its sensitivity, specificity, and throughput.

Refereed Publications

Bahns, J.T., Q. Guo, J.M. Montgomery, S.K. Gray, H.M. Jaeger, and L. Chen, "High Fidelity Nano-Hole-Enhanced Raman Spectroscopy," *Journal of Physical Chemistry C* **113** (2009), 11190-11197.

Laboratory Simulations of Plasma Conditions near Active Galactic Nuclei and Black Holes

2009-146-N0

Elliot P. Kanter, Robert W. Dunford, and Linda Young

Project Description

The objective of this project is to use the Advanced Photon Source (APS) to obtain some of the first measurements of a low-density photoionizing plasma. In this project, the Smithsonian Astrophysical Observatory (SAO) is joining with Argonne to create and characterize exotic photoionized plasma conditions that are representative of the gas near active galactic nuclei and black holes. The SAO will bring two state-of-the-art spectroscopy instruments to Argonne: a new electron beam ion trap (EBIT) designed to produce well-controlled plasmas and a cryogenically cooled microcalorimeter capable of measuring broad-band x-ray spectra with high spectral resolution.

Mission Relevance

The proposed project is tied to DOE's mission in science by investigating (1) the interactions of hard x rays with highly ionized plasmas, a major field of research planned for the Linac Coherent Light Source (LCLS) and other x-ray free-electron laser (XFEL) sources, and (2) the multielectronic atomic transitions, which will be an important signature of hollow atoms created by future XFEL sources. In addition to SAO, the proposed project will be of interest to the National Aeronautics and Space Administration (NASA). An important future effort in the DOE Fusion Energy Science Program will be High Energy Density Laboratory Plasma (HEDLP) research. Our proposed work will provide a unique opportunity to investigate the processes in radiation-dominated plasmas, which may be important in controlling HEDLP.

FY 2009 Results and Accomplishments

This past year we have separately brought into operation the new EBIT and microcalorimeter. Both had been commissioned in laboratory tests at the SAO. Our goal in Stage 1 was to operate the EBIT *in situ* at the APS and to obtain data regarding synchrotron beam intensity and the size of the beam and to develop procedures to align the beam with the EBIT plasma. The information gained was extremely useful for planning the follow-on run in Stage 2 with the microcalorimeter. Figure 1 shows a representative 12-hour spectrum for an 18-keV (kilo electron volt) photon beam interacting with the EBIT plasma. At low energies (below 3 keV), the figure shows the L- and M-fluorescence emissions for Kr (krypton) gas produced when 3-keV electrons from the EBIT electron gun ionize the Kr gas to its Ne (neon)-like ionization state. There is also evidence of radiative recombination into higher energy levels of the Kr

ions within the trap. Also shown is the background-free region where we expect to observe Ne-like K fluorescence for Kr (around 14 keV) from photoionization by the 18-keV photon beam. The high-energy photons induced by x-rays came from fluorescence of the Cu (copper) cold shield in the trap, produced by x-rays scattered from its Be (beryllium) window and small air gaps.

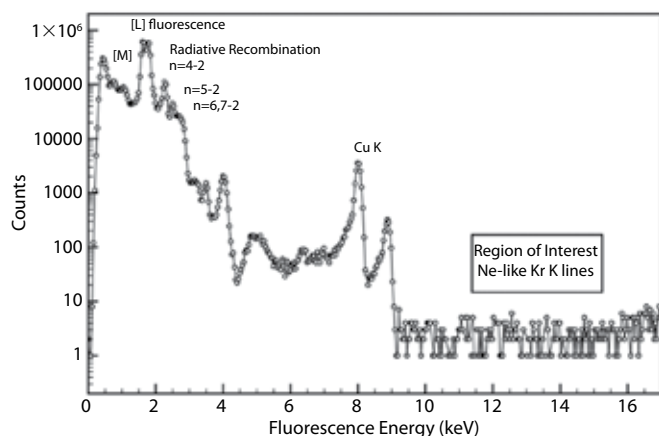


Figure 1. X-ray emission spectrum measured with Si(Li) detector for 18-keV photons interacting with plasma in electron beam ion trap created by 3-keV electrons in krypton gas.

Proposed Work for FY 2010

For the Stage 2 experiment planned for spring 2010, we expect to increase the number of ions by five times with an electron beam current of 150 mA (milliamperes). The microcalorimeter will be used in conjunction with an SAO-patented point-to-point x-ray optic, which will provide a solid angle that is twice that subtended by the Si(Li) (lithium-drifted silicon) detector during this last run. Combined with the enhanced pink beam flux, these and other EBIT improvements will combine to produce a minimum increase of two orders of magnitude in x-ray photoionization yield.

Our principal objective for FY10 is to observe the Fe K α lines (an important physical diagnostic in the x-ray spectra of active galaxies and quasars) that result from photoionization of various charge states of Fe. The major technical hurdle will be interfacing the microcalorimeter with the EBIT and APS beam. We will initially make a conventional collisionally ionized plasma of Fe using the 100-mA electron beam in the EBIT. We conservatively expect an Fe K-emission photon rate of approximately 0.2 counts/s (second). In a 10-hour run, for example, we would obtain over 7,000 counts in the Fe K-emission line alone. We could substantially increase the count rate by cooling the ion cloud and more tightly focusing the photon beam, or by boosting the electron current. The high resolution and broad bandwidth of the microcalorimeter will make it possible to observe the Fe K- and L-fluorescence emissions simultaneously. The data will be time tagged and analyzed as a function of the EBIT trapping period, which can be as long as 2 s. The

resulting spectrum will be extremely rich with new information.

Non-Refereed Publications and Presentations

Kanter, E.P., N. Brickhouse, R. Brissenden, R.W. Dunford, J. Gillaspay, K. Kirby, J. McDonald, D. Schneider, E. Silver, and L. Young, "Laboratory Simulations of Astrophysical Plasmas," presented at 2009 Advanced Photon Source Users Week, Argonne, IL, May 4–6, 2009.

Single Photon Receiver Using Abrikosov Vortices

2009-190-NO

Goran T. Karapetrov, Maria Iavarone, Valentyn Novosad, and Volodymyr G. Yefremenko

Project Description

In the last decade, rapid development and application of thermal superconducting detectors (SDs) or bolometers has provided breakthroughs in many areas of science and industry requiring the detection of single photons. Nevertheless, the major limitation of SD arrays remains the direct proportionality of SD sensitivity to the intrinsic response time, making it difficult to develop fast and highly sensitive receivers, which are needed for many applications, such as observations of far-away pulsars or stand-off explosive detection.

We are developing a sensor element that employs the effect of Abrikosov vortex creep in a type-II superconductor. Radiation impinging on the active area causes penetration of Abrikosov vortices, and the number of flux quanta carries basic information about the radiation. Under continuous influence of radiation, the vortices continuously penetrate from the edges of the superconductor, and their amount needs to be read periodically. This type of detection avoids some of the pitfalls of superconducting bolometers and offers high sensitivity without sacrificing speed. Also, the sensitivity of this detection scheme ideally does not depend on the intensity of the radiation impinging on the superconductor.

Mission Relevance

The project is relevant to DOE's missions in basic science and nuclear security. High-sensitivity, scalable, and high-speed image-forming arrays of direct detectors are required for materials science research (x rays), security screening (THz), remote sensing, medical imaging and surveillance (infrared, THz, and millimeter waves), as well as for ground- and space-based applications, such as in astronomy (x-rays, submillimeter and millimeter waves). Our work is directed toward the design and implementation of novel superior-performance detectors for these applications.

FY 2009 Results and Accomplishments

In the first year of the project, we proved the general concept of detection and manipulation of Abrikosov vortices by fabricating and testing a model device. As a superconducting material, we used 20-nm-thick MoGe films that were deposited on a silicon wafer covered with 500 nm of silicon nitride. In the test structure, the vortices are induced by an applied magnetic field in the leftmost triangular area (Figure 1). By applying a bias current I_{bias} of several microamps, the vortices start experiencing a Lorentz force that initiates their motion along the middle narrow channel. The bias current acts effectively as a “pump” by pushing the vortices from the reservoir in the upper left corner through the narrow superconducting strip and to the collector in the lower right corner (Figure 1). The non-local voltage measured at the terminals V_{nl} is therefore a measure of how many vortices per unit time have been pushed through the narrow strip. This scheme of counting vortices is only feasible if the vortex motion through the superconducting strip is quasi-ballistic (i.e., scattering and pinning effects due to surface roughness are minimized). We have detected a voltage due to ballistic vortex movement as far as 5 μm from the driving current I_{bias} . This is very promising since detection and counting can be spatially separated.

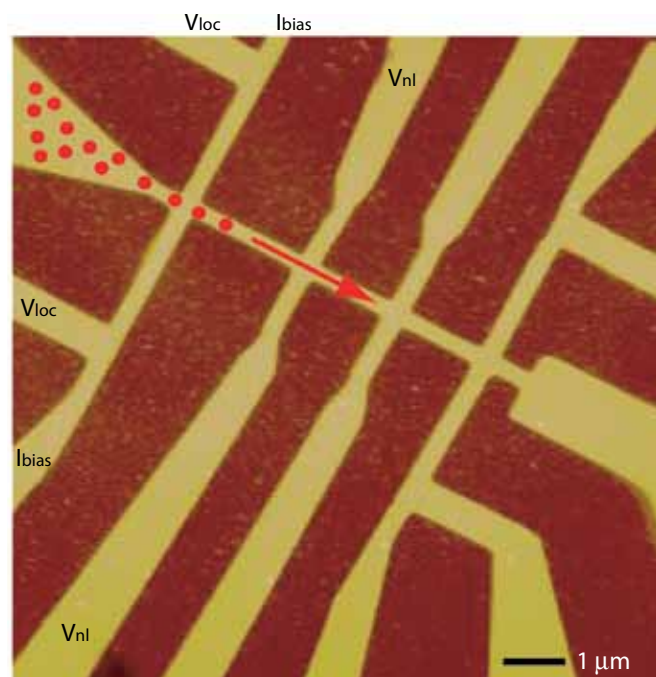


Figure 1. Atomic force microscope image of the 250-nm-wide superconducting MoGe active detector element. The Abrikosov vortices (schematically shown as red dots) are created by the absorbed photons in the superconducting area partially shown in the upper left corner. Application of the bias current I_{bias} exerts a Lorentz force on vortices and pushes them along the superconducting strip (force direction shown by the arrow), inducing a non-local voltage between the terminals V_{nl} . This non-local voltage is proportional to the number of vortices traveling through the superconducting strip in unit of time and thus serves as an effective vortex counter. The V_{nl} is thus proportional to the number of absorbed photons by the superconducting detector.

By introducing changes in the magnetic field, we could evaluate the sensitivity of the device to changes in vortex density. The slope of the curve in Figure 2 shows the effective sensitivity of the device to changes in vortex density at the operating temperature of 4.2 K. Because of the confinement geometry, the vortices form a single vortex chain in the superconducting channel. Any increase in vortex density is accompanied by compression of the chain and results in an increase of the induced voltage. When the distance between the vortices in the chain reaches a critical value of half the width of the channel, there is geometrical phase transition, leading to reordering of the vortex system into a double-chain state. Further compression of the double-chain state leads to a triple-chain state, and so on. We have confirmed this by producing a Ginzburg-Landau simulation for this system with the help of theorists at Antwerp University. Currently, we are examining the observed phase transitions and are correlating them with noise measurements on the same device.

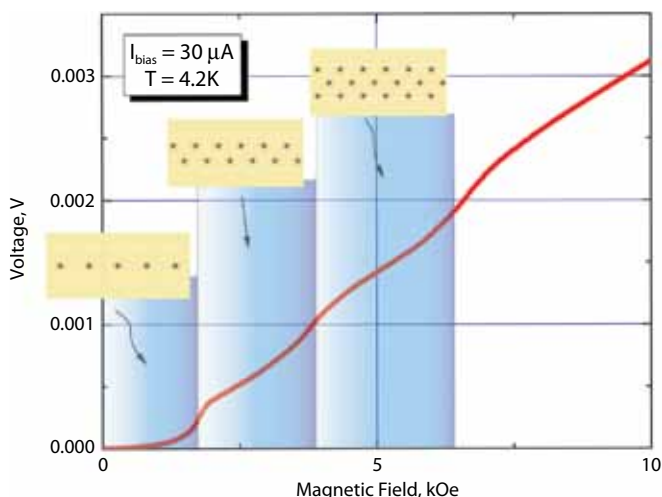


Figure 2. Local voltage V_{loc} as a function of the number of vortices in the channel subject to a constant Lorentz force supplied by the I_{bias} . Reordering of vortices in the channel is shown as a series of kinks. The figures in yellow represent a Ginzburg-Landau simulation of vortex distribution in the linear confinement.

Proposed Work for FY 2010

During the second year, we plan to optimize sensor performance from the standpoint of sensitivity and speed of operation by optimizing geometries and materials. Work will begin on developing a system containing an array of sensors and low-temperature readout electronics. Readout concepts will be implemented and tested. In FY11, we will focus on developing cryogenic readout electronics that could be applied to addressing matrix elements of a 2D sensor array. This development would enable imaging applications in the THz, x-ray, and millimeter wave regimes. Arrays of single-photon receiver sensors will be developed and tested.

Engineering Nanostructures Atom by Atom for Optical Activity and Quantum Coherence

2009-204-N0

Jeffrey R. Guest and Nathan P. Guisinger

Project Description

Bottom-up assembly of nanostructures tailored for specific functions has been one of the most enticing promises of nanoscience and nanotechnology because of its potential to produce novel materials and capabilities. Scanning tunneling microscopy (STM) in an ultrahigh vacuum (UHV) environment ($<10^{-10}$ torr) has led the way not only in characterizing systems at subnanometer length scales, but in assembling novel nanostructures atom-by-atom such as “quantum corrals” and atomic-scale magnets and by controlling molecular adsorption on engineered surfaces. These types of systems could provide chemical and environmental sensing capabilities, ultrahigh-density data storage, or platforms for quantum information processing.

The goal of this project is to develop new methodologies that will bring the power of high-resolution laser spectroscopy and coherent optical control to bear on nanoscale and molecular systems on surfaces that have been characterized or fabricated by UHV STM. We plan to (1) correlate atomic structure with optical function, (2) demonstrate systems with low decoherence rates – or long-lived quantum memories – as platforms for sensing or quantum control, (3) use atom-by-atom fabrication capabilities to engineer structures for novel optical responses, and (4) demonstrate quantum entanglement by quantum structures and lay the groundwork for quantum information processing.

Mission Relevance

The project is relevant to the DOE’s missions in energy and basic science. Combining lasers with scanning probe microscopy has a great potential for scientific applications involving many types of measurements, including investigations of ultrafast and ultraslow phenomena at the core of many fundamental and energy-related areas of research. The work will be well-positioned to contribute to the mission of the Office of Basic Energy Sciences and coincides strongly with the mission of nanoscience centers.

FY 2009 Results and Accomplishments

We made substantial progress in FY09 by (1) fabricating an optically integrated UHV STM, (2) developing a reproducible process for synthesizing high-quality graphene layers, and (3) starting to investigate and characterize molecules that are of optical interest.

We are developing graphene – a monolayer of carbon atoms tightly packed into a nearly ideal two-dimensional hexagonal lattice – as a platform for our studies because our approach requires substrates that are both conducting and transparent. To produce high-quality graphene layers on silicon carbide, we have developed an annealing process that removes deep scratches and results in high-quality surfaces, as shown in Figures 1(a) and 1(b). Following hydrogen cleaning of the silicon carbide surfaces, high-quality films of graphene were successfully grown (by UHV heating) and characterized with our commercial *in situ* UHV STM, as shown in Figure 1(c). Optical transmission measurements were also made, as shown in Figure 1(d).

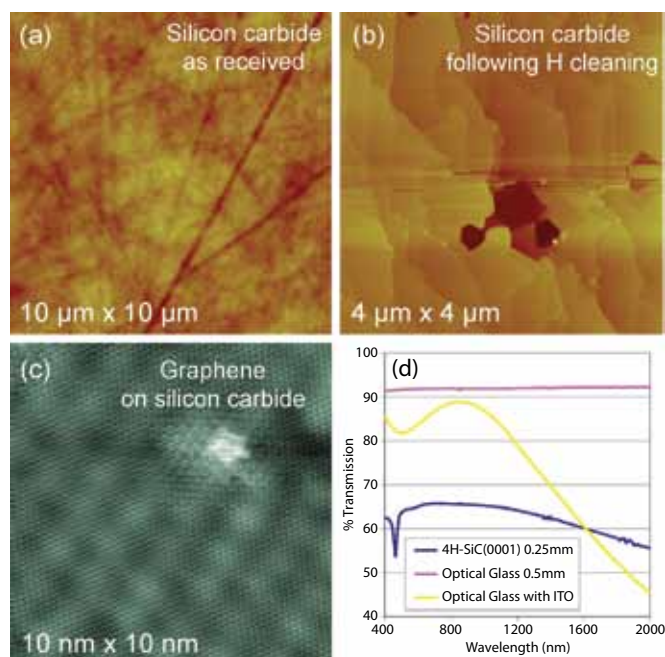


Figure 1. Development of graphene on silicon carbide as a transparent conducting substrate for optical STM experiments. Atomic force microscopy images of silicon carbide (a) as delivered and (b) after hydrogen cleaning; (c) atomic-resolution UHV STM images of graphene prepared on silicon carbide; and (d) comparison of optical transmission of silicon carbide with glass and indium tin oxide on glass.

We have begun to screen and characterize optically active organic molecules. We imaged iron phthalocyanine molecules on metal nanostructures (iron islands on tungsten) concurrently with our graphene development. As seen in Figure 2, we have successfully imaged isolated phthalocyanine molecules and achieved submolecular resolution.

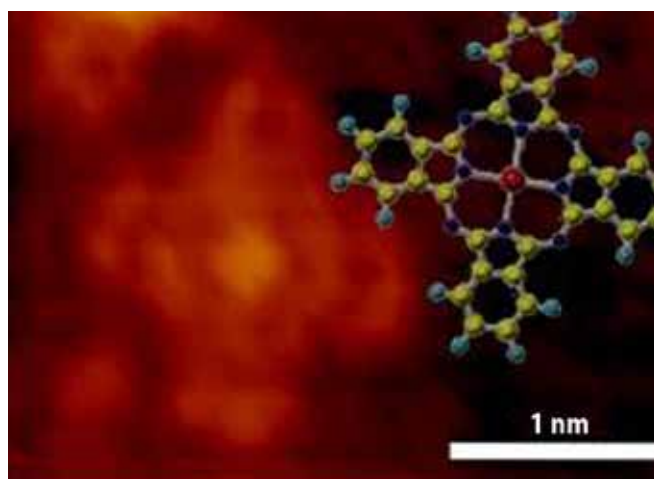


Figure 2. Submolecular-resolution UHV STM image of iron phthalocyanine molecule (with its structure inset).

Proposed Work for FY 2010

In FY10, we will commission the UHV STM instrument with integrated optical access and begin to develop the methodologies for these studies. We will perform our single-molecule STM studies on our transparent conductor (graphene) and perform single-particle laser spectroscopy on molecules that have been characterized by the STM with the goal of correlating structural information with optical function at the atomic level. We will investigate the need for buffer layers or multiple molecular layers in order to preserve optical activity near the graphene surface. Ultimately, we will work toward demonstrating optically active single particles at the surface, which can be characterized by long enough decoherence times that they would be useful for sensing or quantum information applications.

Physics of the Superinsulating State

2009-209-N0

Valerii Vinokour and Andreas Glatz

Project Description

The research project investigates the physical properties of a new state of matter: the superinsulator. Since the superinsulating state is a low-temperature Berezinskii-Kosterlitz-Thouless (BKT) state in a charged system, we plan to theoretically investigate BKT transport in depth, taking into account quantum fluctuations and the effects of disorder and the geometry of the film. We will explore different realizations of the superinsulating system (superconductor-normal metal-superconductor [SNS] structures and artificial Josephson-junction arrays) and investigate nonlinear transport in these systems, focusing on the effects of conductivity and current jumps at the voltage

depinning threshold. Our results will help outline novel ways to design artificial superinsulating materials that will work over a wide range of temperatures and magnetic fields.

Mission Relevance

The proposed project is tied to DOE's mission in science. If successful, the project will lead to technological breakthroughs comparable to those resulting from the discovery of superconductivity. Given the scale of the research and prospective scientific developments (e.g., artificial manufacturing of superinsulating materials with the predefined properties and enhanced critical temperatures/magnetic field/voltage threshold; emerging materials with novel electromagnetic properties), we expect considerable interest in the proposed project, particularly from DOE and other agencies pursuing the creation of new materials for new-generation technology, such as the U.S. Department of Defense's (DOD's) Defense Advanced Research Projects Agency (DARPA).

FY 2009 Results and Accomplishments

During the first year, we developed a general method allowing us to quantitatively describe electronic transport behavior in large SNS arrays. We studied the formation of a regular lattice of superconducting islands on a film/substrate hybrid structure using the Ginzburg-Landau approach (Figure 1). This finding justifies our model, which treats the highly disordered film in the vicinity of the superconductor-insulator transition as a large array of superconducting islands coupled by weak links (Josephson-junction arrays). We developed a numerical simulation and started to conduct large-scale computational analysis of the formation of the lattice of superconducting islands in disordered films and explored the phase diagram in the temperature and elastic coupling parameter space (Figure 2). On the basis of the results, we will extend simulations to explore charge transport in this lattice.

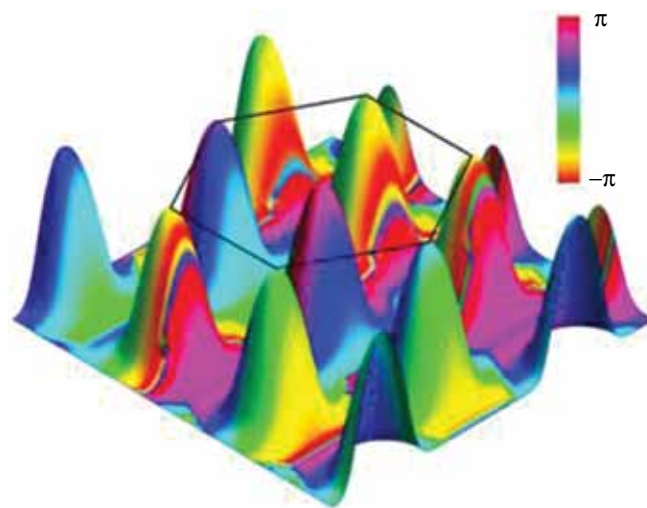


Figure 1. Superconducting islands due to the instability of the homogeneous superconducting state caused by elastic forces. Height indicates the amplitude of the superconducting order parameter, while color indicates phase.

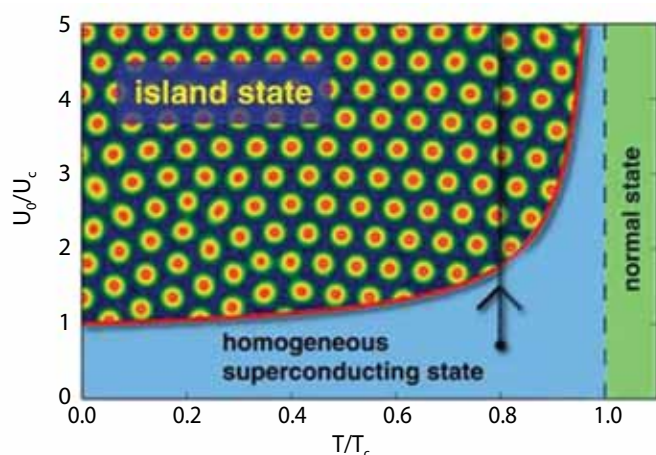


Figure 2. Phases in the elastic coupling constant, U_0 , plane for a thin film. Above T_c , the film is in the normal state, whereas below that temperature, the film can be either a homogeneous superconductor or a textured superconductor consisting of insulated islands.

Using a novel approach, we wrote recurrent relations for the current and formulated correct boundary conditions at the interfaces between the normal metal and superconductors (a graphic representation of such conditions for an SNSNS (S = superconducting layer; N = normal layer) system is presented in Figure 3). The derived equations will form the basis for our future study of electronic transport in the vicinity of the superconductor-insulator transition and in systems of regular superconducting islands. Our technique also allowed us to initiate a separate large-scale project aimed at the extensive study of transport phenomena in the resistive state of large SNS arrays, where a new macroscopic quantum effect, the resonant super-transmission of electron charge, was discovered.

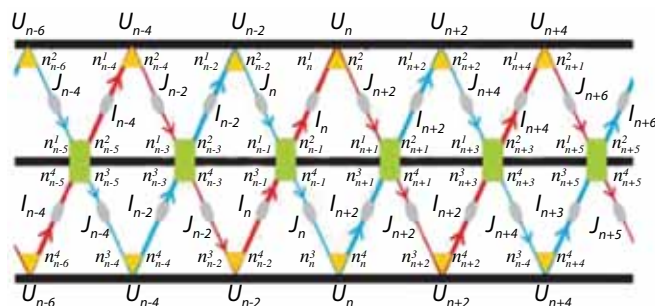


Figure 3. An effective circuit for calculating the current-voltage characteristics of a large SNS junction array at large voltages.

The theoretical part of the project is being carried out in close cooperation with experimental groups studying the superinsulating state. The experimental research related to our project confirmed the predicted hyperactivated behavior of resistivity at low temperatures, below the supposed insulator-superinsulator phase transition.

Proposed Work for FY 2010

We will develop theories for nonlinear charge transport in the vicinity of a superconductor-to-insulator transition and for transport in the low-temperature BKT phase, taking into account quantum and thermal fluctuations and the effects of disorder. We will also investigate the charge depinning process under the combined action of dc and ac fields, and we will simulate charge transport in systems exhibiting regular structures of superconducting islands, both in the weak and strong driving regimes. The latter effort will require extensive computational resources for both massively parallel simulations and the solution of huge linear equation systems.

Refereed Publications

Baturina, T.I., A. Yu Mironov, V.M. Vinokur, N.M. Chtchelkatchev, A. Glatz, D.A. Nasimov, and A.V. Latyshev, "Resonant Andreev Transmission in Two-Dimensional Arrays of SNS Junctions," *Physica C* (2009), doi: 10.1016/j.physc.2009.11.107.

Chtchelkatchev, N.M., T.I. Baturina, A. Glatz, and V.M. Vinokur, "Synchronized Andreev Transmission in SNS Junction Arrays," submitted to *Physical Review Letters* (2009).

Glatz, A., I. Aranson, V.M. Vinokur, N.M. Chtchelkatchev, and T.I. Baturina, "Emergence of Superconducting Textures in Two Dimensions," submitted to *Nature* (2009).

Non-Refereed Publications and Presentations

Glatz, A., "Interplay of Elasticity and Superconductivity in Thin Films: Regular Electronic Textures," presented at the 12th International Workshop on Vortex Matter in Superconductors, Lake Yamanaka, Japan, September 12–16, 2009.

Glatz, A., "Emerging Regular Superconducting Patterns in Thin Films," presented at the 5th International Workshop on Nanomagnetism and Superconductivity, Coma-Ruga, Spain, July 5–9, 2009.

Vinokur, V., "Nonequilibrium Mesoscopic Transport and Superinsulation," presented at the 5th International Workshop on Nanomagnetism and Superconductivity, Coma-Ruga, Spain, July 5–9, 2009.

Development of a Novel Instrument for Argon-39 Analysis

2009-212-N0

Peter Mueller, Zheng-Tian Lu, and William D. Williams

Project Description

We explore the use of atom trap trace analysis (ATTA) for ultra-sensitive detection of the argon radioisotope ^{39}Ar . This isotope has a radioactive half-life of 270 years and occurs naturally in the atmosphere with an isotopic abundance at the parts-per-quadrillion (10^{-15}) level. ATTA is an atom-counting method based on laser cooling and trapping and has been developed by our group at Argonne. This method has so far been capable of analyzing trace isotopes at the parts-per-trillion (10^{-12}) level and has been used to measure the abundance of the krypton radioisotopes ^{81}Kr and ^{85}Kr in environmental samples. Recent progress in the development of our ATTA setup suggests that its sensitivity level can be further improved by three orders of magnitude. This project aims to establish these sensitivity levels for atom trapping of argon and to enable new applications of ^{39}Ar analysis.

Mission Relevance

The project is tied to DOE's missions in science and national security. The proposed instrument for ^{39}Ar analysis would open new applications within geochemistry, cosmochemistry, nuclear/particle physics, and homeland security. In addition to DOE, the National Science Foundation (NSF) will likely be interested in the research; for example, efforts toward ^{39}Ar analysis of water samples are of potential interest to NSF's Division of Earth Sciences. The search for a source of "clean argon" (i.e., argon free of radioactive ^{39}Ar) would be relevant to next-generation liquid-argon dark matter detectors, which are supported by DOE, Office of Nuclear Physics and Office of High Energy Physics.

FY 2009 Results and Accomplishments

In FY09, we achieved two major milestones: (1) we successfully performed high-resolution laser spectroscopy of ^{39}Ar to accurately measure the atomic transition parameters required for laser cooling and trapping (i.e., isotope shift and hyperfine structure) and (2) we demonstrated laser cooling and trapping, as well as single-atom detection of a stable argon isotope with adequate efficiency using an ATTA setup.

The laser spectroscopy effort included production and purification of an enriched ^{39}Ar sample generated through neu-

tron irradiation of potassium fluoride at the Oregon State University Radiation Center research reactor. The spectroscopy work was performed with a dedicated setup at Argonne using a high-resolution technique based on saturated absorption measurements of a laser beam passing through the enriched ^{39}Ar gas. Isotope shift and hyperfine structure of the atomic transition of interest were successfully measured with the required precision. Publication of the results is in preparation.

This project was strongly motivated by efficiency improvements achieved in our existing krypton ATTA system while implementing considerable atomic beamline and laser upgrades. Previously, these improvements had only been demonstrated for the individual components separately. During FY09, we assembled, tested, and optimized the complete system and achieved an overall improvement in krypton trapping efficiency of a factor of ~ 100 over the previous best result. This is a significant breakthrough and is extremely encouraging for the goal of detecting ^{39}Ar . In addition, we have modified the krypton trap system so that it is also able to trap argon atoms. Using this modified system, we have trapped stable argon atoms with an efficiency high enough to achieve ^{39}Ar capture rates of about 1 atom per hour.

We would like to acknowledge Kenneth Rudinger from the University of Chicago for his help in setting up and optimizing the ^{39}Ar laser spectroscopy apparatus and Reika Yokochi from the University of Illinois at Chicago for her support in realizing the gas extraction and purification system to generate the enriched ^{39}Ar sample.

Proposed Work for FY 2010

During FY10, we plan to demonstrate a single-atom detection capability of ^{39}Ar in an atmospheric sample with a trapping rate of about 1 ^{39}Ar atom per hour. Additionally, we plan to develop the ability to perform quantitative measurements of ^{39}Ar abundances with relative accuracies of $\sim 20\%$. Finally, we aim to demonstrate the applicability of our novel technique by analyzing a small number of samples relevant for climate research and for the search for "clean argon."

Refereed Publications

Rudinger, K., Z.-T. Lu, and P. Mueller, "The Role of Carrier Gases in the Production of Metastable Argon Atoms in a RF Discharge," *Rev. Sci. Instrum.* **80** (2009), 036105.



EXASCALE COMPUTING TECHNOLOGY

Membrane Analysis and Simulation System (MASS)

2007-110-R2

Ron S. Faibish, William D. Pointer, Benoit Roux, Adrian M. Tentner, Justin W. Thomas, Yaroslav D. Bodnar, Timothy J. Tautges, Peter Zapol, and YuPo J. Lin

Project Description

The MASS project aims to develop a simulation tool for the prediction of membrane properties and performance. The simulation tool will be sufficiently robust to, *a priori*, describe the fundamental membrane properties and their relationship to membrane processes. The tool will integrate interactions ranging from the molecular level through their mesoscopic and macroscopic effects. It will guide the prediction of membrane properties and performance and ultimately will serve as a valuable resource for predicting the performance and economics of a wide range of separation processes. The tool will combine computational fluid dynamics (CFD), the lattice Boltzmann method (LBM), molecular dynamics (MD), user guidance feedback (UGF) based on artificial intelligence (“thinking model”), and system analysis (Figure 1). The proposed “full picture” modeling tool will provide integrated macro- and micro-scale predictions to guide selection of the proper membrane process, materials, and overall system for the desired separation. The MASS may be applied to (1) process optimization by using existing characterized membranes; (2) design of new membranes based upon macroscopic empirical characterization of membrane materials; and (3) prediction of the behavior of membranes from atomic-scale principles.

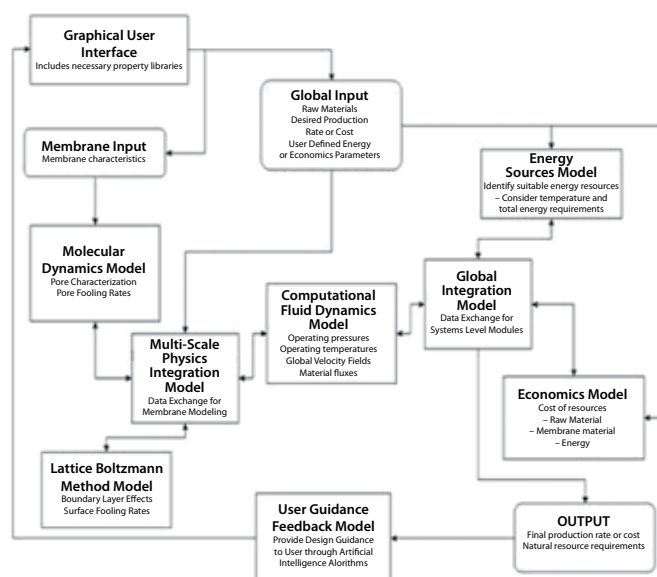


Figure 1. Flow chart showing interaction among primary modules of the comprehensive system-based membrane performance modeling tool.

Mission Relevance

This project is tied to DOE’s mission in energy. MASS will overcome the need for extensive and often costly screening and experimentation. It will benefit researchers in making step changes in membrane and separation processes by providing *in silico* selection and pathways to optimization of the most suitable membrane system (geometry, materials, and properties). Industrial vendors and end-use customers will benefit from a more rapid and efficient membrane development process. DOE has a strong interest in advancing membrane technology in the Energy Efficiency and Renewable Energy (EERE) Industrial Technologies Program (ITP), Office of Biomass Program (OBP), and Office of Fossil Energy (FE) Program.

FY 2009 Results and Accomplishments

Significant progress has been accomplished on all project fronts, particularly on CFD, LBM, and MD model development. The initial development of the overall modeling tool has been tested with a reverse osmosis membrane for water desalination – one of the most common applications of membrane technology.

MD: We created a new method to build and model a polymerized reverse osmosis membrane. Water permeability and ion rejection can now be calculated from a large MD simulation of the model membrane, which has shown excellent agreement with experimental results (same order of magnitude). Both MD and density functional theory calculations were run to elucidate the first steps in the polymerization process at the liquid-liquid interface. In addition, we created a new method to compute the osmotic pressure from the MD model so that one can validate and refine the potential function associated with it. This method was used to test and optimize the force field parameters to model NaCl and KCl aqueous salt solution. Tests showed that the osmotic pressure is reproduced accurately at concentrations up to 5M. To our best knowledge, the proposed heuristic-based MD method for building all-atom structures of polymeric thin-film materials is the most realistic atomistic model of the separation layer in reverse osmosis membranes reported in the literature. This method attempts to capture the inhomogeneous reaction kinetics that gives rise to the complex chemical structure and morphology of these membranes.

LBM/CFD: We expanded the original LB-FLOW code to allow the simulation of one solvent field and two solute fields. The ability to account for the presence of two solute fields allows a realistic representation of reverse osmosis water purification, where Na and Cl ions are present. The code structure was modified to allow the addition of solute fields with relatively little effort if necessary for future research projects. We also developed and implemented new models that mechanistically describe the interactions between the solute and solvent molecules. The diffusion properties of new LBM solute-

solvent interaction models were validated in LBM simulations describing solute diffusion in a finite one-dimensional domain. The results of these LBM simulations showed good agreement with the corresponding theoretical solution (see Figure 2).

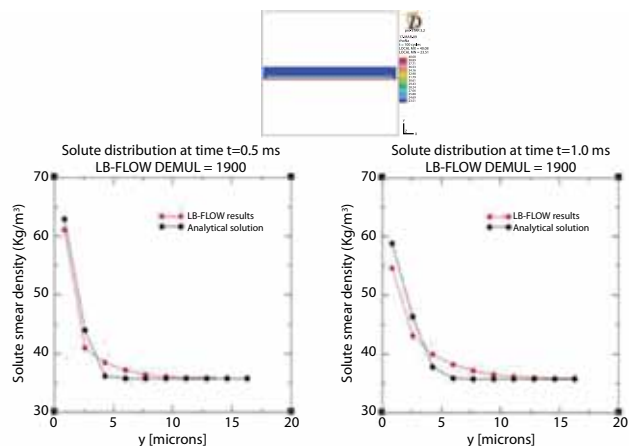


Figure 2. LB-FLOW simulation results of a solute layer (NaCl) diffusing in a stationary fluid (water), compared with the corresponding analytical solution.

We developed a new LBM methodology that expands the velocity domain of LBM simulations to supersonic velocities, as high as 2.4 mach, while the conventional LBM simulations are limited to approximately 0.1 mach. This capability is important in the simulation of solvent-solute systems, where the sonic velocities of the solvent and solute are widely different. In the LB-FLOW code, we implemented a capability to track the electrical charges associated with ionic solute species. Figure 3 illustrates the formation of a stratified charge structure from an initially uniform solute layer near the membrane due to the different diffusion properties of the ionic species.

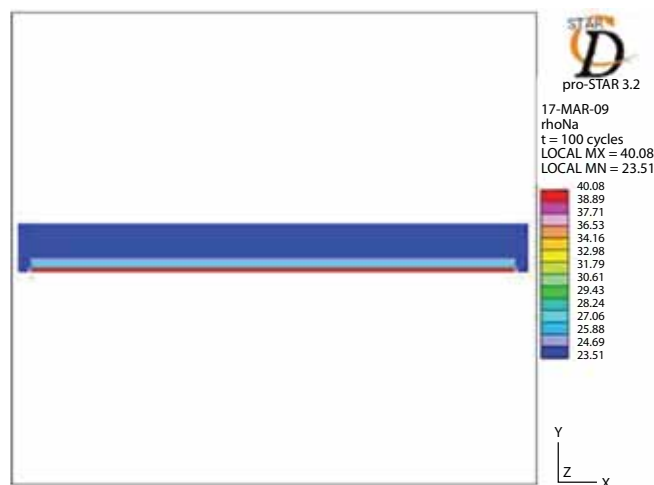


Figure 3. A stratified structure of the initially uniform solute layer that evolves due to the different diffusion characteristics of Na^+ and Cl^- ions.

Also developed and implemented in the LB-FLOW code were models of the electro-kinetic forces that control the interactions among the electrically charged ionic species present in many solvent-solute systems, including reverse osmosis desalination systems.

Finally, we developed and implemented a methodology that couples LBM (LB-FLOW code) meso-scale calculations with the CFD (STAR-CD code) macro-scale calculations to simulate the solvent-solute flow in complex membrane geometries. We also developed a procedure for the use of micro-scale MD results describing the solvent-solute flow through the membrane in the LB-FLOW calculations.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Harder, E., D.E. Walters, Y.D. Bodnar, R.S. Faibish, and B. Roux, "Molecular Dynamics Study of a Polymeric Reverse Osmosis Membrane," *Journal of Physical Chemistry B* **113** (30) (2009), 10177-82.

Luo, Y., and B. Roux, "Simulation of Osmotic Pressure in Concentrated Aqueous Salt Solutions," *Journal of Physical Chemistry Letters* **1** (2010), 183-189.

Real-Time Analysis of Advanced Photon Source Data

2007-165-R2

Ian T. Foster, Francesco De Carlo, Rajkumar Kettimuthu, and Michael E. Papka

Project Description

Time-resolved micro-tomography, x-ray photon correlation spectroscopy, and three-dimensional micro-diffraction can all produce three (or more) dimensional data at rates exceeding 100 megabytes per second (MB/s). However, the utility of these techniques is severely limited by the hours it takes to manually transfer and then analyze the resulting large datasets on the high-performance computing (HPC) cluster. In many situations, the user requires quasi-instant feedback, so that the result of one experiment can guide selection of the next. (Such feedback is crucial in studies of crack propagation or in-situ aluminum corrosion, for example.) In the absence of such quasi-real-time analysis, the utility of these new techniques is greatly reduced.

Our project was created to address this problem by designing, developing, and demonstrating a real-time analysis capability for Advanced Photon Source (APS) beamlines. This new capability will enable beamline scientists to define and execute workflows that automatically take experimental data, transfer it to computational systems, and return the results to the beamline for decision making. The ability to perform real-time analysis (i.e., reliable high-performance data transfers and remote processing driven by on-demand workflows) is a critical requirement for users of large-scale scientific and computing facilities. Such a capability can be compared to the distributed data processing architecture of the LHC (Large Hadron Collider), although the capability being demonstrated under this project is general and can be used by experimental scientists of many kinds; it is not limited to one type of experimental apparatus or one area of research.

Mission Relevance

This project is tied to DOE's missions in energy, environment, national security, and science. The results of this project may also be of interest to the National Institutes of Health, the National Science Foundation, and the Department of Homeland Security. The results of this project will support research and development in disciplines with real-time requirements, such as threat management, climatology, high-energy physics, and chemistry. For example, real-time and on-demand calculations are important for threat management in national security applications, as when using sensor networks and simulation algorithms to analyze the dispersion of airborne biological agents. In chemistry, scientists may determine new thermochemical reaction values through a real-time experiment, while in climatology the path of a tornado needs to be calculated in real time.

FY 2009 Results and Accomplishments

The experimental controls and the workflow tools have been integrated with the data movement capabilities. Integration enables data to automatically flow directly from the experiment to computational resources for analysis as part of an end-to-end experimental workflow. Being able to work flow the data movement is a major capability for the APS.

We ported the Globus GridFTP server to cygwin, a Linux-like environment for windows, and deployed it on the beamline data-acquisition machines for tomography and x-ray photon correlation spectroscopy. We developed a high-performance data transfer library based on GridFTP, a data scheduler, and a graphical user interface (GUI) that allows users to manage their own data. This library incorporates automatic tuning mechanisms to select at runtime the number of concurrent threads to be used for transfers and restart mechanisms capable of dealing with client, network, and server failures.

This data transfer library has been integrated into the TomoScript program used to automate tomography experiments at the APS. TomoScript can acquire data — while unattended — for a group of samples loaded into an automated sample changer and then also can load samples into the x-ray beam and control all of the equipment necessary to obtain the approximately 12 gigabytes (GB) of data generated per sample. In one 24 hour period, the system is capable of running 96 samples and acquiring 1.1 terabytes (TB) of data. These data need to be moved to an on-site computational cluster for processing before users can determine whether critical acquisition parameters are correct for obtaining high-quality data. TomoScript thus relieves the user of the arduous tasks of finding the right data set out of hundreds to move and of monitoring the data movement for proper completion. Transfer failures are noted, and automatic recovery is attempted. If multiple transfer failures occur, the user is alerted so appropriate action can be taken.

This GridFTP-based data management system allows the data to be moved from the beamline data-acquisition machine to the HPC cluster at a rate that is five times faster than the Windows-based native protocol that was used before.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Liu, W., R. Kettimuthu, B. Tieman, R. Madduri, B. Li, and I. Foster, "GridFTP GUI: An Easy and Efficient Way to Transfer Data in Grid," pp. 57–66 in *Proceedings of the 3rd International ICST Conference on Networks for Grid Applications*, Athens, Greece, September 8–9, 2009, Springer.

Developing Analysis Services for Petascale Computing

2007-166-R2

Ian T. Foster, Mark Hereld, Michael E. Papka, and Michael J. Wilde

Project Description

This project enables flexible petascale data analysis by using parallel scripting with scalable task and data management. It applies common middleware to enable scalable analysis across leading petascale systems and evaluates its effectiveness on important applications.

Mission Relevance

This project will benefit DOE's mission in science, particularly DOE's Office of Advanced Scientific Computing. The National Science Foundation, National Institutes of Health, and Defense Advanced Research Projects Agency have a vested interest in petascale computing, and these organizations will be developing research programs applicable to this project. Enabling flexible workflows for petascale analysis increases scientific productivity and cooperation and leverages the investment in leadership computing facilities.

FY 2009 Results and Accomplishments

We ran scaling experiments on visualization algorithms to compare performance on Blue Gene/P (BG/P) architecture with performance on a graphics processing unit (GPU) accelerated cluster. The tests included codes based on the visualization toolkit (vtk) system in order to study the behavior of widely used and widely deployed algorithms. We also ran extensive comparative tests on v13, a high-performance volume rendering code we have developed to take optimal advantage of GPU hardware not exploited by general-purpose graphics libraries (see Figure 1). This work will benefit the future design of hardware and software visualization and analysis systems.

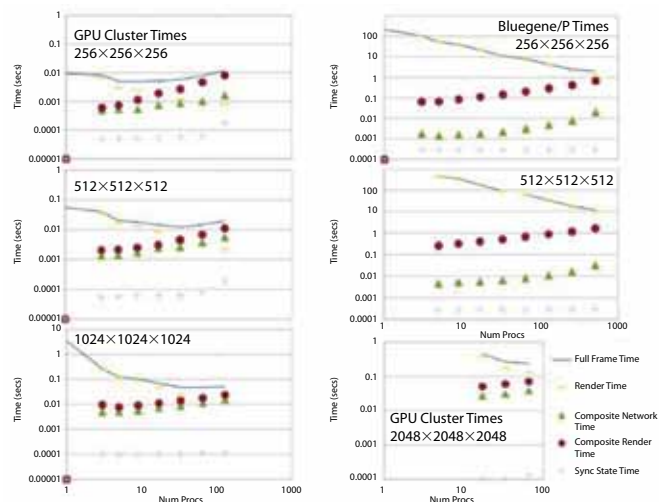


Figure 1. Performance breakdown of optimized volume renderer running on Blue Gene/P and on a large GPU accelerated cluster.

We developed a web portal that allows scientists to browse science scripts without needing programming or command-line access; users of this tool can also select input datasets and parameters, initiate and monitor script execution, and peruse and fetch results. With this portal, users can execute highly parallel application scripts using both Swift and ad-hoc procedures. The tool also enables users to select slices of data for further analysis by using data analysis and plotting tools. The tool is being used in several science projects.

We implemented collective input/output (I/O) and tested it with two structure prediction codes on Argonne's Blue Gene/P. These tests use the broadcast of common datasets and code, local disk for I/O datasets, and copy-back of local output datasets to shared storage using datasets spread across directory trees to significantly reduce or eliminate write contention on the General Parallel File System (GPFS) shared filesystem. We also implemented a broadcast primitive in ZeptoOS for the BG/P. This tool was tested on a proteomics application involving analysis of mass spectrometry datasets for protein post-translational modifications.

We integrated a dataset transmission capability into the "Coaster" resource provisioner and tested it in an application examining neuroscience structural equation modeling. More than 900,000 science jobs have been run successfully on the TeraGrid's Ranger petascale computer with this new capability.

One of our objectives is to manage datasets efficiently on node storage at sizes greater than a single node permits. We applied our analysis framework to large-scale BLAST (basic local alignment search tool) runs on the BG/P. Initial results indicate that our loosely coupled approach is competitive with the more complex mpiBLAST application, which breaks large BLAST problems into smaller ones and then merges statistical results from the decomposed problems.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Hereld, M., R. Hudson, J. Norris, M.E. Papka, and T.D. Uram, "Enabling Scientific Teamwork," *Journal of Physics: Conf. Series* **180**(1) (July 2009), 012085.

Wilde, M., I. Foster, K. Iskra, P. Beckman, Z. Zhang, A. Espinosa, M. Hategan, B. Clifford, and I. Raicu, "Parallel Scripting for Applications at the Petascale and Beyond," *IEEE Computer* **42**(11) (November 2009), 50–60.

Wilde, M., I. Raicu, A. Espinosa, Z. Zhang, B. Clifford, M. Hategan, S. Kenny, K. Iskra, P. Beckman, and I. Foster, "Extreme-Scale Scripting: Opportunities for Large Task-Parallel Applications on Petascale Computers," *Journal of Physics Conference Series* **180**(1) (July 2009), 012046.

Zhang, Z., A. Espinosa, K. Iskra, I. Raicu, I. Foster, and M. Wilde, "Design and Evaluation of a Collective IO Model for Loosely Coupled Petascale Programming," in *Proceedings of the Workshop on Many-Task Computing on Grids and Supercomputers*, Portland, OR, November 16, ACM Press, 2009, pp. 1–10.

Non-Refereed Publications and Presentations

Wilde, M., “Parallel Scripting for Science Applications at the Petascale and Beyond,” presented at the Petascale Active Data Store – Fall Seminar Series, University of Chicago Computation Institute, October 22, 2009.

Wozniak, J.M., and M. Wilde, “Case Studies in Storage Access by Loosely Coupled Petascale Applications,” presented at the 4th Petascale Data Storage Workshop, Portland, OR, November 15, 2009.

Exascale Agent-Based Modeling System

2008-142-R1

Michael North, Charles M. Macal, Michael E. Papka, David L. Sallach, and Rick L. Stevens

Project Description

Agent-based modeling is an emerging computational simulation approach that allows the derivation of system-level consequences from knowledge of individual-level choices. The successful application of this technology to a wide variety of domains demonstrates its potential to advance science, engineering, and policy analysis. However, realizing the full potential of agent-based modeling to find breakthrough results in research areas relevant to DOE’s missions requires far greater computing capability than is available through current agent-based modeling tools. This project is developing a next-generation agent-based modeling system explicitly focusing on exascale computing platforms. The system is leveraging existing world-class Argonne capabilities, such as the Repast Symphony agent-based modeling toolkit and its distributed computing expertise, to target multi-core chips and aims to scale to 10^6 to 10^7 threads. The design and implementation paths of the exascale agent-based modeling system are being determined by using a focused series of stepwise experiments. Each experiment is driven in turn by the chosen pilot application areas, namely microbial biodiversity and cyber security, as well as requirements input for modeling the social aspects of climate science.

Mission Relevance

This project supports DOE’s energy security, national security, environmental, and scientific discovery and innovation missions. The project supports DOE’s energy security mission by developing a platform for testing the performance, feasibility, and utility of potential new energy technologies; studying the possible benefits and impacts of energy policies; and investigating the strengths and weaknesses of existing and proposed

energy supply chains. The project supports DOE’s national security mission by developing a platform for studying national security issues and policies, such as those embodied in the planned cyber-security model of the DOE’s laboratory computing infrastructure. The project supports DOE’s environmental mission by developing a platform for testing environmental technologies and policies. User requirements input from experts on the social aspects of climate science helps to ensure the success of this thrust. The project supports DOE’s scientific discovery and innovation mission by developing a platform for scientific investigation into many areas of basic science, as exemplified by the new microbial biodiversity modeling effort.

FY 2009 Results and Accomplishments

FY09 was the second year of the project. During FY08, we completed user requirements analysis, implementation platform testing and selection, and initial system design and implementation. During FY09, we completed the initial version of the core exascale agent-based modeling platform, completed a supporting Eclipse integrated development environment (IDE) configuration, and initiated design planning for the two pilot application areas (cyber security and microbial biodiversity).

Features of the core exascale agent-based modeling platform include fundamental data structures for simulation, such as dynamic lists, linked lists, hash maps, priority queues, and graphs; an agent identification structure to uniquely track agents; a distributed discrete event priority queue scheduler; distributed discrete grid spaces; distributed network spaces; and aggregate and nonaggregate (i.e., per-process) data collection and logging. During FY09, platform implementation was also upgraded from C to C++. A fundamental ecological test simulation was implemented by using the system components. The system was tested on Blue Gene/P Surveyor, and benchmarked data were generated and documented in a report titled *Exascale Repast Symphony Benchmark Results Report*. Excellent scalability was observed. Most of the software components have been individually documented, a tutorial was written, and the overall implementation was documented in a working report titled *Exascale Repast Symphony C Implementation Report*. The Eclipse IDE configuration was also documented in a working report titled *Exascale Repast Symphony Development with Eclipse*.

Proposed Work for FY 2010

The goals for the project's third and final year, FY10, are to complete the exascale agent-based modeling system's feature set, develop test demonstration models for microbial biodiversity and cyber security, prepare the platform for public release (including extensive verification and validation), and complete refereed publications documenting the research progress.

Refereed Publications

Macal, C., M. North, G. Pieper, and C. Dragan, "Agent-Based Modeling and Simulation for Exascale Computing," *SciDAC Review*, Issue 8, Summer 2008, 34–41.

Exascale Hardware Designs

2008-154-R1

Peter H. Beckman, Raymond A. Bair, Narayan Desai, Ewing L. Lusk, Robert B. Ross, Rick L. Stevens, and Rajeev Thakur

Project Description

Exascale systems will likely require between 10 million and 100 million processing elements and will pose challenges in several key areas, such as processor architecture, power, and fault tolerance. This project provides the hardware infrastructure for research in these and other areas.

Mission Relevance

DOE is embarking on an initiative to develop exascale computing resources within the next 10 years. Exascale computing will fundamentally change our understanding of the world, unlocking secrets in fields that have traditionally used high-end computing and in areas just beginning to leverage the power of computation. Exascale computer architectures will be a radical departure from existing systems; they will involve a very large number of processors that are slower and have large core counts, and there will be a much greater imbalance between processing capabilities and the memory and storage subsystems. Exascale systems will require the use of exotic, power-efficient components to be practical in current facilities — even state-of-the-art facilities.

FY 2009 Results and Accomplishments

The primary focus of this project is the procurement and exploratory operation of a system that has similar properties to those expected of exascale systems. The SiCortex system is a parallel system with a large number of low-power Central Processing Unit (CPU) cores. We made this system, called "Full Disclosure," available to research groups in high-performance computing system software and applications as a part of this project, in order to assess its functionality for a variety of

applications and needs and thereby propose improvements for future systems. Several of these groups are Argonne-based research projects and others are based at other sites engaged in high-performance computing (HPC) research. We describe several of these usage-testing projects below.

The MPICH (portable version of the Message Passing Interface) team at Argonne has used Full Disclosure to develop new collective operation algorithms and implementations well suited to large-scale parallel systems. It also developed a new set of collective operations that are "topology-aware"; they will be critical on upcoming large-scale systems in which hierarchy will be increasingly prominent. The Hydra process manager was developed; it provides a scalable start-up mechanism for parallel processes on large machines.

In addition, the UPC (Unified Parallel C) group from Lawrence Berkeley National Laboratory ported the UPC runtime system to the SiCortex machine and developed low-level drivers for the unique network fabric.

Alternative programming models were also explored on Full Disclosure. The ADLB (Active Directory Load Balancer) system is a dynamic library used to develop scalable applications. Its initial target was the QMC (Quick Media Converter) code developed as a part of the Universal Nuclear Energy Density Functional (UNEDF) project. ADLB has been developed primarily on the SiCortex system, but the QMC application was successfully scaled to 65,536 cores on the Intrepid system.

The PVFS (Parallel Virtual File System) group at Argonne ported I/O code to the SiCortex architecture. Some work on I/O forwarding was also done; it provided insight into the adaptations needed for software on systems with many relatively slow cores. The machine enabled the development of scalable parallel compositing algorithms for data visualization.

Full Disclosure is also a popular setting for code development and tuning in preparation for execution on the Intrepid system at the Argonne Leadership Computing Facility. The UNEDF and Nek5000 projects — both INCITE projects based at Argonne — used the SiCortex system to analyze and tune the performance of applications.

Our work with SiCortex resulted in direct support for the SiCortex fabric in the Argonne parallel I/O stack, which includes PVFS and I/O forwarding software. SiCortex recently shifted to providing its customers with the latest MPICH2 version from Argonne.

Another effort with IBM centered on developing Blue Gene(BG)/Q. This system has many characteristics in common with the SiCortex machine. The process was informed by our experiences operating the SiCortex 5832.

Proposed Work for FY 2010

A major goal is to develop the tools and techniques to prepare a thorough point design of an exascale system. Three E3SGS (Exascale for Energy, Ecological Sustainability and Global Security) reports state that an exascale system is probably feasible, but there are many questions, especially about the choice of processor architecture and the whole-system design. With regard to architecture, a key requirement is finding an approach that can provide sustained performance at low power. (An exascale system requires, at most, 100 gigaflops/watt to keep total system power under a few tens of megawatts.) To address this issue, we partnered with SiCortex to evaluate new technologies. With regard to whole-system design (including the integration of interconnect, processors, and I/O), we plan to operate a test bed that will let us develop and test different approaches for benchmarking, managing, and operating a highly scalable system. This system will be invaluable in supporting the development of an open-source scalable software stack, which is also needed for exascale computing.

Multicore and General-Purpose Graphics Processing Unit (GPGPU) Investigations:

A recent change in central processing unit (CPU) designs has been the move to multicore. BG/P will have four cores per socket; the SiCortex platform has six cores per socket. The performance of individual processors is no longer doubling every 18–24 months; instead, the number of processors is doubling, or other on-chip features are being added. Some suggest this trend will continue until we have hundreds of cores on a die, but our vendors point in a different direction: heterogeneous cores. What should a heterogeneous system look like? What is the best way to integrate one or more GPGPUs with the main processor? In order to scale, multiple GPGPUs may be necessary. How will these components communicate in a high-performance manner? Equally important is the power use of the heterogeneous systems. Because of the increased computational capability of the GPGPUs, more power is consumed. Traditional GPUs are intended for single, stand-alone machines. Power use of large systems must be addressed.

SiCortex Whole-System Design Investigation: SiCortex, Inc., is a small company that developed a power- and space-efficient, parallel computing system. We propose to use it to develop a suite of tools, methods, and experiments to evaluate and construct designs for exascale systems. The heart of the SiCortex system is a six-core system-on-chip (SOC) node based on the MIPS cpu architecture. Each core runs at 500 MHz and can perform two floating-point operations per cycle. The nodes are connected by a Kautz graph that has three incoming and three outgoing edges per node. A key innovation by SiCortex is tiling that allows the nodes to be wired economically. The Kautz graph has many attractive properties and should provide a less topology-sensitive environment for applications.

The SiCortex system is a flexible DMA (direct memory access) engine that allows optimization of MPI and other programming models, such as those represented by the Partitioned Global Address Space languages and even the HPCL (High-Productivity Computer Language) languages. Current MPI latency should be about 2 μ s (microseconds) once tuning is complete. SiCortex uses Argonne's MPICH2 as the basis for the MPI implementation.

All SiCortex system software is open source, so the entire system software stack is available for research and experimentation, and we can explore design issues and evaluate the system at a much deeper level than is possible for other commercial systems. For example, users can modify the microcode for the DMA engines to explore latency tolerance, resilience in the presence of faults, and put/get behaviors. We cannot do such low-level research on the BG/P, which does not have open interfaces to the firmware. This capability makes Full Disclosure a compelling setting for system software research.

We will evaluate the SiCortex architecture in multiple areas, experimenting with the operating system, communication libraries, Kautz interconnect, languages, tools, and parallel I/O. We will develop a suite of tools and methods for understanding how single-node SOC performance is affected by the whole-platform architecture. Our goal is to develop application models and benchmarks that will let us accurately predict the performance of future exascale designs and architectures. In pursuing these objectives, our approach will continue to employ the algorithm used in FY 2009 wherein our research is informed by the experiences of various HPC groups who are invited to use our system for their applications.

Milestones: (1) determine efficient ways to use multicore and GPU components in large-scale parallel machines; (2) develop a series of benchmarks, experiments, and tools to assess and predict the performance of potential exascale applications and apply these to both the SiCortex platform and GPGPU systems; (3) continue our research with SiCortex; and (4) leverage our Argonne Leadership Computing Facility (ALCF) work and our work with IBM on designing the BG/Q platform.

Non-Refereed Publications and Presentations

Peterka, T., D. Goodell, R. Ross, H.-W. Shen, and R. Thakur, "A Configurable Algorithm for Parallel Image-Compositing Applications," published in the proceedings of the International Conference on High Performance Computing, Networking, Storage and Analysis (SC '09), preprint ANL/MCS-P1624-0509, Argonne National Laboratory, May 2009.

Zhu, H., D. Goodell, R. Thakur, and W. Gropp, "Hierarchical Collectives in MPICH2," presented at EuroPVM/MPI (Parallel Virtual Machine/Message Passing Interface) 2009, preprint ANL/MCS-P1622-0509, Argonne National Laboratory, May 2009.

Software Infrastructure to Enable Exascale Computational Science

2008-179-R1

*Robert B. Ross, Peter H. Beckman, Mark Hereld,
Ewing L. Lusk, Boyana R. Norris, Michael E. Papka,
Rick L. Stevens, Rajeev Thakur, and Albert F. Wagner*

Project Description

Our goal is to understand three crucial software areas for exascale computing: tools for understanding and debugging applications at exascale; system software for managing millions of processors, complex networks, and exascale storage systems; and frameworks and algorithms for extracting and representing knowledge contained in exascale data sets.

Mission Relevance

DOE is embarking on an initiative to develop exascale computing resources in the next 10 years. Our project is highly relevant to this initiative. Exascale computing will fundamentally change our understanding of the world, unlocking secrets not only in fields that have traditionally used high-end computing (HEC) resources (e.g., climate modeling) but also in areas just beginning to leverage the power of computation (e.g. economics). Exascale computer architectures will be a radical departure from existing systems; there will be a large number of processors that are slower with large core counts and a much greater imbalance between processing capabilities and the memory and storage subsystems. Advances in software infrastructure will be critical for overcoming these challenges so the new resources can be used to make scientific discoveries.

FY 2009 Results and Accomplishments

To better understand application execution, we extensively searched the literature and software dealing with large-scale debugging and performance analysis. We helped the developers of ScalaTrace and its prerequisites port their trace compression tool chain to Blue Gene(BG)/P. We applied it to analyze the message passing interface (MPI) communication patterns of a set of benchmarks based on the VORPAL commercial electromagnetic code. Our experience with ScalaTrace revealed that its on-the-fly compression methods can result in potentially huge overheads, so we also began investigating other approaches to expressing communication behavior without requiring full traces. We developed a preliminary, matrix-based representation of the communication patterns for pairwise communications, and we began testing different approaches to optimizing the MPI task mapping in order to minimize costs. Our initial focus was on applications using the

Portable Extensible Toolkit for Scientific Computation (PETSc) partial differential equation (PDE) solver library. In our investigation, we considered only regular discretizations using standard stencils.

We continued efforts to develop scalable, fault-tolerant storage software for exascale systems. We developed a software simulator to help us understand the impact of data placement on large-scale distributed storage systems, and we are experimenting with various techniques from peer-to-peer and High-Performance Computing (HPC) storage projects. We are also investigating the access patterns of HPC and many-task applications to better understand the sorts of workloads that exascale systems will likely have. Our work with the IBM BG/Q development team continues; we are interested in in-memory distributed key/value stores for analysis workloads. This effort fits well with prior LDRD work on distributed hash tables over the MPI.

We did comparative testing of visualization codes on Intrepid and Eureka to understand the roles these two architectures may play in exascale computing environments. Volume and isosurface rendering techniques can be implemented on both. For the isosurface algorithm, we used a general-purpose visualization toolkit (vtk). For the volume rendering, we used a custom code (vl3) with graphics processing unit (GPU) optimizations in place when built on Eureka. For both, we measured and analyzed the time spent on data loading, rendering, exchange over network, and compositing as functions of the size of the data set and of the number of processors used.

Discussions with Argonne Leadership Computing Facility (ALCF) partners revealed that one reason for specifying future hardware designs is to better model the impacts of visualization and analysis on computational resources. To understand the issues, we are collecting information from users, system logs, and other sources to correlate the profiles of computational resources (simulation cycles, input/output [I/O] bandwidth, storage, visualization cycles) for actual usage patterns. To do so, we created a database with data from an increasing number of sources that can be mined for these relationships: time spent on analysis and visualization versus time spent on simulation, correlated I/O requirements for producing and analyzing data, and resource footprints for various application types, among others.

With regard to data representation, we continued our work on data compression via general interpolative methods. To test our approach, we developed a test suite of 17 data sets based on combinations of exponential, trigonometric, power, and other functions evaluated over a regular grid of independent variable values. By using a multigrid approach for processing coarser to finer samples from the data set, we have obtained

interpolation functions that reproduce each data set in our test suite with 1% accuracy by using factors of 100–1,000 fewer data elements than achieved with the unprocessed data sets. We are presently making parallel key steps in the algorithm.

Our 2010 Innovative and Novel Computational Impact on Theory and Experiment (INCITE) proposal entitled “Scalable System Software for Performance and Productivity” was selected to receive 5 million processor hours in 2010. This award is up for renewal every 3 years. In response to program announcement 09-26, we submitted a DOE early career proposal entitled “Coupling Storage and Analysis of Extreme-Scale Scientific Data for Greater Scientific Insight” that is still under review. Also, our proposal with Kwan-Liu Ma (University of California-Davis) entitled “Visual Characterization of I/O System Behavior for High-End Computing” submitted in response to NSF 09-530 through the Computation Institute was recently accepted and funded.

Proposed Work for FY 2010

In FY10, we will continue to develop our communication pattern representation to accommodate less regular applications through an approach that utilizes static analysis of the source code. It (1) slices the application code to generate a “light-weight” version that captures communication patterns and (2) inserts annotations that can be used to generate smaller traces, such as loop variables.

We will continue developing our storage simulation system, investigating the use of the ROSS parallel discrete event simulation system for more complex storage system analysis. We will work with the IBM BG/Q team as the hardware is available. Finally, we will develop a working version of our exascale storage software for the existing IBM BG/P system by using our INCITE allocation.

We will create a model of visualization and analysis computations to study a range of possible science pipeline configurations, including in situ analysis, conventional post processing, and opportunities for hybrid approaches. To study the limits and issues associated with interactive visual data analysis at exascale, we will develop and document a visualization experiment of a resource-limited data set and corresponding analysis.

With regard to data compression by interpolation, we will complete our MPI-based parallel code, extend our test suite and methodology to irregular data sets, and evaluate parallel applications of our method to large-scale data sets. In particular, we intend to conduct application studies on data sets on regular grids produced by climate modeling. We also plan to apply our methods to data sets on irregular grids produced by electronic structure calculations.

Refereed Publications

Lang, S., P. Carns, R. Latham, R. Ross, K. Harms, and W. Allcock, “I/O Performance Challenges at Leadership Scale,” in *Proceedings of Supercomputing (SC) 2009*, Portland, OR, November 14–20, 2009.

Peterka, T., R. Ross, H.-W. Shen, K. L. Ma, W. Kendall, and H. Yu, “Parallel Visualization on Leadership Computing Resources,” presented at Scientific Discovery through Advanced Computing Program (SciDAC) 2009, San Diego, CA, June 14–18, 2009; in *Journal of Physics: Conference Series* **180** (2009), 012088.

Wozniak, J.M., and M. Wilde, “Case Studies in Storage Access by Loosely Coupled Petascale Applications,” in *Proceedings of the 4th Petascale Data Storage Workshop at SC 2009*, Portland, OR, November 14–20, 2009.

Presentations and Non-Refereed Publications

Cowen, B., “Field Messaging Schemes for Large-Scale Electromagnetic Simulation,” presented at the International Computational Accelerator Physics Conference, San Francisco, CA, August 31–September 4, 2009.

Gropp, W., E. Lusk, R. Ross, and R. Thakur, “Advanced MPI,” tutorial presented at SC 2008, Austin, TX, November 15–21, 2008.

Latham, R., and R. Ross, “Parallel I/O in Practice,” tutorial presented at SciDAC 2009 Tutorials Day, San Diego, CA, June 19, 2009.

Latham, R., R. Ross, M. Unangst, and B. Welch, “Parallel I/O in Practice,” tutorial presented at SC 2008, Austin, TX, November 15–21, 2008.

Ross, R., “Extreme Scale I/O Systems,” presented at Institute of Electrical and Electronics Engineers (IEEE) Nuclear Science Symposium Data-Intensive Workshop, Orlando, FL, October 26, 2009.

Wozniak, J.M., B. Jacobs, R. Latham, S. Lang, S.W. Son, and R. Ross, “Implementing Reliable Data Structures for MPI Services in High Component Count Systems,” in *Poster Proceedings of the 16th Euro Parallel Virtual Machine (PVM)/MPI Conference*, Espoo, Finland, September 7–9, 2009.

Novel Computing Methodologies for the Simulation of Complex Molecular Systems

2009-047-N0

Benoît Roux

Project Description

Classical simulations based on atomic models play an increasingly important role in a wide range of applications in physics, biology, and chemistry. They are particularly valuable for the study of soft matter systems involving liquids, polymers, membranes, microemulsions, surfactants, and complex biomolecules, such as proteins and nucleic acids. A central issue in classical simulations concerns the accuracy and predictive value of the force field used. Such force fields are mathematical objects constructed from analytical functions, which are parameterized to approximate the Born-Oppenheimer potential energy surface and reproduce known experimental results. In practice, the neglect of induced polarization has severely limited the usefulness of molecular dynamics simulations. The project addresses the urgent need for new and extremely scalable algorithms for accurate simulation of complex systems incorporating induced polarization. An objective method for optimizing the atomic force field used in the simulations is also necessary for a wide variety of applications. This project will provide novel computational approaches for simulating large-scale self-assembled systems with induced polarization.

Mission Relevance

The project is relevant to DOE's mission in basic science. The impact of reliable and physically accurate large-scale simulations of complex molecular systems will be directly beneficial to a number of researchers and DOE. With the significant increase in computational power made available by the Argonne Leadership Computing Facility (ALCF), the impact of molecular simulations based on accurate atomic models for these various projects is expected to continue to grow in the near future. This research advances DOE's long-term mission goals through the development of the relevant mathematical methodologies, as well as through contributions to the understanding of specific material systems with great potential for engineering applications in the energy sciences.

FY 2009 Results and Accomplishments

We have developed rapid and systematic protocols for computing the free energy of solvation. We have also developed a novel replica-exchange free energy simulation protocol for the Blue Gene supercomputer. Lastly, we have developed a new polarizable force field for lipid membranes. All those results were published in peer-reviewed journals.

We started the implementation of the polarizable force field based on classical Drude oscillators in the program NAMD (Nanoscale Molecular Dynamics) developed by the Schulten group at the University of Illinois Urbana-Champaign. This initial implementation was limited and did not support all the aspects that would be necessary to simulate membranes and proteins. The implementation did, however, support the simulation of liquid water via the SWM4-NDP model, and we were able to perform some initial benchmark analyses. A comparison of initial benchmarked data for NAMD with the Drude force field on different boxes of water molecules is shown in Figure 1. As may be seen, the 5-particle Drude SWM4-NDP model (3 atoms, M site, and Drude particle) is a maximum of 3 times slower than the TIP3P model and only 1.2 times slower for the largest system on 4096 processors. This encouraging result indicates that we should focus research in this direction and that we should implement all of the features necessary to fully support the polarizable force field in NAMD.

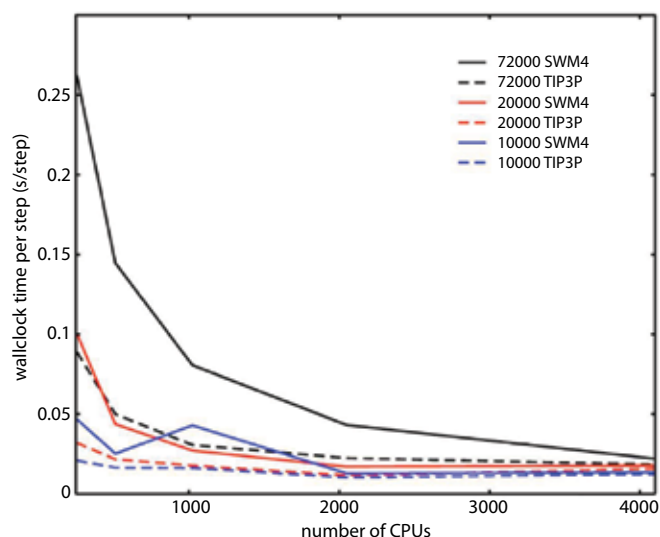


Figure 1. NAMD benchmarks for the SWM4-NDP model compared with TIP3P on the Blue Gene/P at Argonne National Laboratory. Compared are systems with 10,000, 20,000, and 72,000 water molecules. The TIP3P model has 3 interaction sites, and the SWM4-NDP model has 5 sites (3 nuclei, 1 long pair, and 1 Drude). The TIP3P/SWM4-NDP ratio for timing performance varies between 3 (with 256 CPUs) and about 1.1 (with 4096 CPUs).

Proposed Work for FY 2010

We plan to soon have a version of Nanoscale Molecular Dynamics (NAMD) that supports our polarizable force field. NAMD is a parallel molecular dynamics code developed in the laboratory of Klaus Schulten at the University of Illinois at Urbana-Champaign for high-performance classical simulation of large biomolecular systems. NAMD scales to thousands of processors on high-end parallel platforms and hundreds of processors on commodity clusters. Past work has already resulted in complete integration of the functional form of

the polarizable force field based on dual-thermostat classical Drude oscillators with lone pairs into NAMD-Lite, which is the software basis for the NAMD group. Ongoing work to parallelize the model in NAMD includes a Langevin form of the dual thermostat for the Drude oscillator, an approach that is proven to sample the canonical ensemble well with good parallel scalability. Support for the SWM4-NDP water model is already implemented into NAMD, and efforts are under way to implement the general case of the massless auxiliary lone-pair sites in a scalable manner. A comparison of initial benchmarks for NAMD with the Drude force field on different boxes of water molecules shows that the performance will be excellent (Figure 1).

Refereed Publications

Harder, E., A.D. Mackerell, and B. Roux, "Many-Body Polarization Effects and the Membrane Dipole Potential," *J. Am. Chem. Soc.* **131** (2009), 2760–2761.

Jiang, W., M. Hodoscek, and B. Roux, "Computation of Absolute Hydration and Binding Free Energy with Free Energy Perturbation Distributed Replica-Exchange Molecular Dynamics," *J. Chem. Theo. Comp.* **5** (2009), 2583–2588.

Shivakumar, D., Y.Q. Deng, and B. Roux, "Computations of Absolute Solvation Free Energies of Small Molecules Using Explicit and Implicit Solvent Model," *J. Chem. Theo. Comp.* **5** (2009), 919–930.

New Framework for Electromagnetic Simulations on Exascale Supercomputers

2009-155-NO

Paul F. Fischer, Jin Xu, Mi Sun Min, and Timothy J. Tautges

Project Description

This project focuses on developing an innovative computational tool for exploring beam dynamics with accelerator devices. Efficient computations will enable us to predict the geometric parameters for optimal solutions for various accelerating systems at low cost.

Our recent research, based on the development of the time-domain electromagnetic solver NekCEM, has shown significant progress in high-performance electromagnetic modeling at the terascale and petascale. The aim of this project is to add a new framework that will increase both computational capability and efficiency of our high-order code. Specifically, the following key capabilities will be designed and implemented:

(1) enhancement of geometric flexibility with simplicial elements, (2) development of efficient eigenvalue and frequency-domain solvers, and (3) extension of scalable parallel algorithms to exascale simulations.

Mission Relevance

This project is relevant to DOE's Office of Science missions in advanced scientific computing and nuclear physics. After successful completion of this project, the framework can be used as a platform to perform further research involving electromagnetic simulations in several divisions at Argonne, such as the Advanced Photon Source (APS), Center for Nanoscale Materials (CNM), Chemical Sciences and Engineering (CSE), High Energy Physics (HEP), Materials Science (MSD), Nuclear Engineering (NE), and Physics (PHY). Extensions can be added in different disciplines to greatly improve their quality and efficiency. For accelerator devices in APS and PHY, it can provide accurate electromagnetic fields for further physical research. These codes will greatly improve the quality of electromagnetic simulations and design optimization of linear accelerators. More importantly, successful completion of this project will further strengthen Argonne's support of DOE in accelerator simulation.

FY 2009 Results and Accomplishments

During FY09, our main focus was on the development of a time-domain electromagnetic solver based on simplicial elements (triangles and tetrahedra). Both two-dimensional (2D) and three-dimensional (3D) solvers have been incorporated into the NekCEM code, which originally supported only quadrilateral and hexahedral elements.

Our results and accomplishments include the following:

1. Development of a time-domain Maxwell solver for simplicial elements.
2. Completion of accuracy and central processing unit (CPU) time comparisons for simplicial and hexagonal elements (see Figures 1 and 2).
3. Development of parallel algorithms for simplicial elements in 2D and 3D.
4. Development of parallel input/output (I/O) and post-processing tools for simplicial elements in 2D and 3D.
5. Development of a moving window algorithm for wakefield calculations on hexagonal elements.
6. Initiation of development of eigenvalue and frequency-domain solvers.

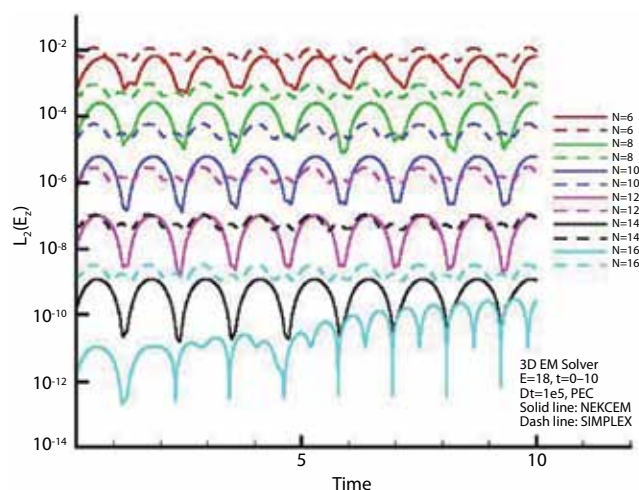


Figure 1. L_2 -error behaviors in time for tetrahedral (dashed lines) and hexahedral (solid lines) elements for 3D sinusoidal waves traveling 15.7 periods. Simulations are based on spectral element discontinuous Galerkin discretizations showing exponential convergence as increasing the orders of approximations $N = 6, 8, 10, 12, 14, 18$ for both approaches. Comparisons on the error behaviors in time demonstrate higher accuracy with hexahedral elements for each N .

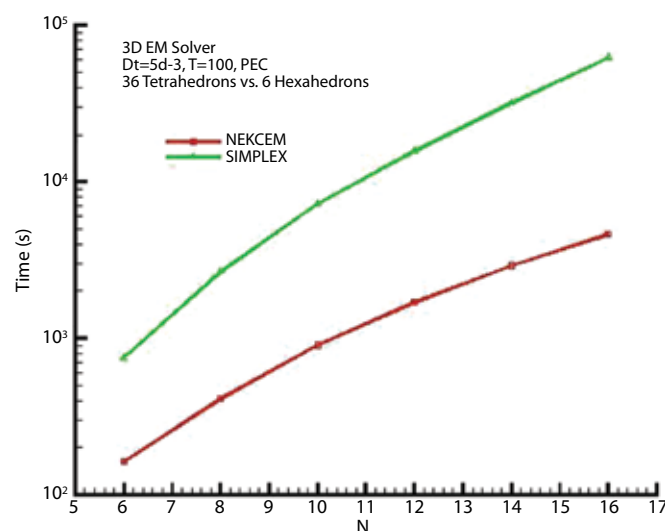


Figure 2. CPU time comparisons between tetrahedral (green lines) and hexahedral (red lines) elements as increasing their resolutions with the orders of the approximations $N = 6, 8, 10, 12, 14, 18$ for 20,000 time-step runs, demonstrating faster speed for the cases with hexahedral elements; For comparison, the total number of elements are properly chosen so that the total number of grids are similar between the cases of tetrahedral and hexahedral approaches.

Proposed Work for FY 2010

In FY10, we will continue to improve the time-domain solver for large-scale applications. We will develop scalable eigenvalue and frequency-domain solvers on high-performance architectures. The essential aspects of our proposed research are as follows:

1. Develop scalable algorithm up to 100K processors for NekCEM (currently, up to 16K).
2. Develop eigenvalue solvers using continuous Galerkin, discontinuous Galerkin, and Nedelec element methods.
3. Develop scalable algorithms for the eigenvalue solvers.
4. Develop a frequency-domain solver with nonreflecting boundary conditions.
5. Enhance meshing and visualization/post-processing components for exascale computing.
6. Simulate application problems for radio-frequency quadrupole resonators, radio-frequency resonators, couplers, and wakefield computations.

Refereed Publications

Min, M., and P. Fischer, "Spectral-Element Discontinuous Galerkin Simulations with a Moving Window Algorithm for Wakefield Calculations," Proc. of Particle Accelerator Conference, TH5PFP037, May 2009 (accepted).

Non-Refereed Publications and Presentations

Min, M., "Spectral Element Discontinuous Galerkin Simulations with Moving Window for Wakefield Calculations," invited talk presented at the International Computational Accelerator Physics (ICAP) Conference, San Francisco, CA, August 31, 2009.

Min, M., and P. Fischer, "Spectral-Element Discontinuous Galerkin Simulations with a Moving Window Algorithm for Wakefield Calculations," poster session presented at the Particle Accelerator Conference 2009, Vancouver, Canada, May 8, 2009.

Min, M., "NekCEM: High Performance Electromagnetic Simulations," invited talk presented at Mathematics and Its Applications Seminar at the University of Illinois, Chicago, IL, February 25, 2009.

Min, M., "High-Performance Electromagnetic Modeling," invited talk presented at the Applied and Computational Seminar at University of North Carolina, Charlotte, NC, January 28, 2009.

Xu, J., "Scientific Computing with High-Order Numerical Methods," invited talk presented at the Computer Science and Mathematics Division at Oak Ridge National Laboratory, Oak Ridge, TN, February 23, 2009.

LARGE-SCALE SCIENCE
USER FACILITY DEVELOPMENT

Development of Concepts for a Super Separator Spectrometer

2007-105-R2

Bela Erdelyi, Christopher J. Lister, Jerry A. Nolen, and Guy Savard

Project Description

SPIRAL 2 is a project to expand the capabilities of the Grand Accélérateur National d'Ions Lourds (GANIL) so that nuclear physics research can be performed with exotic beams. One of the new instruments envisioned is the super separator spectrometer (S^3) for high-intensity heavy ion beams that are stable. In this project, we address the ion optical issues of this device, including the modeling of fringe field effects of large-aperture, short superconducting magnets. The physics that is proposed to be studied with the S^3 instrument includes synthesis and spectroscopy of super heavy elements, fusion and evaporation reactions, nucleon transfers, deep inelastic reactions, some nuclei from secondary reactions, astrophysics at very low energy, and plasma physics.

Mission Relevance

This project in the field of exotic beam research is relevant to the science mission of the DOE Office of Nuclear Physics. This project will provide new techniques in mass separation of stable and unstable ions, contributing to the advanced design of high-intensity machines. Techniques developed for this device will be directly useful in advanced instruments for low-energy nuclear physics research at exotic beam and intense stable beam facilities in the United States and elsewhere.

FY 2009 Results and Accomplishments

A design based on **Momentum Achromat** followed by a **Mass Separator (MAMS)** has now been accepted as the basis for the S^3 project. A preliminary design based on the MAMS concept was proposed in FY08. In FY09 the design was extended further to accommodate constraints arising from new experimental setup requirements and other practical considerations. We proposed two variations to the original MAMS design, which are currently being studied. Also, realistic fringe field effects of magnets are now included in beam-optics calculations.

In parallel to the design effort, work was also done to identify and evaluate technology choices to build individual components of the S^3 device. For the magnets, both conventional (room temperature) and superconducting magnet technology are being considered. A major part of the FY09 effort was devoted to preliminary design of superconducting magnets using both commercial and in-house computer codes. Simulation studies showed the feasibility of building the S^3 multipole magnets using racetrack coils and double-helix technology. Figures 1 and 2 show designs developed on the basis of finite element analysis (with OPERA3D and ROXIE computer codes, respectively) for the proposed S^3 multipole magnet using racetrack-type coils. We have started working with companies to perform complete engineering design studies for different magnet options.

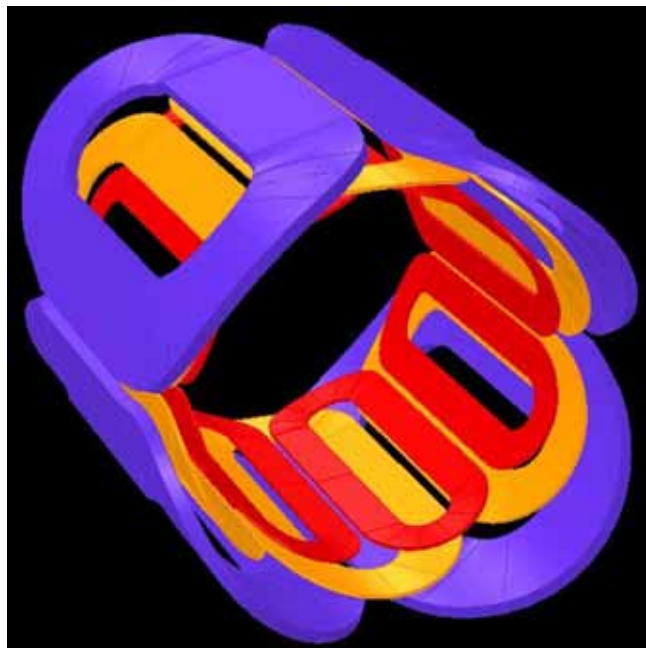


Figure 1. Superconducting magnetic fields are used to guide charged particles in S^3 . The magnetic fields are created by superconducting current-carrying wires, shaped in such a way as to satisfy certain constraints regarding the quality of the magnetic fields they create. One such model, created by the code OPERA3D for a multipole magnet using race-track-type coils, is shown in the figure.

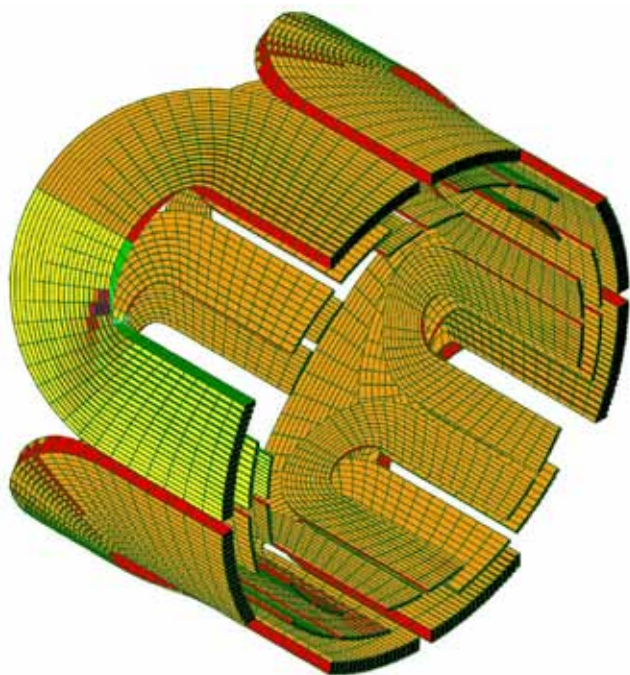


Figure 2. Another model for the magnet shown in Figure 1, created with a different computer code (ROXIE) for cross-checking purposes.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Drouart, A., A.M. Amthor, D. Boutin, O. Delferriere, M. Duval, S. Manikonda, J.A. Nolen, J. Payet, H. Savajols, M.-H. Stodel, and D. Uriot, "The Super Separator Spectrometer (S3) for SPIRAL2 stable beams," *Nuclear Physics A* **834** (Issues 1–4) (March 1, 2010), 747c–750c.

Non-Refereed Publications and Presentations

Nolen, J., "Superconducting Multipoles Option for Super Separator Spectrometer (S3)," presented at Super Separator Spectrometer Workshop, GANIL, Caen, France, June 15–17, 2009.

Nolen, J., "Momentum Achromat Mass Separator Basic Optical Design of S3," presented at Super Separator Spectrometer Workshop, GANIL, Caen, France, June 15–17, 2009.

Manikonda, S., "Optimization of the Proposed S3 Design," poster presented at SPIRAL2 Week, Caen, France, January 26–29, 2009.

Second-Sound Diagnostic Thermometry for ILC Cavities

2007-142-R2

Michael P. Kelly, Joel D. Fuerst, Kenneth W. Shepard, and Zhenchao Liu

Project Description

The goal of our project is to extend and adapt the second-sound diagnostic technique to the 9-cell, 1.3 gigahertz (GHz) superconducting (SC) cavities being developed for the proposed International Linear Collider (ILC), as well as SC cavities, such as spoke and quarter-wave structures for ATLAS and other heavy-ion accelerators.

Mission Relevance

The project is relevant to DOE's mission in science. The project supports DOE by providing an important new tool for locating and identifying defects in the fabrication and processing of high-performance elliptical-cell cavities. The direct beneficiaries include those working to develop high-gradient superconducting radio frequency (SRF) cavities for the ILC; however, the DOE or other organizations with projects that require SC cavities operated at high gradient will also benefit from this technique.

FY 2009 Results and Accomplishments

A simple technique based on an in situ and movable germanium resistance thermometer has been built to measure the quench location in SRF cavities in superfluid liquid helium. SRF cavities are very often limited in operating field level by thermal instability that manifests as a transient "quench" of the electromagnetic field. The field energy is transferred into the superfluid helium bath as a heat pulse and may be detected as a wave of phonons at a thermometer. We have adapted the second-sound diagnostic technique so that it is simple, easy to use, and cost-effective for application with cavities under development today. These include, for example, the 9-cell, 1.3-GHz SC cavities, as well as reduced beta superconducting cavities, such as half-wave and quarter-wave cavities.

Proposed Work for FY 2010

This project does not continue into FY10.

Non-Refereed Publications and Presentations

Kelly, M., M. Kedzie, and Z. Liu, "A Simple Second Sound Detection Technique for SRF Cavities," published in the *Proceedings of the 14th International Conference on RF Superconductivity*, Berlin, Germany, September 20–25, 2009. <http://cern.ch/AccelConf/SRF2009/papers/tuppo032.pdf>

Molecular Machines: The Visualization of Motion

2007-157-R2

Klaus Attenkofer and David M. Tiede

Project Description

Molecular machines are a class of molecules that show a reversible structural change after an electrical, chemical, or photonic excitation. While these molecules function at the core of multiple essential functionalities of living organisms in nature, this concept is new in engineered artificial materials. Within the last decade, there has been remarkable progress in designing and synthesizing device-oriented molecular machines; nevertheless, there remains a debilitating lack of characterization tools that could help deepen the molecular understanding of the excitation and the following structural change. The goals of this project are to (1) develop time-resolved, wave-guide x-ray techniques for the direct, *in situ* detection of impulsively triggered electronic and atomic motions in molecular switches, machines, and motors across the 100 picoseconds (ps) -to-millisecond (ms) timescales and (2) explore detection schemes with 1-ps time resolution. We use newly developed, time-resolved x-ray techniques to visualize the motions of molecular machines across the full, functional timescale, starting from the fundamental charge transfer time to the macroscopic motion of the molecule. To trigger the motion of an ensemble of molecules coherently, we developed a novel sample cell, which is based on the principles of wave-guides. Molecular electronic excitation is achieved either by the direct interaction of molecular films with the pulsed electric fields, or by the three-step process of subsequence, field-driven interfacial electron transfer, and charge transport through the molecular layers. We are investigating opportunities to extend pulsed field technologies to 1-ps rise-times with time-varied, shaped electric pulses that achieve field strengths of up to 0.5 volts (V)/nanometer (nm) at the sample position by using laser-driven, optical-switch technology.

Mission Relevance

This project is relevant to DOE's mission in science. In the fields of bioengineering and nanotechnology, molecular machines play an important role. In particular, the new opportunity to manipulate chemical reaction pathways by manipulating molecular excited-state electronic structures using externally applied, pulsed electric fields with ultrafast time resolution is

central to missions in DOE's Office of Science, including its programs in ultrafast sciences and instrumentation and ultrafast chemical sciences. More generally, the ability to produce an electric cell for ultrafast x-ray analyses will create opportunities for breakthroughs in a broad range of disciplines within energy-related science, including electrochemistry, catalysis, hydrogen production, solar energy, and fuel cells, all of which are central to core missions of DOE.

FY 2009 Results and Accomplishments

We implemented micro-focusing capabilities at beamline 11-ID-D, an optimized Advanced Photon Source beamline for time-dependent spectroscopy and scattering experiments. The beam-stability was tested, and a 40- to 50-micrometer (μm) drift over 8 hours was observed that contributed to thermal instabilities inside the x-ray hutch. An additional periodic 5- μm , short-term drift (caused by the x-ray chopper) with a period length of 32 minutes was detected and contributed to the fact that the crystal chopper provided the single bunch-selectivity in the current experiments. Better thermal control of the hutch temperature and a major detector upgrade will eliminate most of these problems. In addition, we started to develop an ultrafast feedback system, which allows steering the beam within 1 ms on the target (50–100-nm resolution). Our objective was to provide the first time-dependent wide angle x-ray experiments using pulsed electric fields.

Parallel to the x-ray efforts, we developed our capabilities to fabricate stripline sample chambers, which allow a pulse length of 1 ps and shorter. With Professor Thomas Wong of the Illinois Institute of Technology, we were able to extend our simulation capabilities to the 10–50-gigahertz (GHz) range (Figure 1). Various test structures were designed, fabricated, measured, and compared to simulations. On the basis of these experiments and by using micro-electro mechanical device technology, we are currently developing new design rules for striplines in the 100–500-GHz range. The improved simulation capabilities also provide us with the ability to develop stripline structures that fully utilize the polarization sensitivity of this approach to create a highly selective excitation population in the sample. The devices will be combined with an optical switch (i.e., an Austin-switch) and an integrated antenna structure for terahertz absorption. By using the increased time resolution of the new devices, we plan to demonstrate the electron injection with a time-dependent (1-ps time resolution) water dissociation experiment by studying the catalytic reactions on a platinum (Pt) -water interface. This work is currently supported programmatically within the Advanced Photon Source.

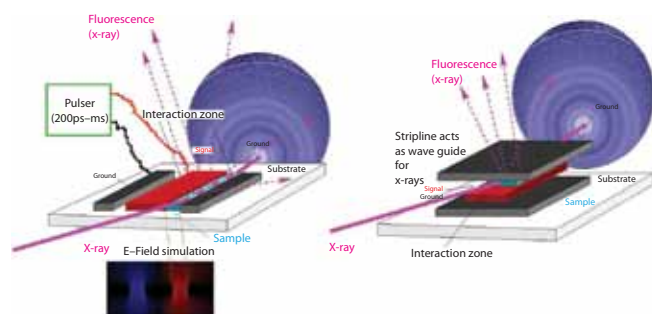


Figure 1. Usage of stripline sample cells for ultrafast x-ray scattering and spectroscopy experiments: the left panel shows a cell with horizontal alignment of the electric field (simulation of the electric field is shown in the inset); the right panel shows a cell with vertical alignment. The horizontal geometry will allow potential gradients of up to 0.5 V over the dimension of one molecule with switching times on the order of 1 ps. The vertical geometry will allow more complex structures that model the materials properties in solar cells and organic light-emitting devices. The present development will include a gold signal electrode coated with a titanium dioxide (TiO_2) surface.

Proposed Work for FY 2010

This project does not continue into FY10.

An Integrated X-Ray/Neutron Approach to Magnetic Depth Profiling in Artificial Nanostructures

2007-158-R2

Daniel Haskel, Suzanne G.E. Te Velthuis, and Evgeny Kravtsov

Project Description

The objective of this project was to develop software to be used for simultaneous refinement of polarized neutron reflectometry (PNR) and x-ray resonant magnetic reflectivity (XRMR). The resulting data allow reliable determination of depth-resolved magnetization density profiles in artificial magnetic nanostructures. The emerging area of spintronics (spin-electronics), which exploits both the spin and charge of the electron for digital processing and storage of information, has the potential to yield improved energy efficiency and computational speed relative to conventional electronics. Further optimization of spin-based technologies will rely on a quantitative understanding of spin-dependent scattering at the interfaces of magnetic nanostructures. Optimization will thus require determination of chemical and magnetic interfacial structure, including chemical and magnetic roughness and magnetization density profile across interfaces.

Mission Relevance

This project supports the mission of the DOE Office of Basic Energy Sciences (BES) to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels. The combined analysis of polarized x-ray and neutron scattering data enhances the reliability with which this information can be obtained benefiting the academic and industrial communities working on fundamental and applied aspects of spintronics and thin-film magnetism.

FY 2009 Results and Accomplishments

During FY07, we developed a unified theoretical formalism for a consistent mathematical description of PNR and XRMR. A generalized computer code based on this formalism was written but was initially limited to *simulate* PNR and XRMR data. The simulation code was successfully tested on data collected on a $[\text{Fe}(35 \text{ \AA})/\text{Gd}(50 \text{ \AA})]_5$ model nanostructure at the Advanced Photon Source and the Intense Pulsed Neutron Source of Argonne National Laboratory, as well as at the National Institute of Standards and Technology reactor. During FY08, the code was extended to include simultaneous *refinement* of PNR and XRMR data. The refinements used a single parameterized model of the chemical and magnetic density profiles and a nonlinear least-squares minimization procedure. The code was successfully used to refine complex magnetization density profiles in the model nanostructure with unprecedented resolution and accuracy (see Figure 1).

We developed a user-friendly graphical user interface (GUI) in FY09. The GUI includes a generalized model-building capability that allows generating parameterized models of magnetization density profiles in either collinear or noncollinear configurations (magnitude and direction of magnetization vector varies along the depth of the nanostructure according to a parameterized functional form). The GUI facilitates all data input operations and provides easy access to most of the code functionality. A *beta* version of the GUI was successfully tested on data from the model nanostructure. Documentation for the GUI and underlying code was also developed. Future work would involve the incorporation of a plotting/visualization capability for on-the-fly monitoring of the evolution of the fitting parameters and resultant model from initial guess to full convergence.

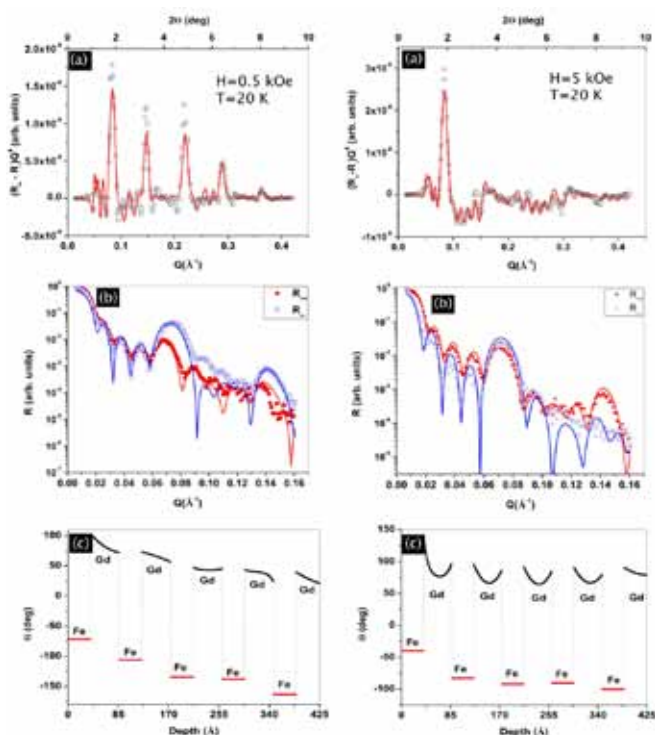


Figure 1. Fit results (solid lines) from simultaneous refinements of (a) XRRM and (b) PNR data (points) obtained for model nanostructure $[\text{Fe}(35\text{\AA})/\text{Gd}(50\text{\AA})]_5$ with two values of the applied magnetic field (data for 0.5 kOe on the left and 5.0 kOe on the right). The derived self-consistent magnetization profiles (c) show the presence of a surface twist of magnetization at low fields, and a bulk twist at high fields, wherein the Fe and Gd magnetization deviates from the applied field direction by a depth-dependent angle, θ (the opposite sign of θ for Fe and Gd is because of their strong anti-ferromagnetic interfacial coupling; i.e., their moments point in exactly opposite directions at the Fe/Gd interface). XRRM measures the difference in reflectivity for opposite helicity of circularly polarized x-rays (R_+ , R_-) while PNR measures the reflected intensity of polarized neutrons (plus sign = up, minus sign = down). Only non-spin-flip neutron scattering ($++$, $--$) is shown.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Kravtsov, E., D. Haskel, S.G.E. te Velthuis, J.S. Jiang, and B.J. Kirby, "Complementary Polarized Neutron and Resonant X-ray Magnetic Reflectometry Measurements in Fe/Gd Heterostructures: Case of Inhomogeneous Intralayer Magnetic Structure," *Physical Review B* **79** (2009), 134438.

Non-Refereed Publications and Presentations

Kravtsov, E., "Complementary Use of Neutron and Synchrotron X-ray Scattering to Probe Magnetic Microstructure in Exchange-Coupled Multilayers," presented at the Australian Nuclear Science and Technology Organization (ANSTO), Menai, Australia, October 20, 2009.

Kravtsov, E., D. Haskel, S.G.E. te Velthuis, S.J. Jiang, and B.J. Kirby, "Application of Polarized Neutron and Resonant X-ray Magnetic Reflectometry to Resolve Inhomogeneous Magnetic Structure in Fe/Gd Superlattices," presented at the 21th Russian School-Seminar, News in Magnetism and Magnetic Materials, Moscow, Russia, June 28–July 4, 2009.

Kravtsov, E., D. Haskel, S.G.E. te Velthuis, J.S. Jiang, and B.J. Kirby, "Inhomogeneous Intralayer Magnetic Structures in Fe/Gd Multilayers," presented at the International Colloquium on Magnetic Films and Surfaces, Berlin, Germany, July 20–24, 2009.

Complex Dynamic Behavior Investigated with Real-Time X-Ray Photon Correlation Spectroscopy

2008-070-R1

Alec R. Sandy, Pete R. Jemian, Brian J. Tieman, and John Weizerick

Project Description

The project focus is to provide a revolutionary improvement in x-ray photon correlation spectroscopy (XPCS) data collection and reduction procedures. XPCS data, gathered in parallel over many length scales, are compressed on the fly and time auto-correlated on a pixel-by-pixel basis, and results are periodically updated on control screens — all in real time. Thresholding and compression will be performed in firmware; in addition, a high-performance computing (HPC) PC-cluster that executes appropriate parallelized analysis code will efficiently calculate time autocorrelations across a wide range of time scales. These developments will allow multi-speckle XPCS to seamlessly probe fluctuations persisting from a few milliseconds to more than thousands of seconds — more than six orders of magnitude in time. Our technical developments will be applied to the study of multi-timescale dynamics in glassy systems.

Mission Relevance

This project is tied to DOE's mission in science. The primary benefit of this project is the ability to probe multi-timescale dynamics in complex glassy and soft materials (such as gels) with dynamics on a variety of length and timescales. The understanding of the glass transition remains a challenge in condensed matter physics. While our primary interest is in addressing fundamental scientific problems, XPCS also has important potential applications within the food, cosmetics, and paint industries (among others); these developments will facilitate access to the technique of XPCS to researchers with

more expertise in technologically important materials than in synchrotron x-ray science. Also, with the successful development and deployment of such a system, we will be able to offer Advanced Photon Source (APS) users the ability to seamlessly probe equilibrium and non-equilibrium sample fluctuations ranging from milliseconds to thousands of seconds. We expect that many new sample systems will be studied with XPCS because the need to match “predicted” sample dynamics beforehand into the available length scale and frequency window will be greatly reduced. This functionality will truly revolutionize the breadth and applicability of XPCS to a wide range of fascinating scientific problems.

FY 2009 Results and Accomplishments

On the basis of the extensive feasibility studies performed in FY08, we finalized the architecture of our system. The adopted architecture, illustrated in Figure 1, reduces the data flow from the charge-coupled device (CCD) detector to disk by at least a factor of 16 and decreases the data reduction time by more than a factor of 10.

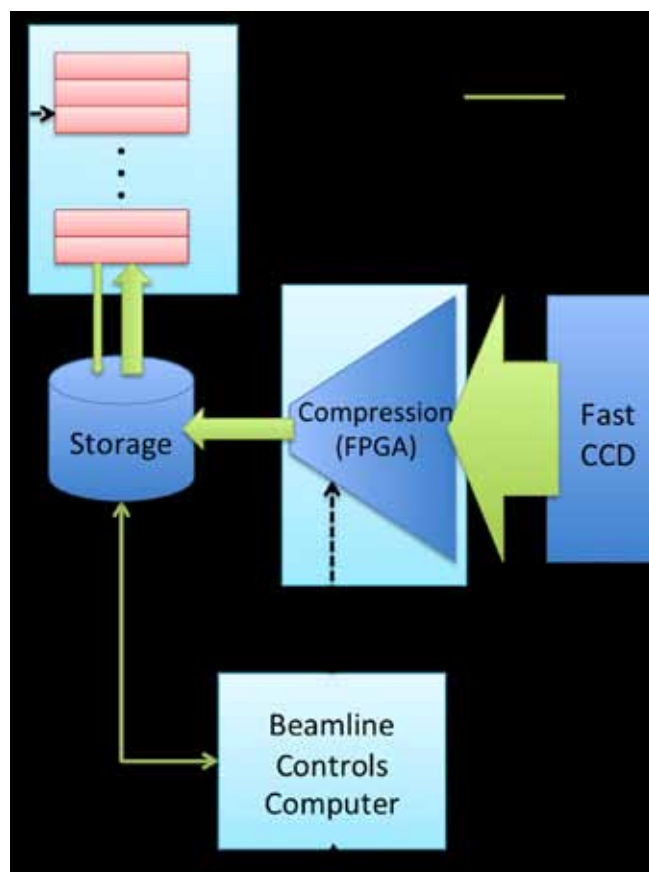


Figure 1. Fast XPCS data acquisition, compression, and reduction architecture at beamline 8-ID at the APS.

During FY09, extensive proofing of legacy software against the parallelized version of the same software was completed. Subsequently, the HPC aspect of the project was placed into production at an APS beamline. This development led to the factor-of-10 reduction in data processing time and markedly increased the efficiency of XPCS experiments. Most importantly, it has also generated an ambitious scientific study to investigate the connection between rheology and nanoscale dynamics near the glass transition in selected materials. This research will directly benefit from the HPC and firmware developments that we are implementing.

In addition, we are seeking to implement field-programmable gate array (FPGA) detector firmware that reduces the volume of data output by fast XPCS detectors by a factor of 16 or more via on-the-fly dark subtraction, thresholding, and, most significantly, compression. This development allows fast XPCS detectors to run as quickly as possible for extended periods without exhausting network bandwidth and disk space. We tested this software and placed it into production at the end of calendar year 2009.

Proposed Work for FY 2010

In FY 2010, we will place the thresholding and compression firmware described above into production. We will also continue experiments to fully exploit this new infrastructure, namely by examining the dynamics of probe particles in a molecular glass as it is slowly cooled through its glass-transition temperature. Finally, we will extend the infrastructure described above to real-time operation so that time–auto-correlated or reduced data are available as fast as the raw data are acquired.

Non-Refereed Publications and Presentations

Sikorski, M., Fernandez, P.B., Jemian, P.R., Madden, T.S., Narayanan, S., Sandy, A.R., Sprung, M., Tieman, B.J., and Weizeorick, J., “Real-Time Multi-speckle XPCS Data Reduction via a Field-Programmable Gate Array and High-Performance Computing,” presented at the 2009 IEEE (Institute of Electrical and Electronics Engineers) Nuclear Science Symposium and Medical Imaging Conference, Orlando, FL, October 25–31, 2009.

Beam Dynamics for an ERL Upgrade of the APS

2008-136-R1

Michael D. Borland, Xiaowei Dong, Louis Emery, Katherine C. Harkay, Vadim Sajaev, and Aimin Xiao

Project Description

An ERL (Energy Recovery Linac) is a possible upgrade to the Advanced Photon Source (APS) that promises to provide a two orders of magnitude increase in average x-ray brightness. This project addresses critical beam dynamics issues for an ERL upgrade, including production and preservation of high-brightness electron beams, optimization and practicality of accelerator optics, and prediction and control of beam loss.

Mission Relevance

The project is relevant to DOE's science mission. This upgrade will have revolutionary consequences for x-ray-based science, as a result of the x-ray brightness, coherence, and temporal properties. Principal beneficiaries are DOE, which is seeking a meaningful path for an APS upgrade, and x-ray scientists, who will benefit from the revolutionary science the upgrade will enable.

FY 2009 Results and Accomplishments

A number of related investigations were undertaken this year, as summarized in the following paragraphs.

We developed an ERL upgrade configuration for the APS that incorporates up to nine 48-m-long undulators, taking full advantage of the beam brightness. This gives an average brightness approaching 10^{23} in standard units (photons/s•0.1% bandwidth/mm²•mrad²). We looked in detail at the effect of insertion devices on the ERL and showed that short booster cavities following each long undulator are feasible as a compensation mechanism. We revisited energy optimization for this design and concluded even more strongly that a 7–8 GeV ERL is highly advantageous.

We completed a generic optimization of the ERL injector including the merger, obtaining solutions for 19 and 77 pC/bunch, which meet the requirements for nominal high-coherence and high-flux operation. Using these results, we performed the first-ever start-to-end simulation of an x-ray ERL. In particular, we explored the effect of the intrinsic electron energy from the cathode. At the 120 meV level (corresponding to a green laser on a gallium arsenide cathode), we found that the high-charge case outperforms the low-charge case and gives results that are superior to the nominal high-coherence parameters. This result was surprising and is an excellent example of the utility of a start-to-end simulation.

We extended our Monte Carlo simulation of the Touschek effect to allow use of the real beam distribution from tracking, rather than a Gaussian distribution. We extended our intra-beam scattering (IBS) simulation to use longitudinal slicing, which gives more accurate results for photo-injector-generated beams. We applied this to the APS upgrade design and determined that IBS not a concern.

We extended our work on a single-pass beam optics correction to include x-y coupling, determining that the number of presently installed skew quadrupoles (19) is inadequate and would have to be increased four-fold.

Proposed Work for FY10

The project does not continue in FY10.

Refereed Publications

Borland, M., X. Dong, and Y. Li, "Progress on an Energy Recovery Linac Upgrade to the Advanced Photon Source," submitted to 2009 Synchrotron Radiation Instrumentation Conference proceedings.

Non-Refereed Publications and Presentations

Borland, M., "Choice of Optimum Operating Energy for an ERL X-ray Source," presented at ERL09 workshop, Ithaca, NY, June 8–12, 2009.

Borland, M., G. Decker, X. Dong, L. Emery, and A. Nassiri, "APS ERL Upgrade with Many Long Undulators," presented at ERL09 workshop, Ithaca, NY, June 8–12, 2009.

Borland, M., X. Dong, K. Harkay, Y. Li, R. Lill, A. Nassiri, V. Sajaev, C.-X. Wang, A. Xiao, and B. Yang, "Advanced Photon Source ERL R&D Activities," presented at ERL09 workshop, Ithaca, NY, June 8–12, 2009 (invited).

Dong, X., and M. Borland, "Using IMPACT-T to Perform an Optimization of a DC Gun System Including Merger," presented at ERL09 workshop, Ithaca, NY, June 8–12, 2009.

Sajaev, V., "Simulation of Optics Correction for ERLs," presented at ERL09 workshop, Ithaca, NY, June 8–12, 2009.

Xiao, A., and M. Borland, "Detailed Simulation of Touschek Scattering in ERLs," presented at ERL09 workshop, Ithaca, NY, June 8–12, 2009.

Xiao, A., and M. Borland, "Simulation of Intrabeam Scattering for Non-Gaussian Beams," presented at ERL09 workshop, Ithaca, NY, June 8–12, 2009.

Borland, M., G. Decker, X. Dong, L. Emery, and A. Nassiri, "Possible Upgrade of the Advanced Photon Source with an Energy Recovery Linac," *Proceedings of the 2009 Particle Accelerator Conference*, Vancouver, May 4–8, 2009 (invited).

Dong, X., and M. Borland, "An Optimization of a DC Injector with Merger for the Energy Recovery Linac Upgrade to the APS," *Proceedings of the 2009 Particle Accelerator Conference*, Vancouver, May 4–8, 2009.

Sajaev, V., "Simulation of Linear Lattice Correction and Coupling Correction of an Energy-Recovery Linac Designed for an APS Upgrade," *Proceedings of the 2009 Particle Accelerator Conference*, Vancouver, May 4–8, 2009.

Xiao, A., and M. Borland, "Intrabeam Scattering Effect Calculated for a Non-Gaussian Distributed Linac Beam," *Proceedings of the 2009 Particle Accelerator Conference*, Vancouver, May 4–8, 2009.

Development of the Emittance Exchange Technique for Improved Accelerator Facility Performance

2008-141-R1

John G. Power, Wei Gai, and Kwang-Je Kim

Project Description

The objective of this research is to develop a novel accelerator scheme for generating beams capable of meeting the most demanding accelerator requirements for the next generation of particle accelerators. The goal of this proof-of-principle Emittance Exchange eXperiment (EEX) is to exchange the initial (low) longitudinal emittance (ϵ_{z0}) with an initial (high) transverse horizontal emittance (ϵ_{x0}) and also to incorporate room for possible parametric studies (e.g., using an incoming flat beam with tunable horizontal emittance).

Mission Relevance

The project relates to DOE's science mission. Next generation accelerator applications will require charged particle beams with an optimized phase space partition. For example, high-gain free-electron lasers will potentially benefit from high transverse quality at the expense of reduced longitudinal quality. Proper phase space partitioning of electrons may eliminate the need for an electron damping ring for the International Linear Collider. A megawatt-scale average-power free-electron laser based on an energy-recovery linac would benefit from an emittance exchange to significantly reduce the energy spread before the beam dump.

FY 2009 Results and Accomplishment

Our first experiments have been carried out. The goal was to determine if the Argonne Wakefield Accelerator (AWA) facility beamline could achieve the desired initial emittance, (ϵ_{x0} , ϵ_{z0}) = (17, 3). The transverse emittance was measured with a quadrupole scan while the longitudinal emittance was measured by a linac phase scan. The measured values were (19.5, 7.4) respectively, close to the expected values. A jitter analysis study of our optimized exchange parameters (Figure 1), (ϵ_x , ϵ_z) = (17, 3) $\rightarrow$ (6, 18), showed that in order to keep emittance dilution under 20% we have to maintain the phase jitter of the deflecting cavity within 1 degree. The stripline and associated radio frequency receiver board for the EEX diagnostics are now nearly complete. Finally, based on the limited space currently available, we developed a new plan that uses half of the EEX beamline to directly measure the longitudinal phase space; the associated simulations were also carried out.

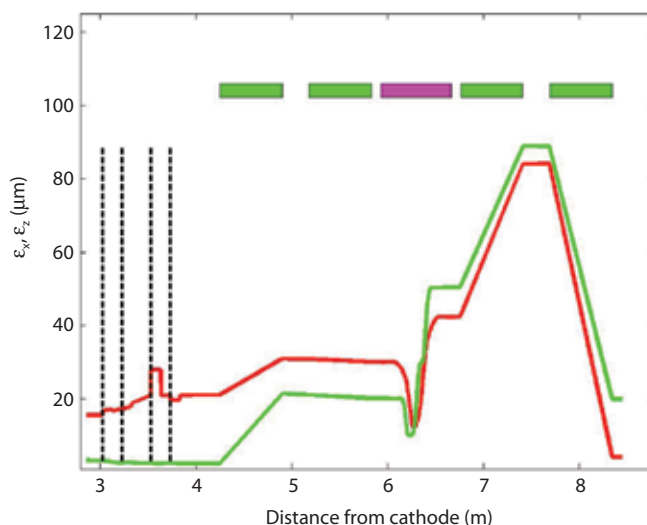


Figure 1. Evolution of horizontal (red) and longitudinal (green) trace space emittances along the beamline are shown. The dashed black line and the green and cyan rectangles, respectively, correspond to the locations of the quadrupoles, dipoles, and the deflecting cavity. A clear exchange between the transverse and longitudinal emittance is seen after the full exchanger.

Proposed Work for FY 2010

The half-EEX beamline (2 magnetic dipoles and 1 deflecting cavity, as well as a table, 2 vacuum chambers, 3 quadrupoles, and 3 YAG [yttrium aluminum garnet] screens) will be installed and used to measure the longitudinal phase space, bunch length, and half-EEX characterization. The calibration of these measurements will be one of our most challenging tasks, and we will verify the longitudinal charge distribution measurement using another method. Finally, we will prepare for the installation of the full EEX beamline when the AWA facility tunnel expansion is completed.

Non-Refereed Publications

Rihaoui, M.M., P. Piot, W. Gai, and J.G. Power, "Limiting Effects in the Transverse-to-Longitudinal Emittance Exchange Technique for Low Energy Relativistic Electron Beams," to be published in *Proceedings of PAC09* (IEEE, Piscataway, NJ), Vancouver, 2009.

Rihaoui, M.M., D. Mihalcea, P. Piot, W. Gai, and J.G. Power, "Verification of the AWA Photoinjector Beam Parameters required for a Transverse-to-Longitudinal Emittance Exchange Experiment," to be published in *Proceedings of PAC09* (IEEE, Piscataway, NJ), Vancouver, 2009.

Design and Fabrication of a Preliminary HOM-Suppressed High Beam Power CW Superconducting RF Structure and Cryomodule for Light Source Energy Recovery Linacs

2008-152-R1

Alireza Nassiri, Joel D. Fuerst, Michael P. Kelly, Geoff Waldschmidt, and Marion M. White

Project Description

The next-generation, high-performance light sources, including energy recovery linacs (ERLs) and x ray free electron lasers (XFELs), will most likely be superconducting. Our goal is to develop a highly efficient, high-current, multi-cell superconducting radiofrequency (RF) structure and cryomodule that will meet the performance requirements of future superconducting accelerators. The superconducting RF (SRF) structures envisioned for the Argonne Advanced Photon Source (APS) upgrade will be required to operate in continuous wave (CW) mode (100% duty factor) with a moderate field gradient and high cavity quality. A high-quality SRF cavity is needed to reduce total RF power and surface residual resistance and thus lower the overall wall-plug power of the cryogenic plant operation. The goals of this project are to develop and build a suitable multi-cell SRF structure, investigate methods and apply a suitable surface process to enhance the accelerating gradient and improve the cavity quality, and design and build a multi-cell structure cryomodule.

Mission Relevance

This project is relevant to DOE's mission in science. Future DOE accelerator facilities, including light sources, will benefit greatly from recent advances in SRF technology. Future accelerators will be aiming for higher energies, and light sources, in particular, will be required to operate in a wide range of modes to meet the requirements of x-ray science experi-

ments. The stringent technical requirements of the machines will be met best by SRF technology, which can deliver the best accelerator performance. However, large SRF facilities tend to be very expensive. Design optimizations and the application of novel niobium surface treatments could make such large machines more affordable and competitive with their normal conducting counterpart. This effort addresses some key issues related to developing SRF technology for future light sources.

FY 2009 Results and Accomplishments

We successfully completed the development and testing of a 1,400 MHz five-cell copper cavity. After tuning, 98.8% field flatness was measured by using an on-axis field perturbation method. The measured dipole modes and corresponding simulation results are shown in Table 1. Six major dipole modes were found and measured in the copper cavity; they were in good agreement with the simulation results. The π (π)-mode frequency error was about 0.1 MHz for the copper cavity. We also completed the beam breakup (BBU) and higher-order mode (HOM) simulations and analyses. The BBU threshold for stability indicated that this cavity can easily support 200 mA. This structure also efficiently damped higher-order modes while maintaining high impedance (ratio of shunt impedance and quality factor, R/Q) for the operating π mode and high geometry factor.

Table 1. Comparison of Six Major Dipole Modes

Major HOMs	Frequency (GHz) Simulation/Copper Cavity
TE111	1.74273/1.7457
TM110	1.85807/1.8611
TM110	1.99041/1.9918
TE111	1.81258/1.8158
TE111	1.95653/1.9583
TM110	2.00725/2.0082

In addition, a single-cell, large-grain 1,400-MHz niobium cavity was developed and cold tested to determine its accelerating field gradient and surface properties. Initial cryogenic vertical tests at 2 K indicated a good field flatness and quality factor up to 16 MV/m and a soft multipacting barrier at about 20 MV/m followed by Q-drop at about 25 MV/m (Figure 1). The initial vertical tests also showed a lower Q value at 2K (Figure 1), indicating a higher-than-expected residual resistance that is attributed to the short stainless-steel beam pipes attaching to the cavity. There is enough field at the stainless-steel coupling pieces at the end of the beam pipes to add losses to the niobium losses. For the next test, the beam pipes will be extended to reduce this loss. We expect the multipacting at 20 MV/m will be mitigated by increasing the cavity processing time.

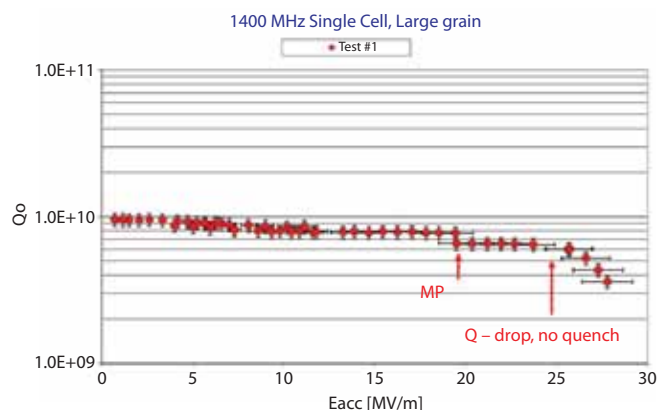


Figure 1. Plot of the cavity Q value versus the accelerating field gradient.

Proposed Work for FY 2010

We will fabricate a five-cell niobium structure, perform a vertical-drop test for accelerating field characterizations, and measure and characterize higher-order modes.

Refereed Publications and Presentations

Liu, Z., and A. Nassiri, "Novel Superconducting rf Structure for Ampere-Class Beam Current for Multi-GeV Energy Recovery Linacs," *Phys. Rev. ST Accel. Beams* 13, 012001 (2010).

Non-Refereed Publications and Presentations

Nassiri, A., Z. Liu, and G. Waldschmidt, "Superconducting 5-Cell Cavity Design and Copper Prototype Cavity for an Energy Recovery Linac at the Advanced Photon Source," presented at the 14th International Conference on RF Superconductivity, Berlin, Germany, September 20–25, 2009.

An X-Ray Free-Electron Laser Oscillator in an Energy Recovery Linac

2008-156-R1

Kwang-Je Kim and Yuri Shvydko

Project Description

The goal is to develop an x-ray free-electron laser oscillator (XFEL), which is a fully coherent source of x-rays, with an extremely narrow spectral bandwidth. The peak spectral brightness of an XFEL is about the same as a self-amplified spontaneous emission (SASE) source, such as the Linac Coherent Light Source (LCLS). The average spectral brightness of an XFEL is higher by at least two orders of magnitude than a state-of-the-art SASE source, such as the European x-ray free-electron laser (XFEL).

Mission Relevance

This project is relevant to DOE's mission in science. The results of the project will be of interest to various offices within DOE, other light source laboratories, and leading experts in dynamical diffraction theory. The x-ray science community will benefit from this novel source of fully coherent x-rays. The x-ray photons from an XFEL will be an ideal source for applications, particularly those that demand a very high degree of spectral purity, such as inelastic x-ray scattering and Mössbauer spectroscopy.

FY 2009 Results and Accomplishments

We implemented the full complex reflectivity of the Bragg crystals into the two-dimensional FEL simulation code GINGER, and we studied the harmonic contents and another mode of XFEL operation using shorter (100 femtosecond) bunches with a higher peak current (100 A).

A tunable scheme for an x-ray cavity was found. The scheme also allows selection of the crystal material independent of the spectral range to be covered. Thus, diamond crystals can be used for all spectral regions since they have the highest reflectivity and excellent mechanical and thermal characteristics.

The qualities of diamond crystals have been studied at a beam line at Argonne's Advanced Photon Source (APS). Small but sufficiently large regions for XFEL application ($\sim 0.5 \times 0.5 \text{ mm}^2$) could be identified; the measured energy bandwidth was close to the theoretical value, and the measured reflectivity of 87% was not far from the expected theoretical value of 91%.

The heat load on a diamond crystal due to the impinging x-ray pulses was studied. In the temperature range of 50–100 K, the induced temperature gradients relax to the initial homogeneous state well before the arrival of the next pulse as a result of the very high thermal diffusivity. Thus, the inter-pulse heat loading appears to be avoidable. The intra-pulse heat loading depends on the thermal expansion coefficient β , the value of which has not been known for diamond crystals at temperatures lower than 100 K. By using hard x-rays from a high-resolution monochromator, β was measured for the first time; it was so small that the intra-pulse heat loading problem appears to be manageable.

The angular stability of XFEL crystals should be better than 10 nanoradian (nrad). A null-detection feedback system was implemented at the high-resolution multichannel x-ray monochromators at the APS Sector 30 beamline. A stability of 50 nrad was achieved for the monochromator's crystals; the flux throughput was stabilized over 6 hours (the green line in Figure 1), despite the large swing of the correction signal (the brown line) in response to a refill of liquid nitrogen.

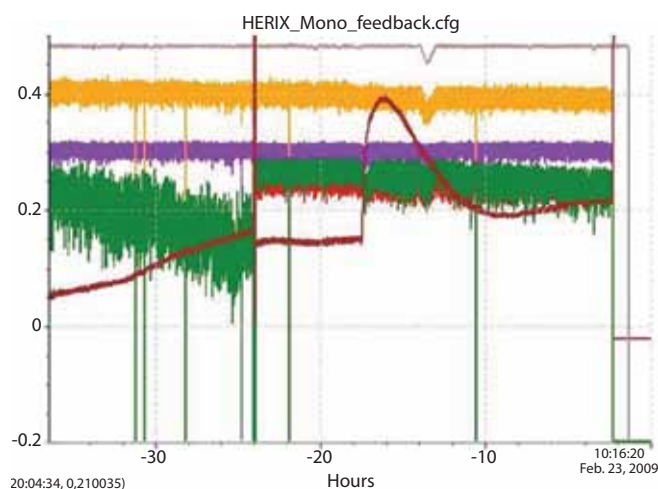


Figure 1. Variation of x-ray intensities with time: IC1 (purple line), IC2 (red line), IC3 (green line), and the feedback correction signal (brown line). The vertical scale reflects x-ray intensity in arbitrary units for all curves, except the brown line.

For the brown line, the units are voltage (V); all other lines are arbitrarily scaled to be on the same plot. These color lines correspond to x-ray intensity measured by different detectors along the path of the x-ray beam; the yellow (orange) line corresponds to output x-ray intensity of the high-heat load monochromator, the blue (purple) line is the output intensity after the first crystal pair of the high-resolution mono (IC1), the red line is the intensity after the second crystal pair of the high-resolution mono (IC2), and the green line is the intensity after the third crystal pair or the output intensity of the high-resolution mono (IC3).

Proposed Work for FY 2010

We plan to (1) further develop the FEL simulation capability to include transverse-temporal coupling of the crystal response; (2) study the optical performance of a grazing-incidence, curved mirror to include the surface roughness and figure error; (3) take measurements of diamond reflectivity in back-scattering geometry to demonstrate that the reflectivity of commercially available diamond crystals could be close to the theoretically predicted 98%; (4) continue the feedback study for the multiple-axes case and tighter angular stability; and (5) prepare for a test x ray cavity to be operated at an APS beam line.

Refereed Publications

Kim, K.-J., and Y.V. Shvyd'ko, "Tunable Optical Cavity for an X-Ray Free-Electron-Laser Oscillator," *Phys. Rev. ST Accel. Beams* **12**(3) (2009), 030703.

Lindberg, R., and K. J. Kim, "Mode Growth and Competition in the X-Ray Free-Electron Laser Start-Up from Noise," *Phys. Rev. ST Accel. Beams* **12**(7) (2009), 070702.

Non-Refereed Publications and Presentations

Kim, K.-J., "Promises and Challenges of X Ray FEL Oscillator," presented at X Ray FEL Workshop, Lawrence Berkeley National Laboratory, Berkeley, CA, Oct. 23, 2008.

Kim, K.-J., "Recent Advances in Hard X Ray FEL Oscillator," presented at the Advanced Photon Source Meeting, Pittsburgh, PA, March 17, 2009.

Lindberg, R., and K.-J. Kim, "Parameter Study for the X Ray Free-Electron Laser," presented at Particle Accelerator Conference (PAC09), Vancouver, British Columbia, Canada, May 4–8, 2009.

Shvyd'ko, Y., "X-Ray Free Electron Laser Oscillator: A Future Fully Coherent X-Ray Source," presented at Physics of Quantum Electronics (PQE) -2009, Snowbird, UT, Jan. 4–8, 2009.

Ultra-Fast X-Ray Tracking of Laser-Controlled Molecular Motions

2008-161-R1

Linda Young, Bernhard W. Adams, Dohn A. Arms, Klaus Attenkofer, Lin X. Chen, Eric M. Dufresne, Elliot P. Kanter, Bertold M. Kraessig, Yuelin Li, Robin Santra, Stephen H. Southworth, Donald A. Walko, and Jin Wang

Project Description

A fundamental and enduring challenge in science has been the quest to understand the relationship between structure and function in complex systems. Ultrafast x-ray science allows us to observe motion on atomic time and length scales. Advances in optical laser technology permit photonic control of atomic and electron motion. In this project, we merge these two frontiers to tackle a 21st century challenge: observation of laser-controlled electron and atomic motion using ultra-fast x rays.

Mission Relevance

This project is relevant to DOE's mission in science. As the steward of advanced photon sources in the United States, the Office Basic Energy Sciences (BES) is interested in advancing the capabilities of these tools. Historically, x-rays have been used primarily for structural studies. This project will expand capabilities for time-domain x-ray studies by providing high-repetition-rate laser excitation sources that allow efficient use of the x-ray flux, enhancing statistical precision 6,500-fold to enable a wide array of applications.

FY 2009 Results and Accomplishments

During FY08, we prepared specifications for and procured a custom master oscillator power amplifier laser system (DUETTO), operating at 1.06 μm (micrometers) with 10-Watt average power, variable pulse width (10 and 130 picoseconds), and variable repetition rate (50 kHz–6.5 MHz). We also designed a passive enhancement cavity.

During FY09, we implemented laser synchronization, built an enhancement cavity, and developed solution-phase targets. For laser synchronization, we built customized synchronization/pulse-picking electronics to lock the master oscillator of the DUETTO (78 MHz) with the 352-MHz storage ring radio frequency to a precision of 250 femtoseconds over the entire range of repetition rates. Variable repetition rate is a valuable tuning parameter to adjust excitation conditions to match the sample requirements.

We procured optics for and fabricated a passive enhancement cavity operating at 6.5 MHz using a Herriot cell to achieve the requisite 46-meter path length (Figure 1). The cavity is designed to allow coherent addition of successive laser pulses to amplify individual pulse energies by approximately 500 times, as required for strong-field molecular alignment experiments. The cavity was tested at the Joint Institute for Laboratory Astrophysics (JILA) by using a continuous wave laser having excellent phase stability and has now been transferred to Argonne for testing with the DUETTO.

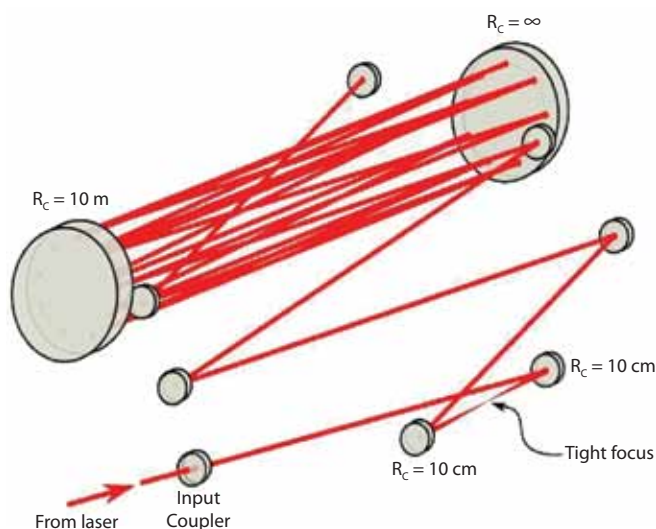


Figure 1. Passive enhancement cavity for coherent addition of pulses at a repetition rate of 6.5 MHz. The optical path length is 46 m. Active stabilization with a piezoelectric transducer (PZT)-actuated mirror was demonstrated to 250 kHz.

Also in FY09, we designed a fast-flowing liquid jet target system with the optical quality required to achieve an optical laser focus of a few microns for x-ray spectroscopy. Surrounding the liquid jet target are fast, large, solid-angle x-ray fluorescence detectors that allow signal processing within 150 nanoseconds. We also designed an *in situ* absorption monitoring system consisting of a white light source and spectrometer to detect optical- or x-ray-induced damage.

Proposed Work for FY 2010

Our principal objective for FY10 is to perform first experiments with the high-repetition-rate laser system at the Advance Photon Source (APS) and understand laser-/x-ray-induced damage as a function of laser and x-ray fluence. The simplest demonstration is a measurement of the near-edge spectrum of a transient excited state of a metal ligand charge transfer complex in solution. We initially plan to test the fast-flowing liquid jet target, absorption damage monitor, and single-photon counting detection system by using x rays. We will concurrently test the enhancement cavity offline by using the DUETTO. Following this testing, the DUETTO will be moved to the APS and used for initial solution-phase experiments with photo-excited targets. These first experiments will quantify laser- and x-ray-induced damage, explore the range of useful repetition rates for solution-phase experiments, and quantify the enhanced spectroscopic precision available at higher repetition rates.

Non-Refereed Publications and Presentations

March, A.M., S.H. Southworth, E.P. Kanter, B. Krässig, A. Stickrath, L.X. Chen, D. Tiede, Y. Li, E.M. Dufresne, D. Yost, T. Schibli, J. Ye, and L. Young, "Ultra-fast/Ultra-small Laser/X-Ray Techniques at High Repetition Rate," X-Ray Science Gordon Conference, Waterville, ME, August 2–7, 2009.

Stickrath, A.B., J.V. Lockard, X. Zhang, K. Attenkofer, L.X. Chen, and R.J. Sension, "Watching Chemical Reactions in Action: Time-Resolved XAFS Characterization of a Light-Triggered Metal-to-Ligand Charge Transfer (MLCT) Intermediate State in the B12 Cofactor Methylcobalamin," Poster Presentation at the X-Ray Science Gordon Conference, Waterville, ME, August 2–7, 2009.

Young, L., S.H. Southworth, E.P. Kanter, B. Krässig, A.M. March, A. Stickrath, L.X. Chen, D. Tiede, Y. Li, E.M. Dufresne, D. Yost, T. Schibli, and J. Ye, "Ultra-Fast/Ultra-Small Laser/X-Ray Techniques at High Repetition Rate," APS User Meeting, Argonne, IL, May 2009.

Coherent Diffraction Imaging of Nonperiodic Materials

2008-171-R1

Ian McNulty, Paul H. Fuoss, Jörg M. Maser, Stephen K. Streiffer, and Linda Young

Project Description

Coherent x-ray diffractive imaging (CDI) is a rapidly advancing method for determining the structures of objects by numerically inverting their coherent diffraction patterns. The forward-directed CDI geometry is suited to imaging noncrystalline and

highly disordered systems. The Bragg geometry provides sensitivity to strain and substructure in crystalline specimens at specific lattice configurations. Both approaches offer imaging at diffraction-limited resolution without the limitations of x-ray optics. We combined theory and experimental efforts to address high-impact questions in materials science, nanoscience, and biological science.

Mission Relevance

This project is relevant to DOE's mission in science. Hard x-ray science and nanoscale research contribute to work that requires high-resolution x-ray microscopy, x-ray scattering, and nanomaterials synthesis and characterization. Establishing and strengthening CDI approaches will leverage DOE's existing instrumentation and give DOE a qualitatively new leading-edge characterization capability, with both instrumentation and computing strengths.

FY 2009 Results and Accomplishments

We continued applying our theoretical and experimental capabilities to pursue coherent diffractive imaging. We established Bragg, small-angle scanned (ptychographic), and Fresnel coherent diffractive x-ray imaging methods and developed resonant and nonresonant approaches in both the soft and hard x-ray ranges. We made significant progress on theory tools, which now encompass Fresnel CDI, ptychography, and Bragg CDI. Instruments developed in this effort include an annealing stage and an *in situ* dealloying cell, a magnetic field environment, a cryostat for the Bragg CDI diffractometer, a refurbished deep-depletion Peltier cooled detector, and a liquid-nitrogen-cooled detector with high sensitivity.

Our experimental efforts focused on materials and materials systems of scientific interest and technological relevance, including ferromagnetic domains in multilayer GdFe films, phase separation in manganite crystals, morphological changes in InO films, and porosity in dealloyed and coarsened Au nanofoams. The experiments were performed at Argonne's Advanced Photon Source (APS) beam lines. Figure 1 shows a reconstruction of ferromagnetically ordered domains in a multilayer GdFe film obtained by scanning CDI. The domain configuration of this system depends strongly on temperature and magnetic field. We studied its dependence on applied in-plane and out-of-plane fields up to 2 kG. This approach is sensitive to spin state at the nanoscale and is promising for element-specific nanoscale imaging of buried magnetic structures beyond the resolution of lenses. Figure 2 shows transmission x-ray microscope (TXM) and Fresnel CDI reconstructions of nanoporous gold specimens. The interface shape and surface normal distributions obtained from the TXM data show that the coarsening process does not proceed by bulk diffusion and the morphology is anisotropic to the 50 nm scale. The topology is consistent with a bicontinuous structure.

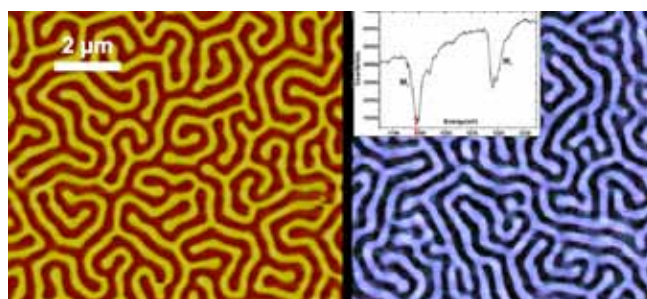


Figure 1. (Left) Magnetic force micrograph. (Right) Scanning CDI reconstruction of 260 nm ferromagnetic domains in different areas of the same GdFe multilayer film. Inset shows the Gd M4 and M5 resonances exploited for magnetic scattering contrast. This scan took 30 minutes to acquire.

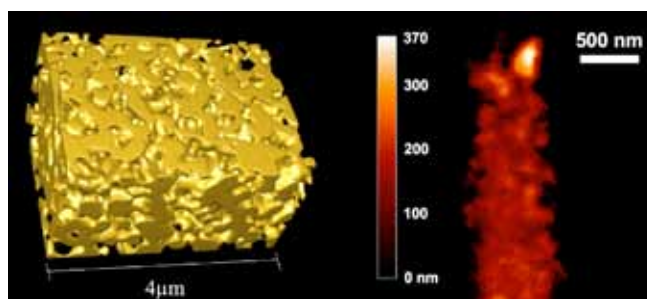


Figure 2. (Left) TXM reconstruction of a $2 \times 3 \times 4 \text{ mm}^3$ volume extracted of a dealloyed and coarsened nanoporous gold rod. (Right) FCDI reconstruction of a nanoporous gold rod, showing the $\sim 30 \text{ nm}$ pore structure after dealloying but not annealing-induced coarsening.

Proposed Work for FY 2010

We will emphasize experiment and the refinement of reconstruction algorithms. In the experiments, we will continue studying magnetically and electronically ordered complex oxide materials; systems such as phase change memory alloys, perpendicular anisotropy multilayers, core-shell nanoparticles, and lithographically fabricated GaN posts; and other novel nanocomposite films. We will focus on making these experimental and computing capabilities available to users so that coherent diffraction capabilities, which to date are mostly used by experts, will be used by the broader scientific community.

Refereed Publications

Abbey, B., G.J. Williams, M.A. Pfeifer, J.N. Clark, C.T. Putkunz, A. Torrance, I. McNulty, T.M. Levin, A.G. Peele, and K.A. Nugent, "Quantitative Coherent Diffractive Imaging of an Integrated Circuit at a Spatial Resolution of 20 nm," *Appl. Phys. Lett.* **93** (November 2008), 214101.

Shen, Q., "Coherent X-Ray Optics and Microscopy," Volume V, Chapter 27 in *Optical Society of America Handbook of X-Ray Optics*, edited by M. Bass, C. DeCusatis, J. Enoch, V. Lakshminarayanan, G. Li, C. Macdonald, V. Mahajan, and E. Van Stryland, Optical Society of America, McGraw-Hill, New York, NY, in press, November 2009.

Non-Refereed Publications and Presentations

Maser, J., “Hard X-Ray Microscopy – Status, Opportunities and Challenges,” presented at the European Synchrotron Radiation Facility (ESRF) NIMA and MIA Brainstorming Workshop, Grenoble, France, November 12, 2008.

Maser, J., “Analysis at the Nanoscale Using the Hard X-Ray Nanoprobe at Argonne National Laboratory,” presented at ICXOM20 International Conference on X-Ray Optics and Microanalysis, Karlsruhe, Germany, September 16, 2009.

McNulty, I., “Soft and Hard X-Ray Microscopy,” presented at Cheiron Summer School, Asia-Oceanic Forum for Synchrotron Radiation Research (AOFSSR), Super Photon Ring 8 (Spring-8), Harima Science Park City, Hyogo Prefecture, Japan, October 2008.

McNulty, I., “Coherent Imaging in Condensed Matter and Biology,” presented at National Science Foundation (NSF) Reverse Site Visit for the Wisconsin FEL Project, Arlington, VA, November 2008.

McNulty, I., “Opportunities for Nanoscale Imaging at High Pressure by Coherent X-Ray Diffraction, presented at Workshop on High-Pressure Synchrotron Science, Annual Users Meeting of the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, May 2009.

McNulty, I., “Coherent Diffractive X-Ray Imaging of Biomaterials,” presented at Workshop on Imaging Structural Hierarchy in Biological Systems, Annual Users Meeting of the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, May 2009.

High Brightness CW Injector Technology and Design Studies for the Energy Recovery Linac

2008-177-R1

Katherine C. Harkay, Yuelin Li, Karoly Nemeth, and Marion M. White

Project Description

Future energy-recovery linacs (ERLs) and free-electron lasers (FELs) can provide greatly enhanced x ray brightness and coherence. The performance parameters that are required for the electron injectors are an order of magnitude beyond the present state of the art. Our goal is to study the technology options suitable for an ERL injector (which are also suitable for an FEL) by conducting a physics characterization of

the cathode emission properties and designing and carrying out experimental studies related to the injector and emittance preservation. Our final goal is to be able to propose a full research and development effort for a specific injector or set of injectors that meets the requirements for next-generation light sources.

Mission Relevance

This work supports DOE’s basic energy science mission to develop and operate premier national scientific user facilities. Synchrotron light sources, such as the Advanced Photon Source (APS) at Argonne National Laboratory, are excellent tools for advancing many scientific frontiers. DOE recognizes the importance of using such tools for basic energy research and supports the development of next-generation light sources, such as the (LCLS) at Stanford Linear Accelerator Center (SLAC). A major accelerator upgrade is envisioned for APS in the next 10–20 years.

FY 2009 Results and Accomplishments

The main focus was on physics characterization of cathode photoemission properties. The effort is divided into two parts. First is developing the experimental study, which will implement angle-resolved photoemission spectroscopy (ARPES) surface analysis techniques. Second is conducting theoretical investigations of electron band structures for crystal surfaces; these are used to predict the transverse momentum distribution of the photoemitted electrons and thereby the emittance.

We made excellent progress in setting up the experiment. We were helped by R. Rosenberg (APS X Ray Science Division), who developed hardware for the ARPES ultra-high vacuum chamber, and L. Spentzouris (Illinois Institute of Technology), who developed the experimental system requirements. We also have most of the hardware for the analysis chamber. A simple time-of-flight (TOF) electron detector and an assembly that allows control of the detector angle with respect to the sample were developed. A detailed layout was made of the ARPES system. An internal technical note describes the experimental requirements in detail; it will be a key reference document.

On the theoretical side, a surface model was developed by fabricating a crystal surface slab with two-dimensional periodic boundary conditions and by computing the band structure by using density functional theory (DFT) analysis. The band structure and work functions were computed for several single crystals, and the agreement with experimental values is reasonable. We investigated a potential photocathode consisting of MgO monolayers on Ag, a well-studied material used in catalysis that exhibits negative electron affinity for Au clusters on the surface. DFT computations suggest that this system has a very small surface-parallel-momentum surface band, strongly correlated with the number of MgO monolayers (see

Figure 1). A potential configuration for a practical photocathode is shown in Figure 2. The analysis suggests an approach for other thin-layered systems. The quantum efficiency is under investigation.

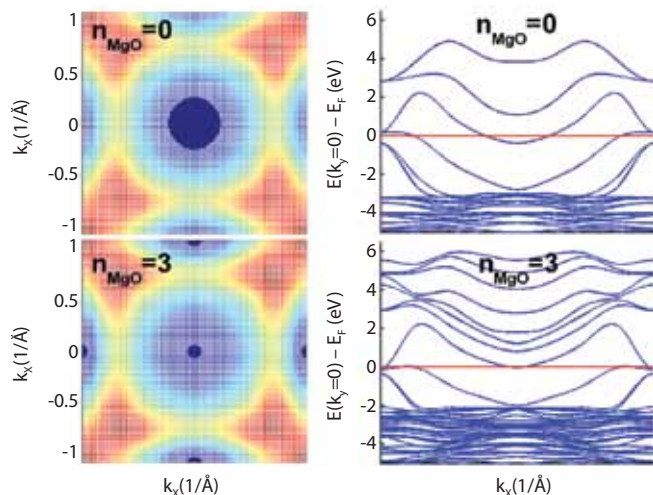


Figure 1. Lowest-energy electronic surface bands (left) and the band structure relative to the Fermi energy (right) in the Brillouin zone for $\text{MgO}[n_{\text{MgO}}]/\text{Ag}(001)[4]/\text{MgO}[n_{\text{MgO}}]$ system, where the bracketed value gives the number of monolayers. Dark blue regions denote momentum-space regions with occupied electrons.

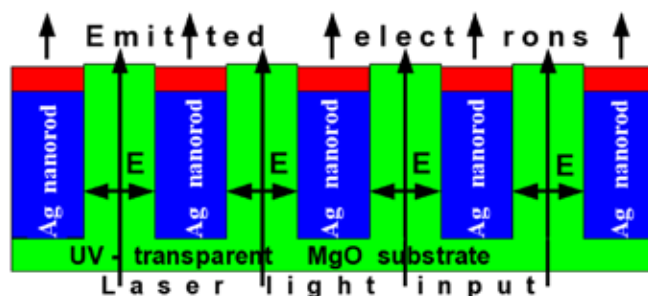


Figure 2. Schematic of a proposed photocathode based on a Ag/MgO (red) multilayer-topped Ag-nanorod array embedded in an ultraviolet-transparent MgO substrate. Typical dimensions of the nanorods are 50–200 nm in width and several microns in length. The laser electric field E is perpendicular to the nanorods and the Ag/MgO interface.

Proposed Work for FY 2010

Phase 1 of the ARPES system will be commissioned. Well-studied metallic crystals, including Cu(110) and Ag(100), will be characterized first. In phase 2, a sample transfer mechanism will be commissioned. Physics simulations will be used to model and optimize the ARPES system. An important goal of the experimental study is to verify theoretical predictions of the beam emittance based on the DFT electron band structure calculations. Follow-on funding will be required to study other crystals with favorable calculated properties.

Presentations and Non-Refereed Publications

Li, Y., S. Chemerisov, and J. Lewellen, "Laser Pulse Shaping for Generating Uniform three-Dimensional Ellipsoidal Electron Beams," *Phys. Rev. ST Accel. Beams* **12** (2009) 020702.

Nemeth, K., K.C. Harkay, M. van Veenendaal, L. Spentzouris, M. White, K. Attenkofer, and G. Srajer, "High Brightness Photocathodes through Ultra-Thin Surface Layers on Metals," submitted to *Phys. Rev. Lett.*

Non-Refereed Publications and Presentations

Harkay, K., "Ultra-Bright Electron Source Study for Accelerator Applications," presented at Photocathode Workshop, The University of Chicago, Chicago, IL, July 2009.

Li, Y., "Laser Pulse Shaping," presented at Energy Recovery Linac (ERL09) Conference, Cornell University, Ithaca, NY, June 8–12, 2009.

Harkay, K.C., Y. Li, K. Nemeth, R. Rosenberg, M. White, and L. Spentzouris, "Photocathode Studies for Ultra-Low Emittance Electron Sources," presented at 2009 Particle Accelerator Conference, Vancouver, British Columbia, Canada, May 4–8, 2009.

Harkay, K. (on behalf of Y. Li), "Laser Pulse Shaping Results at APS," presented at A0 Photoinjector Workshop, Fermi National Laboratory, Batavia, IL, January 29–30, 2009.

Development of Nanofabricated Superconducting RF for Improved SRF Performance

2008-178-R1

Michael J. Pellin and James H. Norem

Project Description

This project aims to produce superconducting radio frequency (SRF) cavities for accelerators by using atomic layer deposition (ALD). ALD seems ideal for coating SRF cavities. It offers precision synthesis of ultra-thin films on complex surfaces, films that are adherent and are pinhole-free — even at 1–2 nm (nanometer) film thicknesses. The goal is to produce cavities with higher gradients (acceleration per unit length) and significantly lower losses (determining the quality factor, $1/Q$; high Q means low loss).

Mission Relevance

The project is relevant to the DOE's missions in energy and basic science. About a dozen superconducting accelerators are being planned or are under construction around the world. Increases in gradient would decrease the length and capital cost of the machine. In addition, almost half of the cost of these facilities lies in the cryogenic plant to keep the modules cool, with the result that the power cost for these facilities can be as much as \$500 million over the life of a machine (~20 years). Use of ALD could result, for example, in dropping the cost of materials in accelerator facilities by as much as \$0.5 billion for the International Linear Collider and increased Q would significantly reduce refrigeration costs, and so operating costs would decrease significantly as well.

FY 2009 Results and Accomplishments

During FY09, we studied aspects of the chemistry of depositing superconducting materials via ALD. At the end of the fiscal year, the best result was a critical temperature of about 4.5 K for niobium nitride, the first superconducting measurement of this compound synthesized by ALD. Since then, the results improved to 9 K, which is equal to the performance of the best single-element superconductor. Studies also proceeded on the deposition of titanium nitride and niobium, with some synthetic success. We are studying improvements possible in the synthesis of these highly active materials and will begin using plasma-assisted ALD to produce higher-quality materials.

The low conductivity of current cavities seems to be a "local" phenomenon dominated by poor regions called "hot spots." Point-contact tunneling measurements as part of this project showed that defects in superconducting cavities caused significant differences in the zero bias current values between "good" and "bad" regions of the cavities. These results indicate that there are differences in the superconducting properties of these two regions, primarily in the electron density of states at the center of the superconducting band gap. This is new fundamental information pointing to the physical reasons hot spots arise and to new strategies for ameliorating their effects.

As part of this project, superconducting radio-frequency (srf) cavities have been coated by ALD and tested at Jefferson Lab. Of the three cavities we have tested, we improved the maximum gradient for one and reduced losses by a factor of 2 in the other two cavities (see Figure 1, which shows an improvement in Q [inverse of losses] by almost a factor of 2). In principle, this is just the beginning, since synthesis of better superconductors should improve both characteristics, making accelerators both shorter (lower construction cost) and more efficient (lower construction and operating costs).

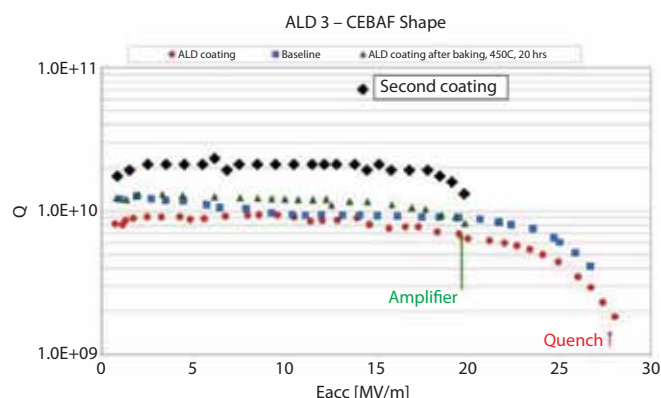


Figure 1. The effects of ALD coating on the acceleration gradient (horizontal axis is accelerating field) and Q (vertical axis). of an rf cavity measured at the Continuous Electron Beam Accelerator Facility (CEBAF) superconducting radio-frequency (srf) cavity in vertical test.

Proposed Work for FY 2010

In FY10, we will continue optimizing the chemistry of superconducting ALD surfaces, testing the coatings on coupons and in cavities. This testing will include modifications to the ALD synthesis process. We will also seek to extend our understanding of superconducting losses due to hot spots.

Refereed Publications

Proslier, Th., J. Zasadzinski, L. Colley, M. Pellin, J. Norem, J. Elam, C.Z. Antoine, R. Rimmer, and P. Kneisel, "Tunneling Study of SRF Cavity-grade Niobium," in *Proceedings of the Applied Superconductivity Conference*, Chicago, IL, August 17–22, 2008.

Proslier, Th., J.F. Zasadzinski, L. Cooley, C. Antoine, J. Moore, J. Norem, M. Pellin, and K.E. Gray, "Tunneling Study of Cavity-grade Nb: Possible Magnetic Scattering at the Surface," *Appl. Phys. Lett.* **92** (2008), 212505.

Proslier, Th., J. Zasadzinski, J. Moore, M. Pellin, J. Elam, L. Cooley, C. Antoine, J. Norem, and K.E. Gray, "Improvement and Protection of Niobium Surface Superconductivity by Atomic Layer Deposition and Heat Treatment," *Appl. Phys. Lett.* **93** (2008), 192504.

Insepov, Z., J. Norem, D. Huang, S. Mahalingham, and S. Veitzer, "The Problem of RF Gradient Limits," in *Proceedings of NuFact09*, Chicago, IL, July 20–25, 2009, AIP Conference proceedings (in press).

Proslier, Th., J. Norem, J. Elam, M. Pellin, J. Zasadzinski, G. Ciovati, and P. Kneisel, "Results from Point Contact Tunneling Spectroscopy and Atomic Layer Deposition," in *Proceedings of SRF1009*, Berlin, September 20–25, 2009 (in press).

Non-Refereed Publications and Presentations

Proslir, Th., Y. Ha, J. Zasadzinski, G. Cipvati, P. Kneisel, C. Reece, R. Rimmer, A. Gurevich, L. Cooley, G. Wu, M. Pellin, J. Norem, J. Elam, and C. Antoine, "Recent Results from Tests of Atomic Layer Deposition (ALD) for Superconducting rf," in *Proceedings of the Particle Accelerator Conference*, May 4–8, 2009, Vancouver, Canada.

Novel Concepts in Streak-Camera Development and Applications

2008-183-R1

Bernhard W. Adams, Klaus Attenkofer, Lin X. Chen, Eric M. Dufresne, John Lee, Antonino Miceli, Tijana Rajh, and Stephen Ross

Project Description

The need for x-ray detectors with ultrahigh time resolution has been evident for many years, as x ray scattering and spectroscopy have been increasingly applied to study the elementary processes of chemistry and condensed-matter physics. X ray structural studies and x-ray spectroscopy are important tools for obtaining information on chemistry and condensed-matter dynamics at the elementary length scale of the chemical bond. Many important processes in these fields take place on the time scale of a few picoseconds (ps). To observe these processes at their elementary level in space and time, x rays need to be recorded with ultrahigh time resolution. A better understanding of the dynamics of light-induced electronic charge transfer helps in, among other goals, developing artificial photosynthesis. Like all synchrotron radiation sources, the APS has an intrinsic time resolution on the order of 100 ps, which is given by its electron bunch length. Higher time resolutions can be reached only with fast x ray detectors, such as streak cameras. The goals of this effort are to improve the time resolution of x ray streak cameras, mitigate some of their weaknesses, and use an x ray streak camera in time-resolved x ray science at the Advanced Photon Source (APS). A streak camera is an electron-optical device that can very rapidly deflect an electron beam, thus streaking it out over a phosphor screen. A time-dependent electron current due to rapidly changing x ray intensity on a photocathode inside the streak camera produces a spatial modulation of the streak, imaging time along a spatial coordinate.

Mission Relevance

This project is tied to DOE's missions in science, energy, environment, and national security. Research and development in such critical areas as femtochemistry, structural biology, materials research, and plasma physics will be directly enhanced by this project. The improved technology will also likely be of interest to the National Institutes of Health, the Nuclear Regulatory Commission, and the Department of Defense.

FY 2009 Results and Accomplishments

We put a test chamber for the quantitative measurement of photoelectron emission yield from photocathode materials into service and took our first measurements with it.

We fabricated a test station for photoconductive switches in the laser laboratory of the APS sector 7 beamline. We successfully tested a photoconductive switch designed to control the shape of the deflection pulse. An improved version of the switch is being tested now.

We developed a computational model of a streak camera with magnetic focusing as a basis for further improving the electron optics. This work is ongoing.

We used an x-ray streak camera in experiments to study the dynamics of laser-induced intramolecular charge transfer in iron pentacarbonyl and to study the collective structural relaxation following laser-induced charge transfer in a molecular crystal of DIABN.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Dufresne, E.M., B. Adams, D.A. Arms, M. Chollet, E.C. Landahl, Y. Li, D.A. Walko, and J. Wang, "Time-Resolved Research at the Advanced Photon Source Beamline 7-ID," in *Proceedings of the 10th International Conference on Synchrotron Radiation Instrumentation (SRI09)*, Melbourne, Australia, September 27–October 2, 2009; (in print) <http://proceedings.aip.org/proceedings/>.

Non-Refereed Presentation

Dufresne, E.M., "Time-Resolved Research at the Advanced Photon Source Beamline 7-ID," presented at SRI09, Melbourne, Australia, September 27–October 2, 2009.

Feasibility Studies and Pre-Conceptual Design of Continuous Wave (CW) Superconducting, RF-Deflecting Cavities for the Generation of Short X-Ray Pulses at the Advanced Photon Source

2008-190-R1

Alireza Nassiri, Michael D. Borland, Katherine C. Harkay, and Geoff Waldschmidt

Project Description

This project focuses on the design and development of superconducting transverse RF structures (“crab cavities”) for the production of short x-ray pulses at the Advanced Photon Source (APS) (Figure 1). In this concept, known as Zholents’ scheme¹, transverse-deflecting, superconducting radio frequency (SRF) cavities are used to impose a correlation (“chirp”) between the longitudinal position of an electron within the electrons population density, known as the “electron bunch” and its vertical momentum. The x-rays emitted by each electron tend to travel along the path of the electron itself. Hence, by placing an undulator just downstream of the crab cavity, for example, we can produce a chirped x-ray beam. At a sufficient distance (e.g., 30 m) from the undulator, this angular chirp will have evolved into a spatial chirp, so that a strong correlation appears in the x-ray pulse between arrival time and vertical coordinate. Use of vertical slits then permits filtering the pulse in the time dimension, allowing production of an x-ray pulse that is shorter than the electron.

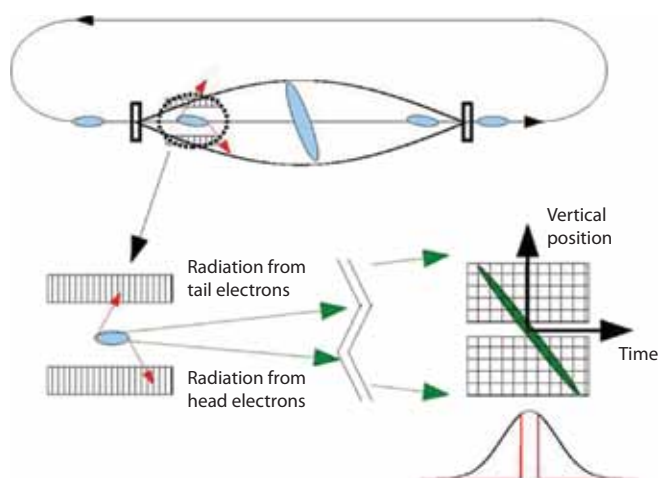


Figure 1. Illustration of Zholents’ scheme for short x-ray pulse production using deflecting RF cavities in a storage ring.

Mission Relevance

This project is tied to DOE’s mission in science. The immediate beneficiaries of this work will be members of the short-pulse, time-resolved x-ray science community, because this scheme will make it possible to deliver picosecond (ps) -type x-ray pulses at very high repetition rates. If successful, it will be the first synchrotron-based, ps-scale x-ray pulse user facility. This work will also lay the groundwork for the R&D efforts for the generation of pico- or sub-picosecond x-ray pulses for APS’s energy recovery linac (ERL) upgrade. In addition, other synchrotron facilities around the world may be interested in implementing such a scheme to extend their synchrotron x-ray source capabilities to include the generation of short x-ray pulses for time-resolved experiments.

FY 2009 Results and Accomplishments

In FY09, the design and fabrication of a niobium single-cell structure with an on-cell waveguide damping (Figure 2) and a niobium 2-cell structure (Figure 3) were completed. These structures were fabricated and tested in association with the Jefferson National Accelerator Laboratory. Initial tests results in achieving the required deflecting field gradient and the cavity quality factor (Q) was encouraging. These measurements also revealed multipacting (breakdown) activities in the vicinity of the on-cell damping waveguide. The multipacting issues are being analyzed by using a three-dimensional simulation code in association with Stanford Linear Accelerator Laboratory. On the basis of this analysis, the cavity’s shape and fabrication process will be modified to mitigate this problem. In FY09, we also designed and fabricated a novel 2.5-cell deflecting structure (Figure 4) made of copper as part of our cavities modeling effort. This cavity is now being tested.



Figure 2. A single-cell niobium RF-deflecting cavity with an on-cell waveguide damper.



Figure 3. Model of a 2-cell niobium RF-deflecting cavity.



Figure 4. Model of a 2.5-cell copper RF-deflecting cavity.

Proposed Work for FY 2010

In FY10, our proposed work includes the following:

- Final design of a single-cell cavity with on-cell or beam pipe waveguide damping
- Final design of a three-cell SRF niobium deflecting cavity
- Development of an optimized single-cell niobium cavity with waveguide damper
- Development of a final three-cell niobium cavity
- Completion of vertical cold test and characterization
- Modeling and simulation of deflecting cavity RF control system
- Development of LLRF measurement techniques
- Publishing of results

Non-Refereed Publications and Presentations

Waldschmidt, G., L.H. Morrison, A. Nassiri, R.A. Rimmer, K. Tian, and H. Wang, "Superconducting Multi-Cell Deflecting Cavity for Short-Pulse X-Ray Generation at the Advanced Photon Source," *Proc. of the 2009 Particle Accelerator Conference (PAC09)*, Vancouver, BC, Canada, paper TU5RFP003 (2009), to be published (<http://www.jacow.org>).

Wang, H., G. Cheng, G. Ciovati, P. Kneisel, R.A. Rimmer, K. Tian, L. Turling, A. Nassiri, and G. Waldschmidt, "Design of Superconducting Parallel Bar Deflecting and Crabbing RF Structures," *Proc. of the 2009 Particle Accelerator Conference (PAC09)*, Vancouver, BC, Canada paper WE5PFP059 (2009), to be published (<http://www.jacow.org>).

¹ See: Zholents, A., P. Heimann, M. Zolotarev, and J. Byrd, *Nuclear Instruments and Methods (NIM) A* **425** (1999), 385–389

Catalyst Station at APS Beamline 9-BM

2009-050-N0

Steve M. Heald, Trudy B. Bolin, Jeffrey T. Miller, Peter C. Stair, and Randall E. Winans

Project Description

This project readies and upgrades beamline 9-BM and the associated laboratory for catalyst research. Synchrotron radiation methods have important applications in catalyst research, and the completion of the project will allow us to make concurrent x-ray absorption fine structure (XAFS) spectroscopy and powder diffraction measurements on catalysts under operando conditions.

Mission Relevance

The project is relevant to DOE's missions in basic science, energy, and the environment. Catalysis is an essential technology for economic prosperity, energy security, and environmental preservation in the 21st century. The use of synchrotron radiation to study catalysts has a long history, and most synchrotron facilities have beamlines with equipment for catalyst research. This project will bring the APS to the state of the art for catalyst research at synchrotron facilities. It will provide the capability for concurrent operando XAFS and powder diffraction, a capability found at only a few beamlines worldwide. It will also be the first step in facilitating catalyst research at other beamlines at the APS.

FY 2009 Results and Accomplishments

Most of the effort in 2009 was aimed at getting the 9-BM-C station ready for *in situ* experiments. Beamline 9-BM already has a station (9-BM-B) optimized for low-energy operations, but with limited capabilities for *in situ* work. Additionally, we began upgrading the associated laboratory and characterizing the beamline monochromator.

The additions to 9-BM-C include a new experimental table and a heavy-duty sample positioner. To run these, we have installed a full set of power supplies, motor drivers, and a new VME (Virtual Machine Environment) crate for control. We also transferred a full XAFS ion chamber detector setup from the 33 BM beamline. All of these have been mounted on X95 rails for flexible positioning of detectors and sample stages. Ventilated gas cabinets, hazardous gas alarms, and an automated gas handling system were installed, allowing the use of hazardous gases. A mass spectrometer was also commissioned for characterizing reaction products. These additions allowed us to make the first experimental runs with catalysts in *in situ* cells in 9-BM-C. Figure 1 shows an example of the data. We chose to test our set up by looking at a system already under study programmatically. The sample was $\text{Os}_3(\text{CO})_{12}$ supported on MgO powder, with an osmium loading of 1 wt% (typical of supported metal catalysts). The aim of the experiment was to determine the temperature at which the triosmium clusters were decarbonylated and began aggregating into larger clusters; the results complement those obtained from similar experiments with Os-Ru bimetallic catalyst.

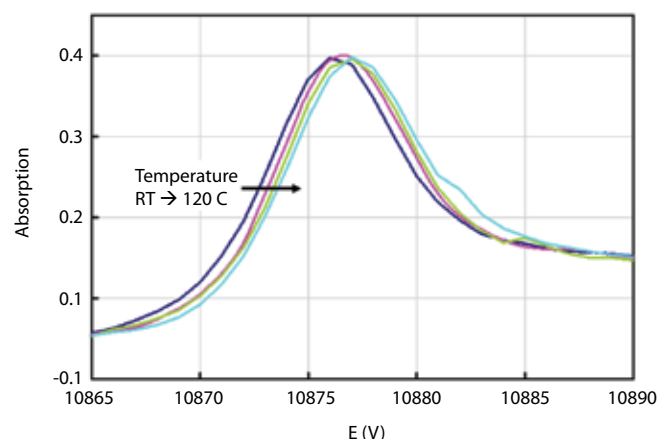


Figure 1. Example of *in situ* x-ray absorption near edge structure data taken in hutch 9-BM-C showing a valence change as the sample temperature was ramped continuously from room temperature to 120 C. The sample is the supported Osmium catalyst described in the text. The data was collected at the Os L_3 edge.

The associated laboratory was also upgraded to support catalyst research. Foremost was the commissioning of a high quality glove box for sample preparation and handling. This was a key capability enabling the early experiments. We also began outfitting the lab with many common sample preparation tools including a pellet press and precision balance.

Proposed Work for FY 2010

A postdoc has been hired who will assist in the upgrade activities and conduct the further experiments to test the equipment. Although initial experiments have been performed with the flow system, commissioning the full capabilities of the flow system and beam line operation will require further testing and troubleshooting. The 9-BM-C hutch upgrade will continue with installation of more user friendly data acquisition software. This will include better integration of the gas handling system and mass spectrometer into the software to allow automated sequencing of the sample preparation and data acquisition. The overall hazardous exhaust capabilities for 9-BM will be upgraded with a new blower and expanded ductwork. We will also continue to upgrade the sample preparation capabilities with an additional glove box for handling “dirty” samples (i.e., samples containing sulfur compounds). To support the glove boxes, a dry nitrogen gas supply will be connected to the nearby liquid nitrogen supply. This installation will be shared with Sectors 9, 10, 11, and 12, helping to support catalyst research at all of these sectors.

We will provide a larger variety of *in situ* sample cells, including cells allowing for powder diffraction concurrent with spectroscopy. We will be installing the software and electronics to support a 13-element germanium detector. This will either be an existing Princeton Gamma-Tech detector from Sector 20 or, if funding allows, a new Canberra detector. Powder diffraction studies will be demonstrated by using area detectors available from the APS equipment pool.

In the following months, we expect to characterize materials that have been used as a catalyst in glycerol and/or formic acid conversion, as we try to elucidate the state of the supported metal during catalysis. These catalysts will contain nanometer and/or sub-nanometer-sized clusters of group-8 metals (e.g., Pt, Pd) supported over a variety of supports. Experiments such as XAS-TPR and XAS-TPO will be performed to assess the state of the metal during catalysis.

Non-Refereed Publications and Presentations

Heald, S., R. Winans, P. Stair, J. Miller, and T. Bolin, “Catalyst Center at the Advanced Photon Source beamline 9-BM,” poster presentations at the 14th International Conference on XAFS, Camerino Italy, July 2009; at the Advanced Photon Source Users meeting, May 2009; and at the Catalysis Club of Chicago Spring Symposium, May 2009.

Large-Scale Beam Dynamics Optimization for More Efficient Operation of Large User Facilities

2009-071-N0

Peter N. Ostroumov, Brahim Mustapha, Jerry A. Nolen, Richard C. Pardo, and Jin Xu

Project Description

We plan to develop a realistic computer model that could be reliably used to operate an accelerator-based user facility. This would require the development of a realistic 3D model for every element on the beamline and a good understanding of the initial beam parameters at the source by combining source models and beam measurements. It will also require the development of specific interfaces between the beam diagnostic devices and the beam dynamics code, in addition to the development of all possible optimization tools.

Mission Relevance

The project is relevant to DOE's basic science mission. The successful application to the Argonne Tandem Linac Accelerator System (ATLAS) and the Californium Rare Isotope Breeder Upgrade (CARIBU) under development will improve beam transmission, which is critical for radioactive beams, and should also reduce facility downtime. It will additionally serve as an important development for the future Facility for Rare Isotope Beams and other high-power linac-based facilities.

FY 2009 Results and Accomplishments

Preliminary Efficiency Studies of ATLAS. We have a full 3D model of the existing ATLAS starting from the ion source to the end of the linac. We recently performed preliminary efficiency studies of the Positive Ion Injector (PII), the initial part of the linac. The injector section is one of the most critical parts of any accelerator because it is responsible for initial beam formation, which directly affects the quality of the output beam. The results of these studies helped us to better understand the limitations of the existing ATLAS and to clarify the path for future upgrade options. Figure 1 (top) shows the transverse and longitudinal acceptance of the PII. It reveals a small longitudinal acceptance, which often results in coupling between the transverse and longitudinal motion and limiting the transmission of the beam and, consequently, the maximum beam intensity. Figure 1 (bottom) shows the same acceptance plots for a proposed radio-frequency quadrupole (RFQ) replacing the first cryomodule of the PII. The RFQ has a much larger longitudinal acceptance and controls much better the for-

mation of the initial beam, thanks to its adiabatic bunching. After installing the RFQ, we expect to increase the intensity of most ATLAS beams by a factor of 10. The characterization of the beam from the ion source and experimental studies of the transmission for the different sections of ATLAS are under way.

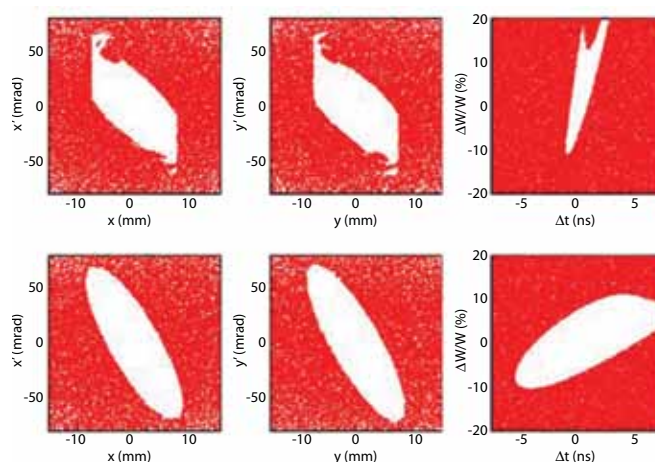


Figure 1. (top) Horizontal, vertical, and longitudinal acceptance plots for the PII; (bottom) the same plots for the proposed RFQ replacing the first cryomodule of the PII.

Implementation and Application of Parallel Genetic Optimization. Very recently, we implemented an evolutionary genetic optimizer into the beam dynamics code TRACK. As a first application, we tried to optimize the phases and amplitudes for the four harmonics of a multi-harmonic buncher (MHB) used as a pre-buncher in front of the RFQ being designed for the ATLAS Efficiency and Intensity Upgrade. Starting from a manually optimized case with only 72% of the beam captured by the RFQ, we were able to reach 80.5% capture after optimization. Note that 80% is the practical limit for an MHB-RFQ setup. To study the convergence of the genetic optimizer, we compared its result to the result from a 2D map in the case of a two-parameter optimization. Figure 2 shows the results for both cases, proving the convergence of the genetic optimizer. Larger-scale optimizations are now being developed.

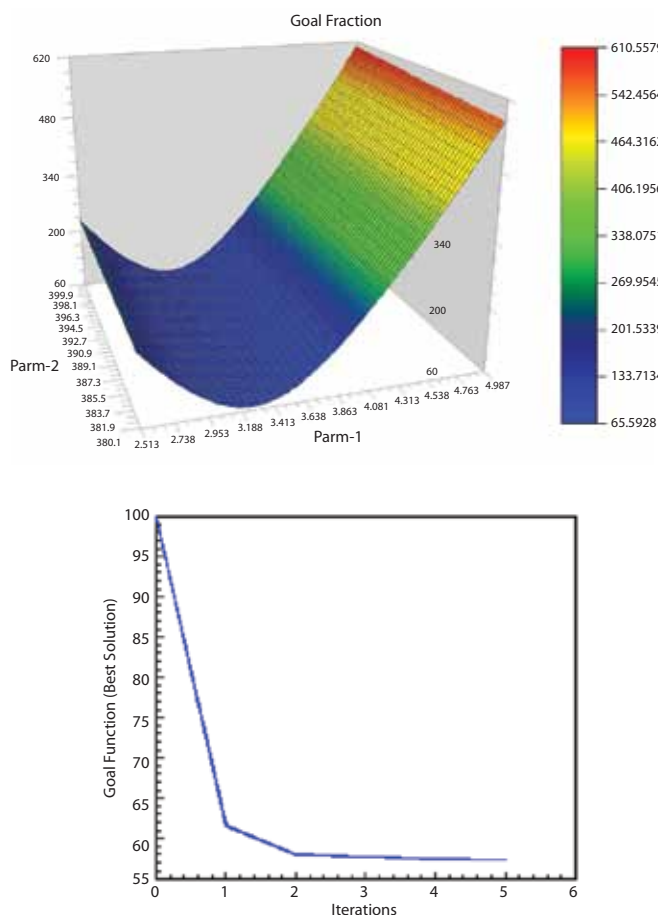


Figure 2. Comparison of the result of a 2D map (top) with the result of the newly implemented genetic optimizer (bottom) for a two-parameter optimization problem. The top plot shows the goal function to be minimized on the vertical axis (the function values are decreasing from red to blue) as a function of the two parameters of the problem mapped uniformly in one hundred steps each. The bottom plot shows the same goal function as function of the iteration number of the genetic optimizer, proving its convergence to the same minimal value obtained from the 2D map (top plot) in 5 iterations.

Proposed Work for FY 2010

We will develop a good understanding of the initial beam conditions at the electron cyclotron resonance ion sources; perform appropriate measurements for general characterization of the beamline; and develop specific optimization tools to help reproduce the measured data.

Refereed Publications

Ostroumov, P.N., S.A. Kondrashev, B. Mustapha, R. Scott, and N.E. Vinogradov, "Analysis and Recombination of Multiple-Charge-State Beams from an Electron Cyclotron Resonance Ion Source," *Phys. Rev. S. T. Accel. Beams* **12** (2009), 010101.

Non-Refereed Publications and Presentations

Mustapha, B., V.N. Aseev, and P.N. Ostroumov, "A Realistic Corrective Steering Algorithm: Formalism and Applications," *Proceedings of PAC (Particle Accelerator Conference) 2009*, May 4–8, 2009, Vancouver, Canada.

Mustapha, B., and P.N. Ostroumov, "Optimization Algorithms for Accelerator Physics Problems," (invited talk) *Proceedings of ICAP (International Conference on Applied Physics)*, August 31–September 4, 2009, San Francisco, CA.

Mustapha, B., J. Xu, P.N. Ostroumov, and J.-P. Carneiro, "Large Scale Simulations of the Fermilab 8 GeV H-minus Linac: Beam Loss Studies from Machine Errors and H-minus Stripping," *Proceedings of PAC 2009*, May 4–8, 2009, Vancouver, Canada.

Photocathodes Development for Accelerator R&D

2009-076-N0

Zikri Yusof, Matthew J. Virgo, Katherine C. Harkay, John Noonan, and Alexander V. Zinovev

Project Description

We propose to develop the next generation of photocathodes by using new semiconductor-based materials. This is a broad-based effort toward understanding the material properties of photocathodes and how such properties translate to photocathode performance in an accelerator. This will be an effort to fabricate, process, and study high-performance photocathodes that fulfill the needs of current and future accelerator-based user facilities. In particular, we will seek photocathodes that can produce a high-brightness electron beams, have high quantum efficiencies (QEs), and have the potential to produce very low beam emittance.

Mission Relevance

This project is tied to DOE's mission in science. Plans for next-generation accelerators are now being defined. Notably, DOE's Office of Basic Energy Sciences is interested in developing next-generation light sources, and Office of High Energy Physics is preparing for a future linear collider. The U.S. Navy and the U.S. Air Force continue to work toward a high-power free electron laser. Because the cathodes available today will not meet the needs for many of these machines, the funding agencies will have to fund cathode research and development if they are to become a reality. Very few laboratories in the world have the capability to produce high-QE cathodes for photoinjectors, and the pool of experienced workers in this area is similarly small. There is a clear need for such expertise.

The project's impact would be broad, benefiting a large number of diverse facilities that require high brightness or more efficient light sources.

FY 2009 Results and Accomplishments

This effort embraces three broad areas: (1) the development and deployment of large (~1.2-inch-diameter) cesium telluride (Cs_2Te) photocathodes for accelerator photoinjectors; (2) the design of a response-time experimental system and the subsequent study of the response times of photocathodes; and (3) the investigation of other semiconductor photocathode materials, such as the gallium nitride family.

Development and deployment of Cs_2Te photocathode. The Cs_2Te photocathode has been shown to have a relatively high QE and to be quite robust in the hostile environment of an accelerator photoinjector. This has been chosen to be the photocathode for the Argonne Wakefield Accelerator's new photoinjector. The main thrust of the project is to fabricate a high-QE photocathode (>1%) and to design an ultrahigh vacuum transfer system connecting the fabrication system to the photoinjector beamline. Both goals have been accomplished.

Design, fabrication and study of the photocathode response time. This investigation addresses how long it takes for all electrons to be emitted after light impinges on a photocathode. The characteristic distribution time for the emitted photoelectrons is the response time. While metals typically have the shortest response time (on the order of femtoseconds), high-QE photocathodes, which are semiconductors, tend to have longer response times (picoseconds or longer). Proper and accurate characterization of the response times of high-QE photocathodes may be especially important for free-electron laser sources and for fast photodetectors.

The first phase of this effort has been devoted predominantly to the development of the anode assembly and the cathode processing system (see Figure 1). The experimental equipment needed for this purpose is under development. This includes an upgrade to an existing setup for measuring quantum efficiency, as well as a second chamber that will interface with a streak tube, which will be used to characterize response times. Samples will be transported between these two vacuum chambers via a load-lock. Design of the system is progressing toward completion. The designs that have been completed are in Figure 1.

We are investigating what samples are available for time-response characterization.

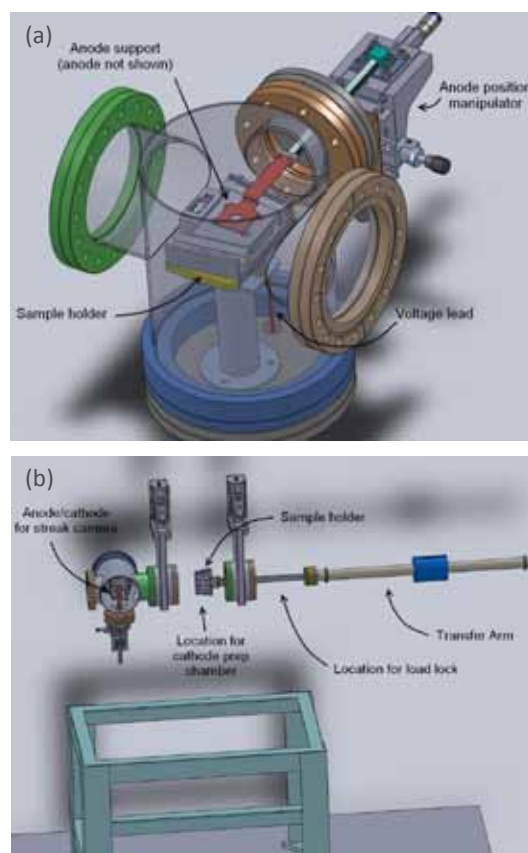


Figure 1. Rendering of the design of the apparatus to characterize the QE and response time of photocathodes: (a) Station for extracting picosecond-length electron bunches. These bunches are fed to the streak camera tube (not shown). The sample station is isolated from ground to support the accelerating voltage. (b) Complete system. The electron extraction station is on the left. The sample transfer arm is used to move the sample between the stations, which are separated by gate valves. The center station will be a preparation chamber where the samples are cleaned and activated. The load lock station will be on the right.

Proposed Work for FY 2010

The study of the high-QE photocathode fabrication process continues in the hope of refining the "recipe" and producing a higher QE. Future studies will involve the investigation of the lifetime of the QE both in pristine vacuum conditions and in the hostile environment of a high-gradient photoinjector. Design of the anode assembly and the cathode processing system will continue. The streak tube will be provided by the Ultrafast Physics Group (Sector 7) at the Advanced Photon Source. The design is a modification of their existing device. Many of the components are on hand.

We will be able to study GaN, as well as InGaN and AlGaN. We also plan to study AlGaN layers deposited on a conducting substrate, which would simplify their use in a radio-frequency gun. These studies may also include investigation into possible activation of the photocathode surface with cesium and the measurement of the QEs of these photocathodes.

Improving Charged Particle Optical Device Designs: From Realistic 3D Field Maps to Transfer Maps

2009-080-N0

Bela Erdelyi, Shashikant L. Manikonda, and Jerry A. Nolen

Project Description

Although accelerators and other particle-beam devices have been ubiquitous in science for over a century, to date there is no seamless way to bridge the gap between measurements of electromagnetic fields and realistic modeling of the devices based on these fields, including their design optimization. The latter has been elegantly solved over the last three decades by using transfer maps. In this project, we propose to develop methods and software that would solve the “from field maps to transfer maps” problem, as well as achieve design optimization by using extracted transfer maps.

Mission Relevance

This project is tied to DOE’s mission in science. The project will provide a general framework that will benefit facilities that require high-precision modeling, simulation, and optimization of the creation, acceleration, transport, and manipulation of charged particle beams. The project also will be of interest to the National Science Foundation and to commercial magnet manufacturers.

FY 2009 Results and Accomplishments

We have done preliminary studies on transfer map extraction techniques by using measured electromagnetic field data. Work was done to improve the transfer map extraction algorithm and to port it to high-performance clusters. The code was implemented in the COSY INFINITY scripting language. We also identified several respects in which the accuracy and speed of execution of the map extraction technique can be further improved. The map extraction algorithm has been applied to multipole magnets in the Super Separator Spectrometer project at GANIL (Le Grand Accélérateur National d’Ions Lourds), France; the BigRIPS quadrupole magnets for the Radioactive Ion Beam Facility in Japan; and the CARIBU electric hexapole magnet at ATLAS.

Proposed Work for FY 2010

The map extraction tool will be optimized further for speed and accuracy. A framework for using the extracted maps for full beam-optics design optimization will be developed and ported to high-performance computing platforms.

Non-Refereed Publications and Presentations

Nolen, J., “Superconducting Multipoles Option for Super Separator Spectrometer (S³),” presented at Super Separator Spectrometer Workshop, GANIL, France, June 15–17, 2009.

Concept of Ultra-Low Emittance Injector for Future X-Ray FEL Oscillator

2009-085-N0

Kwang-Je Kim, Alireza Nassiri, Nicholas S. Sereno, and Michael D. Borland

Project Description

An X-ray free electron laser oscillator (XFEL) is promising to provide record high spectral coherence and record high average power. This instrument requires a continuous sequence of electron bunches with ultra-low emittance but with a low bunch charge, repeating at a rate between 1 MHz and 3 MHz. The standard system for a low-emittance injector producing high-bunch charges for high-gain free electron lasers (FEL) begins with a *photocathode* gun. For XFEL applications, a more promising alternative is to start by extracting low-current, long-pulse beams from a *thermionic* cathode, thus minimizing the space charge effect and the need for its compensation. In this project, we are developing a means for the production of ultra-low emittance electron beams (50 MW, 50 MeV) as an injector for an XFEL.

Mission Relevance

This project is tied to DOE’s mission in science. DOE has a mandate to provide the higher-performance x-ray facilities that are essential for developing advanced materials and techniques. As such, DOE is seeking to develop one or more of these high-performance x-ray facilities, and the XFEL is one of the serious contenders. XFELs that can be fabricated by using the injectors of the kind specified in this project may be regarded as a new option for the next-generation x-ray sources, in addition to the high-gain FELs and spontaneous sources from energy recovery linacs (ERLs). Project success will make the case for the XFEL, either as a part of an ERL or as an independent, green-field facility. Beneficiaries of this injector development will be current light-source users who are looking for the higher-performance facilities of the future.

FY 2009 Results and Accomplishments

The general layout of an injector producing a continuous stream of ultra-low transverse emittance bunches with low intensity suitable for an XFEL is schematically shown in Figure 1. The design is inspired by the recent success of a thermionic gun injector employing pulsed direct-current voltage by

the RIKEN Spring 8 group for its FEL project. For our purpose, we employ a smaller cathode to produce smaller emittance and a low-frequency (100 MHz), continuous-wave (CW) radio-frequency (rf) cavity.

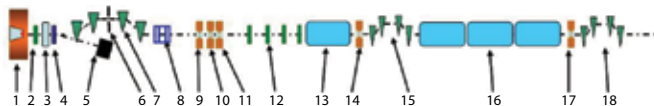


Figure 1. General Layout of the Ultra-low Emittance Injector:

- 1 – RF cavity with thermionic cathode (100 MHz, 1 MV)
- 2 – focusing solenoid
- 3 – rf chopper to form bunch repetition rate of 1 MHz to 3 MHz
- 4 – quadrupole
- 5 – beam dump
- 7 – chicane and slits (six) as an energy filter
- 8 – quadrupole triplet
- 9 – 100-MHz rf cavity
- 10 – monochromator of the beam energy ($f = 600$ MHz)
- 11 – velocity buncher ($f = 300$ MHz)
- 12 – focusing solenoids
- 13 – booster linac section ($f = 400$ MHz)
- 14 – high-harmonic cavity (1,300 MHz)
- 15 – bunch compressor-I
- 16 – superconducting linac section (552 MeV, $f = 1,300$ MHz)
- 17 – high-harmonic cavity (1,300 MHz)
- 18 – bunch compressor-II

Extensive optimization calculations were performed with the BlueGene/P supercomputer at Argonne, showing that the system can deliver the required beam performance.

We initiated a preliminary study of the candidates for the 100-MHz CW gun cavity. In parallel, we are also developing a 300-kV pulsed e-gun with low duty factor to demonstrate production of ultra-low emittance employing a CeB_6 (cerium hexaboride) thermal cathode with diameter less than 1 mm. The initial concept for a Marx-type pulse modulator was completed. The e-gun is followed by a beamline with diagnostics system to provide emittance measurements.

Total beam power extracted from the rf gun operating at 100 MHz will be too high for the slits of the energy filter. In addition, back-bombardment power to the cathode could be an issue. We are designing an experiment at the injector test stand of the Advanced Photon Source to test whether laser heating of the cathode at a repetition rate of the desired 1–3 MHz will obviate these issues.

Proposed Work for FY 2010

We will continue the optimization of the beam dynamics to determine whether a simpler injector configuration is feasible. We will complete a detailed concept of a test gun using a pulsed 300-kV voltage and proceed with fabrication of injector components. We will perform electrodynamics, structural,

and thermal optimization of the 100-MHz copper cavity for the electron gun suitable for 1-MV operation. We will fabricate and test a 300-kV Marx-type modulator and develop and fabricate a programmable logic controller-based system for the modulator.

Non-Refereed Publications and Presentations

Ostroumov, P.N., K.-J. Kim, and P. Piot, “Development of Ultra-Low Emittance Injector for Future X-Ray FEL Oscillator,” in *Proceedings of the LINAC-08*, p. 678 (2009), Linac 08, Victoria, BC, Canada, September 29–October 3, 2008.

Ostroumov, P.N., D. Capatina, K.-J. Kim, S.A. Kondrashev, B. Mustapha, and A. Nassiri, “Optimized Design of an Ultra-Low Emittance Injector for Future X-Ray FEL Oscillator,” presented at Particle Accelerator Conference, Vancouver, Canada, May 4–8, 2009.

Ostroumov, P.N., K.-J. Kim, and P. Piot, “Development of Ultra-Low Emittance Injector Based on Thermionic RF Gun,” presented at Workshop on X-Ray FELs, Lawrence Berkeley National Laboratory, October 23–25, 2008.

Advances in 2 Kelvin Superconducting Cavities for Future Accelerators

2009-158-NO

Michael P. Kelly, Joel D. Fuerst, Alireza Nassiri,
Scott M. Gerbick, and Mark J. Kedzie

Project Description

The objective of this project is to build and test a 2 (K) Kelvin superconducting radio-frequency (SRF) test cryostat applicable to the elliptical-cell cavities in the International Linear Collider (ILC) and the superconducting cavities for transmission electron microscopes (TEM). This capability will also allow testing SRF cavities by using new thin films coated by atomic layer deposition.

Mission Relevance

This project is relevant to DOE’s mission in science by establishing the next-generation particle accelerators for the delivery of intense, high-power, and/or very low emittance beams. For the next decade, SRF cavities will be the only viable technology capable of meeting these demands. Building and maintaining a world-leading 2 K SRF cavity and continuing to advance the state of the art for SRF cavity performance would be of great interest to the ILC and Project X at Fermi National Accelerator Laboratory (Fermilab).

FY 2009 Results and Accomplishments

We installed a new 2 K test cryostat in the SRF test area. Separately, we tested a set of TEM-class cavities, including six high-performance quarter-wave resonators, and assembled a half-wave resonator for testing in the new 2 K test cryostat in June 2009. We also tested six 1.3-GHz (gigahertz) single-cell elliptical cavities, which exceeded the ILC specification for accelerating gradient of 35 MV/m (megavolts/meter). Thus far, final testing has been performed at Fermilab, and the cavities need to be transferred to Argonne.

Proposed Work for FY 2010

Today's SRF cavities are typically limited due to a quench in the RF field at a corresponding surface magnetic field of $\sim 1,000$ gauss or just over half the theoretical limit for niobium. At present, we poorly understand the precise origin of the quench. To develop a systematic method that will achieve better performance, we propose to test cavity quench by exploiting recent investments in cavity processing, 2 K testing, and second sound capabilities. We will use recently developed RF systems for L-band (1.3 GHz) cavities for this test.

Non-Refereed Publications and Presentations

Kedzie, M., J.D. Fuerst, S.M. Gerbick, M.P. Kelly, and K.W. Shepard, "A Top Loading 2 Kelvin Test Cryostat for SRF Cavities," 14th International Conference on RF Superconductivity, Berlin, Germany, September 20–25, 2009.

Kelly, M.P., S.M. Gerbick, D.J. Bice, and G. Wu, "Electropolishing at ANL/FNAL," 14th International Conference on RF Superconductivity, Berlin, Germany, September 20-25, 2009.

A High-Performance Computational Framework for Structure Determination at Large-Scale Facilities

2009-226-NO

Raymond Osborn, Jorge J. Moré, and Brian H. Toby

Project Description

We are developing a computational framework that will advance the joint analysis of x ray and neutron measurements for the structural refinement of crystalline and disordered materials. Although sophisticated tools for such refinements have been developed, they are not optimized for high-performance computing, not well-adapted to the latest advances in instrumentation, and not flexible enough to cope with simultaneous refinements of a variety of experimental techniques. In this project, we are developing advanced numerical algorithms, high-performance tools for scientific data management, and powerful frameworks for modular programming.

Mission Relevance

This project is tied to DOE's science mission and, in particular, to the Office of Basic Energy Sciences (BES) goal to "significantly augment its theoretical and computational programs coupled to experimental research at its major facilities." DOE operates major x-ray and neutron user facilities that enable more than 10,000 scientists to perform world-class science each year. A significant limitation in the use of these facilities is the current focus on individual measurement techniques. It is often advantageous to combine the results from x-ray and neutron experiments, with each probe providing a different experimental constraint on the theoretical interpretation. This computational framework is designed to enable such analyses in a high-performance computing environment.

FY 2009 Results and Accomplishments

A principal need is to develop efficient methods of transforming neutron and x-ray data from instrumental coordinates into the reciprocal space and energy coordinates required for analysis by materials science models. Since the size of these datasets will soon exceed 10 gigabytes (GB), it is essential to develop scaleable meshing solutions that will allow real-time access to transformed data during the experiments. Meshing techniques for treating x-ray data taken under crystal rotation have been developed to generate three-dimensional reciprocal space volumes. A general Python interface using the common neutron and x-ray data format, NeXus, is in an advanced stage of development.

The design of a next-generation programming environment for crystallographic software, GSAS II (General Structure Analysis System), was started. The first goal was to port a tool for computing anomalous scattering coefficients as a function of x-ray energy. The resulting program, pyFprime, which runs on Windows, Mac, and Linux, served as an exercise for learning techniques for creating platform-independent graphical display and interface programs. Different approaches to organizing and displaying diffraction data and materials structural parameters were investigated for GSAS-II. The resulting tree design provides a mechanism that will handle as many experimental and model objects as a user wishes to import and that allows each object to be expanded as needed. This interface was then used to develop a tool for the initial stages of powder diffraction crystallographic analysis, dealing with needs that are not currently addressed in GSAS: versatile data visualization, peak picking, and peak fitting.

Proposed Work for FY 2010

We will extend the functionality of the Python framework by integrating various standard crystallographic tools, including auto-indexing, crystal orientation refinement, the extraction of integrated intensities, detector calibration using powder standards, and enhanced three-dimensional visualization.

As functionality is extended within the core framework, the simplified graphical user interface (GUI), which provides visualization and access to the scripting command line, will be extended. We will also begin developing more advanced data analysis tools within the framework, including model fitting and simulations. We will study optimized methods of meshing event-mode data used at the Spallation Neutron Source in Oak Ridge, Tennessee. In event mode, every neutron is recorded with its time stamp in an event file, and other metadata are stored asynchronously. Strategies for the continual processing and sorting of events during an experiment, in order to reconstruct any two-dimensional slice through the four-dimensional data in real time, will be developed.

For GSAS-II, indexing algorithms will be addressed, a Pawley intensity extraction tool will be developed, and the development of a structure solution tool, such as charge-flipping, will be attempted. This work will allow GSAS-II to address all the steps needed for an initial analysis of powder diffraction data up to the point where GSAS can be used. At that point, we will start the slow migration of GSAS features into GSAS-II. We will also generalize the GSAS-II interface to use more open data structures and import/export interfaces. This will allow new features to be added to the code much more rapidly, particularly by external collaborators. Finally, we plan to solve the challenge of providing easy mechanisms for users to install crystallographic applications with installation tools.



NATIONAL SECURITY

Standoff Monitoring of Acoustic Signatures by MMW Modulated Scattering Technique

2007-113-R2

Sasan Bakhtiari, Nachappa Gopalsami, and Apostolos C. Raptis

Project Description

In remote vibrometry, the current state of the art is based predominantly on optical technology, which suffers from several limitations (e.g., strict range and alignment requirements). The use of millimeter wave (MMW) technology (with frequencies between 30 and 300 gigahertz) for vibration monitoring has promise. To close the technology gap in remote vibrometry at far-field standoff distances, we are conducting proof-of-principle studies toward development of an MMW counterpart to an optical vibration monitoring system. Millimeter wavelengths provide the optimal trade-off between sensitivity and range for detecting the characteristic acoustic vibrations of operating machinery or the reverberations at long stand-off distance from an intended target. The primary objective of this project is to demonstrate the feasibility of remotely detecting the operation of machinery associated with nuclear proliferation activities. Because of its operation at longer electromagnetic wavelengths, an MMW sensor is not as affected by either adverse environmental conditions or the reflectivity of the target. Furthermore, the use of MMW integrated circuit technology allows the fabrication of compact systems that can be operated from either a fixed or a moving platform, making these systems ideal for clandestine operations. Future applications of the MMW technology could include noncontact inspection of civil engineering structures and industrial machinery, nonintrusive diagnosis of biological membranes, and remote monitoring of vital signs and biometric signatures.

Mission Relevance

This project is relevant to DOE's mission in national and homeland security missions. Standoff monitoring of processing plants is the most desirable scenario for the nonintrusive detection of proliferation-related activities. This capability is vitally important to DOE's missions. Advanced remote sensors, such as the kind being developed under this project, will help attain this capability.

FY 2009 Results and Accomplishments

Feasibility studies were initially performed to demonstrate the ability of an MMW sensor to remotely detect characteristic acoustic signals from vibrating structures. A bench-top interferometer, including both hardware and software, was assembled for this purpose (see Figure 1). The MMW front-

end assembly employed all-solid-state components with a homodyne receiver configuration. The electronic block of the system consisted of tunable bandpass filters and amplifiers. Data acquisition hardware and software were implemented by adapting commercially available products for this purpose. Various signal processing and data analysis algorithms have since been developed and integrated into a graphical user interface (GUI) that enables on-line and off-line manipulation of data obtained as a function of time and frequency. Subsequent efforts were associated with more detailed sensitivity analyses to optimize MMW system parameters. Additional experiments were also performed to help assess the influence of key variables (such as signal strength, target range, and atmospheric conditions) on the signal-to-noise ratio.

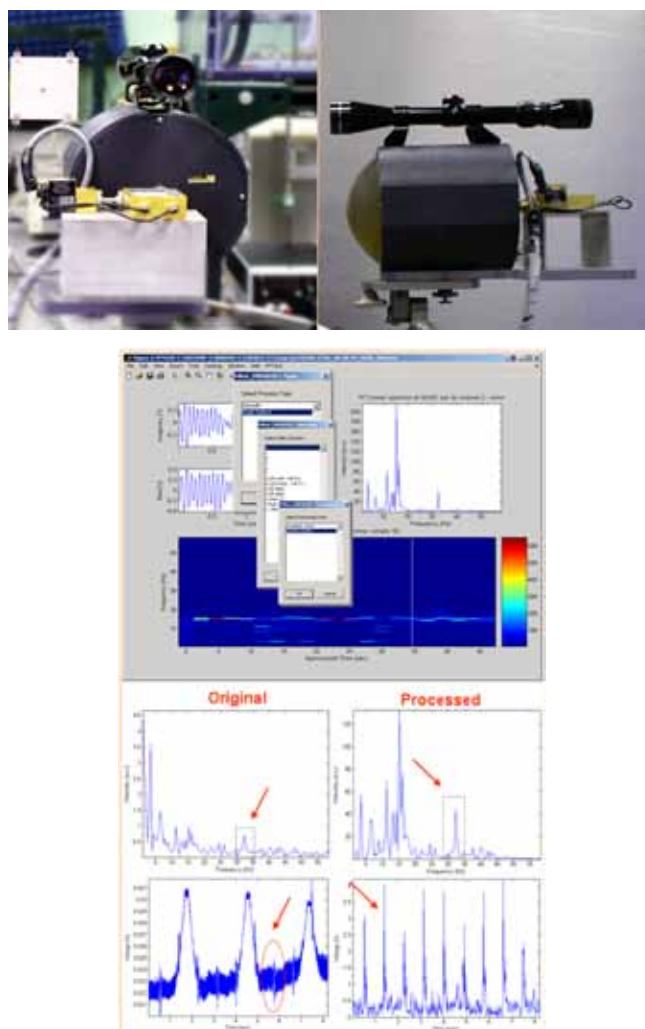


Figure 1. Millimeter wave system developed for remote detection of acoustic vibrations. Shown here are (top, right and left) different views of the MMW sensor's front end; (bottom left) Graphical User Interface (GUI) developed for manipulation of multichannel data; and (bottom right) examples of simulated vibrometry and biometric data before and after processing for extraction of characteristic spectra from different targets.

The work during FY09 focused primarily on development of appropriate signal processing and data analysis routines for extraction of faint signals in the presence of a high level of background noise. Refinements were made to the previously developed algorithms for selective detection and identification of characteristic target signatures. More elaborate noise suppression, feature extraction, and signal identification algorithms were also implemented and tested. The results of feasibility studies clearly demonstrated the ability of the MMW sensor to remotely detect characteristic acoustic signatures from mock-up vibrating structures. For the tests conducted so far, the system consistently provided better than 5- μ m accuracy in measuring displacement at fence-line standoff distances and finer resolutions at distances closer to the target. On the basis of comparative studies performed so far, the MMW technology's main advantages are increased detection range, ease of alignment, and reduced sensitivity to the surface condition of the target. Experiments using simulated targets were also performed to test the applicability of this technology for remote detection of biometric signals. The results confirmed that subtle displacements associated with human vital signs can be detected at relatively long standoff distances.

The following invention report resulted from this project: Bakhtiari, S., N. Gopalsami, T.W. Elmer, and A.C. Raptis, "Millimeter Wave Sensor for Far-Field Standoff Vibrometry," Invention Disclosure ANL-IN-08-041, 2008

Proposed Work for FY 2010

The project does not continue into FY10. Work in this area will continue under a federally funded project sponsored by the Defense Intelligence Agency's National Consortium for Measures and Signatures Intelligence Research.

Refereed Publications

Bakhtiari, S., N. Gopalsami, T.W. Elmer, and A.C. Raptis, "Millimeter Wave Sensor for Far-Field Standoff Vibrometry," in Review of Progress in Quantitative Nondestructive Evaluation, AIP Conference Proceedings Volume **1096** (2009), D.O. Thompson and D.E. Chimenti, eds., pp. 1641–1648.

Non-Refereed Publications and Presentations

Bakhtiari, S., N. Gopalsami, T.W. Elmer, and A.C. Raptis, "Millimeter Wave Sensor for Far-Field Standoff Vibrometry," presented at the 35th Annual Review of Progress in Quantitative Nondestructive Evaluation (QNDE), Chicago, IL, July 20–25, 2008.

Bakhtiari, S., N. Gopalsami, and A.C. Raptis, "Cognitive Processing of Biometric Information for Determination of Intent," presented at the NCMR Technology Review, New Mexico State University, Las Cruces, NM, May 19–22, 2009.

Gopalsami, N., S. Bakhtiari, and A.C. Raptis, "Microwave/Terahertz Radar," presented at the Through Barrier Imaging Technologies Workshop, Argonne National Laboratory, Lemont, IL, January 29–31, 2007.

Risk-Based Decision System toward Risk Excellence

2008-119-R1

Shih-Yew Chen, Maryka Bhattacharyya, Bruce M. Biwer, David B. Chamberlain, Richard D. McKnight, Frederick A. Monette, Edward A. Tanzman, and John A. Volmer

Project Description

A "risk-based approach" has become an element of general guidance in the nation's efforts to ensure national security. The approach addresses a wide range of risk concerns, including human (nuclear, biological, and chemical) risks, critical infrastructure risks, cyber security risks, and a host of other risks that are important considerations for national security. The objective of our project is to develop a basic framework and implementation methods for a national risk-based decision system that will serve as an overarching approach that addresses threat, vulnerability, and consequences for decision makers responsible for homeland security and the battle against terrorism.

For Task 1 of the project, we will develop a framework and methodology to characterize risk and its application to homeland security. For Task 2, we will apply the basic framework to a specific instance in which system components and protocols could be individually tailored to the problem. In doing so, we expect to identify the methodology for applying the general framework to any specific issue. A model risk-based decision system will be developed in the third and final task to be based on Tasks 1 and 2. Once developed, the system and protocols will be tested, and example cases (such as a radiological dispersal device event or an event involving bioterrorism) will be conducted for the purposes of demonstration.

Mission Relevance

This project will benefit the DOE's national security mission areas related to cyber security, emergency response, and counterterrorism. Other federal agencies, including the Department of Homeland Security (DHS), Department of Defense (DoD), and the Nuclear Regulatory Commission (NRC), will likely be interested in the results of this project.

FY 2009 Results and Accomplishments

A review of existing strategies was performed as part of Task 1 in the prior year's work and determined that existing frameworks were hampered by a lack of reliable data, primarily in the application of relevant technologies. The use of technology can minimize risk by reducing threat (event avoidance), lowering vulnerability (enhanced protection), and mitigating consequences (management of the aftermath). Threat reduction can be achieved through intelligence and surveillance/detection. Enhancement of protection relies on technology robustness and defense-in-depth. Consequence management requires assessing the impacts and removing hazards to restore normality, which rely on the accessibility and effectiveness of relevant technologies.

Work in FY09 focused on the application of technology to reduce risk in the three areas discussed above. The work involved consultation with DHS staff in the Office of Policy and the Office of Science and Technology and interactions with Environmental Protection Agency staff in various agencies (National Homeland Security Research Center, Consequence Management Office [North Carolina], Office of Solid Waste [D.C.], Office of Radiation and Indoor Air [D.C.], Office of Water Security [D.C.], National Homeland Security Center [HQ, Cincinnati, OH]). Investigation showed that larger programs geared to detector technology development are more relevant to reducing threat and lowering vulnerability, but do little to mitigate consequences. To perform a proper risk assessment and provide a decision maker with the best potential options, a model must account for mitigation of consequences. In other words, the model must be able to properly account for the technologies available for a widespread cleanup after a potential terrorist event, including their effectiveness, cost, and the types and amounts of waste generated. Such a capability is lacking and sorely needed by federal, state, and local agencies for emergency response planning purposes. The remainder of the year's efforts focused on how to provide such information for practical use in a risk model. The first step was to obtain a representative set of technologies that could be applied to such a problem.

Cleanup technologies from various industries were identified, including those specifically modified to handle chemical, biological, or radioactive agents. Technologies developed for the nuclear power industry, oil and gas industry, wastewater treatment, Superfund cleanup, military applications, and hazardous material response were among those compiled. This compilation serves as the nucleus for the work proposed in FY10.

Proposed Work for FY 2010

A cleanup campaign following a hypothetical terrorist event will be modeled by using a suite of technologies previously identified in the project. The rationale for technology selection will be developed for the risk model on the basis of such parameters as availability, effectiveness, waste volume, cost, and mitigation of human exposure. We will incorporate a suitable database design stemming from the desired characteristics of the compiled technologies and their applications into the risk model's methodology. Such an example will show the optimization process for selecting the proper technology for the situation and set the stage for expansion of the method (the risk framework) to other areas, such as cyber security and infrastructure protection.

Identification of Infectious and Toxin Threat Agents within 15 Minutes

2008-120-R1

Daniel S. Schabacker

Project Description

The surveillance, detection, and diagnostic challenges imposed by a bioterrorist threat justify the need to simultaneously detect protozoa, bacteria, viruses, and toxins. The importance of toxins clearly indicates that current nucleic acid tests will not completely meet the biodefense challenge because of their inability to detect such targets. Accordingly, this project focuses on the development of an antibody-based biochip capable of detecting multiple targets of any nature. Typical biochip substrates include glass, silicon, or plastic, with probes deposited directly on the surface. The fundamental difference between the three-dimensional arrays under development in our laboratory and commercially available substrates is that individual polymeric gel elements literally create a high-density array of three-dimensional hemispheres. Therefore, each gel element retains a solution-phase test environment throughout manufacturing and testing, and biomolecular interactions proceed according to well-understood, liquid-phase thermodynamics and kinetics without the uncharacterized or unknown surface effects that plague conventional microarray substrates and protein arrays, in particular. The antibody-based biochip under development will provide rapid analysis (<15 minutes) with minimal sample preparation requirements, thus affording significant advantages over current nucleic acid technologies. The entire system (i.e., imager, computer, sample collection and preparation devices, and biochips) may be transported in a Pelican briefcase.

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 detect such weapons, specifically biological systems. The development of a rapid assay (<15 minutes) capable of discerning multiple targets with a high degree of accuracy would benefit the initiatives of the Department of Homeland Security and the National Institutes of Health–Biodefense. Additionally, licensees of the technology would provide a direct path for the development of commercial products for national security stakeholders. A rapid test that can be easily undertaken in the field by minimally trained staff has broad applications within the diagnostic, surveillance, first responder, and environmental sampling communities.

FY 2009 Results and Accomplishments

After completing proof-of-concept experiments with individual targets, we performed multiplexed analysis. Test reagents and assay parameters were optimized for multiplexed analysis and limits of detection determined. Detection levels of 10 ppm (parts per million) were easily attained in a full-length (4.5 hours) multiplexed analysis of *Yersinia pestis*, *Francisella tularensis*, Venezuelan equine encephalitis, ricin, Botulinum toxin A/B, and the 1 part-per-billion (ppb) level was attained for *Staphylococcal enterotoxin B* (SEB).

A time study was undertaken with SEB to determine the minimal assay time required to maintain optimum performance. In the current configuration, a 30-minute test from sample to answer was the most rapid time course feasible because of the handling requirements of multiple reagents and wash steps. The limit of detection determined for the 30-minute test for SEB was 1 ppb, the same as the full-length test, displaying the high sensitivity and potential of the rapid test.

Initial studies in our laboratory indicate that colorimetric assays present a viable option; therefore, colorimetric signal development was evaluated as an alternative to fluorescent detection. Limits of detection on multiplexed tests performed with colorimetric development proved comparable to those of fluorescent detection. The benefit of this detection method is that no instrumentation would be required. The biochip would be scored visually as positive or negative, similar to the way in which results are displayed for a pregnancy test. If necessary, an inexpensive imager could be employed after initial visual scoring to obtain more sensitive readings and accommodate archiving of the results.

The ultimate goal of the project was to develop an easily performed detection system capable of rapid multiplexed analysis. Accordingly, one of the main milestones of the third year was to embed the biochip within a fluidic cartridge. As a result

of the rapid progress of the project, evaluation within a fluidic cartridge was accomplished in the current year of the project. Because of time limitations, only SEB was evaluated in the fluidic cartridge, resulting in a detection limit of 1 part per million.

Proposed Work for FY 2010

This project does not continue in FY10.

Plasmonics-Based Methods for Fast, Selective Chemical, Biological, and Explosives Detection

2008-122-R1

Nachappa Gopalsami, Hual-Te Chien, Stephen K. Gray, Alexander Heifetz, Apostolos C. Raptis, and Hsien-Hau Wang

Project Description

New field deployable chemical, biological, and explosive (CBE) detection methods are urgently needed to provide early warning against terrorist attacks. Detection of improvised explosive devices (IEDs) also poses a particular challenge in view of their easy deployment/concealment and potential for mass casualties. We propose a two-pronged approach to address this broad spectrum of threats by developing plasmonics-based methods in the terahertz and optical spectral regions. Central to these approaches is use of the properties of surface plasmon excitations in metals. We will develop a new terahertz spectrometer based on surface plasmon resonance with the goal of ultra-sensitive, selective detection. We will also work to develop novel nanostructured interferometric chemical sensors that turn colors in the visible region upon exposure to IED molecules.

Mission Relevance

This project addresses the national security mission of DOE by developing early warning sensing techniques and devices to thwart terrorist activities involving CBE threat agents. The plasmonics-based sensing is useful to other DOE programs in characterization of nanoscale materials, energy process instrumentation/diagnostics, and environmental sensing/emission control. This project will directly benefit the Department of Homeland Security and the Department of Defense by developing a simple thin film-based sensor that changes color upon exposure to molecules characteristic of explosives.

FY 2009 Results and Accomplishments

In FY09, we modeled the propagation of electromagnetic waves in slit structures with a finite difference time domain technique for the purpose of designing a sensitive, selective,

and compact sensor for chemical and biological detection. Test results showed that a stepped cavity offers desirable features for sensing: good transmissivity, high-quality factor Fabry-Perot resonances, compactness, and ruggedness.

Toward the goal of designing nanostructured interference color sensors for IED detection, we identified organic molecules with guest-host functioning that would selectively bind IED molecules such as trinitrotoluene (TNT) and dinitrotoluene (DNT). We found that anthracene is about one order of magnitude more sensitive toward DNT in terms of fluorescence quenching than aminoanthracene (Figure 1a). However, aminofluorescein is 20 times more sensitive toward DNT than a very similar fluorescein dye (Figure 1b). These highly sensitive fluorescence quenching molecules will help us to develop new IED sensors. We also developed anodized aluminum oxide nanowells and modified their surfaces to attract IED molecules that would result in interference-based spectral changes.

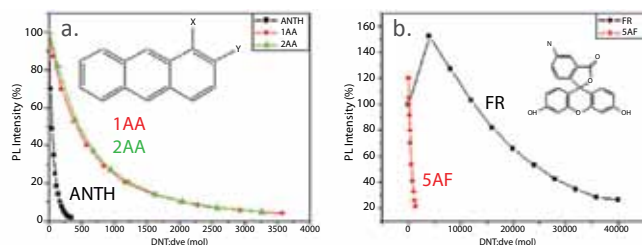


Figure 1. Tests showing: (1a) anthracene (ANTH, $X=Y=H$) is one order of magnitude more sensitive than aminoanthracene (1AA and 2AA, either X or $Y = H$), on the basis of the slopes (quenching rates) of the curves, and (1b) aminofluorescein (SAF) is 20 times more sensitive than fluorescein (FR) in DNT quenching.

Proposed Work for FY 2010

We plan to carry out fluorescence quenching experiments for TNT in FY 2010. Promising candidates will form the basis for additional chemical sensor selection. We will collaborate with a theoretician (P. Zapol) to better understand chemical selectivity toward IED molecules such as anthracene versus aminoanthracene. We would like to test the reactivity of 6-mercaptopyridine-3-carboxylic, a new molecule that has a demonstrated affinity toward TNT, and compare it to our own current results. We will also build upon these discoveries and investigate multi-nanowell arrays. The interference-based color enhancement will also be studied with the use of metal nanoparticles in terms of the surface plasmon effect.

Non-Refereed Publications and Presentations

Gopalsami, N., A. Heifetz, H.-T. Chien, and A.C. Raptis, "Terahertz Subwavelength Structures for Sensing and NDE," in *Proceedings of the 36th Annual Review of Progress in Quantitative Nondestructive Evaluation*, AIP Conf. Proc., University of Rhode Island, Kingston, RI, July 26–31, 2009, in press.

Gopalsami, N., H.-T. Chien, S. Bakhtiari, and A.C. Raptis, "Surface Plasmon THz Resonators for Security Applications," in *Review of Progress in Quantitative Nondestructive Evaluation*, AIP Conf. Proc. 1096 (2008) 440–446.

Wang, H.H., L. Ding, Y. Huang, J.E. Indacochea, and C.Y. Han, "AAO Membrane Fabrication and Applications in Security and Energy," Interdisciplinary Science and Engineering Materials Research Group, ISEMRG Workshop/Spring '08, University of Illinois, Chicago, IL, April 16–17, 2008.

Liu, Y., H.H. Wang, J.E. Indacochea, and M.L. Wang, "Interference Color of Anodized Aluminum Oxide (AAO) Films for Sensor Application," SPIE Smart Structures and Materials & Nondestructive Evaluation and Health Monitoring, San Diego, CA, March 8–12 2009.

Global Modeling Initiative for National Security Event Dynamics

2008-138-R1

Charles M. Macal, David L. Sallach, and Jonathan Ozik

Project Description

The social dynamics domain presents some of the most challenging scientific problems, as well as some of the most important policy consequences. The emergence of complexity science and computational modeling capabilities allows researchers to take an innovative approach to these problems and suggests an effective strategy for making concrete progress. The last decade has been one of dramatic advances in the computational modeling of social processes. The focus has been on heterogeneous agents using simple but intuitive rules and exploring the consequences that emerge from such models. However, these advances only lay the groundwork for what is possible in the computational social sciences. One of the strengths of computational social science is its ability to construct models that integrate previously diffuse knowledge.

The Global Modeling Initiative (GMI) project will provide a computational tool with the capability to identify and better understand emerging worldwide threats to U.S. national security by modeling the social dynamics that are the antecedents to such threats. As part of the GMI, we will develop the Global Modeling Simulation (GMS) to model the dynamic social and cultural processes that germinate threats to U.S. national security. The technical approach of this project is multi-layered, consisting of macro-, meso-, and micro-layers. At the macro-scale, a selected set of worldwide databases will

be linked into a graphical user interface that makes relevant information accessible on a geo-spatial basis. At the meso-scale, social and organizational networks will be the primary relational medium for data presentation and indexing; such networks could include terrorist networks and proliferation networks. At the micro-scale, processes that embody social mechanisms (such as incentives) will allow for the dynamic interactions of individuals and groups that result in emergent social structure, such as terrorist networks. Argonne's capabilities and experience in computational social sciences, agent-based modeling, and analysis of dynamic social networks will be combined to develop this unique tool.

Mission Relevance

The proposed work is tied to DOE's mission in national security. In addition, the Department of Defense (DoD), which now recognizes that the planning process for anticipating future threats and missions for defense must be revamped on the basis of more in-depth consideration of human, social, and cultural factors, will be interested in the results of the project. The Defense Advanced Research Projects Agency (DARPA) will also be interested, particularly now that it is pursuing computational social science. The Department of Homeland Security (DHS) and other agencies also have components of their science and technology portfolios that include human and social factors, and so the outcome of our project will be of interest to these organizations as well.

FY 2009 Accomplishments and Results

In FY09, we achieved several milestones, including substantial progress in developing the capability for visualizing and analyzing unstructured data, such as those from text, web pages, and other unstructured data sources. We also developed the capability to analyze networks that use key networks statistics, including centrality, "betweenness," and closeness, which are often used to infer leadership, importance, and other roles of individuals in the network. In addition, we developed logical directives for combining data from multiple sources to indicate intersections, unions, complements, and other logical operations on the unstructured data sets.

Proposed Work for FY 2010

The GMS has a graphical user interface that functions as an information hub, focusing on the integration of information on key factors from a number of disparate data sources. In FY10, we will implement the mathematical relationships depicting dynamic interactions among variables in the database for the most salient processes. Databases will be dynamically linked to the GMS global user interface through the implemented meta-databases. We will also implement an ontology for weapons of mass destruction to supply contextual information and add the capability to display networks according to thematic layer, such as geo-spatial, nuclear materials supply chain, and financial support, among others.

Science and Technology for Development of High-Sensitivity Biosensors

2008-157-R1

Orlando H. Auciello, Derrick C. Mancini,
Anirudha V. Sumant, Muruganathan Ramanathan,
and David A. Czaplewski

Project Description

This project focuses on the fundamental science needed to develop a portable, high-sensitivity, real-time biosensor. The proposed biosensor is based on the ultrananocrystalline diamond (UNCD) film technology developed at Argonne — specifically, microelectromechanical and nanoelectromechanical systems (MEMS/NEMS) -based resonant cantilevers, in which selective attachment of biomolecules produces resonant frequency changes.

Mission Relevance

The development of high-sensitivity biosensors is critical to the DOE national security mission, which requires swift, accurate detection of potential biological attacks involving such viruses as anthrax. Current detection methods are slow because of the long analysis time required in laboratories far from the attack location. The development of high-sensitivity, portable, personal biosensors with immediate biological response to exposure would save lives.

FY 2009 Results and Accomplishments

UNCD layer characterization work enabled us to identify a functional group that worked to functionalize the UNCD surface. In addition, atomic force microscopy (AFM) studies showed the linkage of the T7-phage to the surface of UNCD layers (Figure 1).

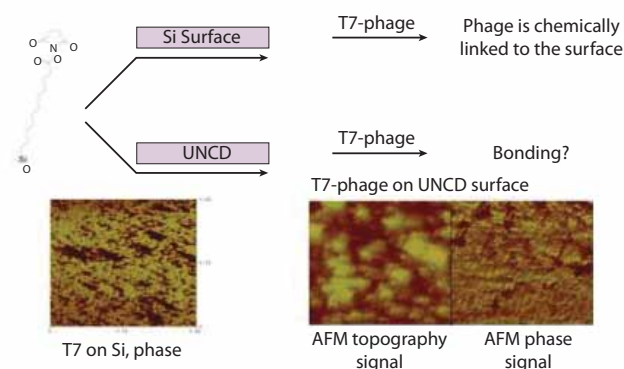


Figure 1. Functional groups investigated for functionalization of the UNCD surface. The functional group based on OH-3F molecules reacted with H_2SO_4 to form the linker molecule 2O-3F (linker #4 in figure seems to be the most promising for functionalizing the UNCD surface for biomolecules attachment).

We analyzed UNCD functionalized surfaces using infrared absorption spectroscopy, which showed the potential of this technique to identify functional groups on the surface of UNCD layers (Figure 2).

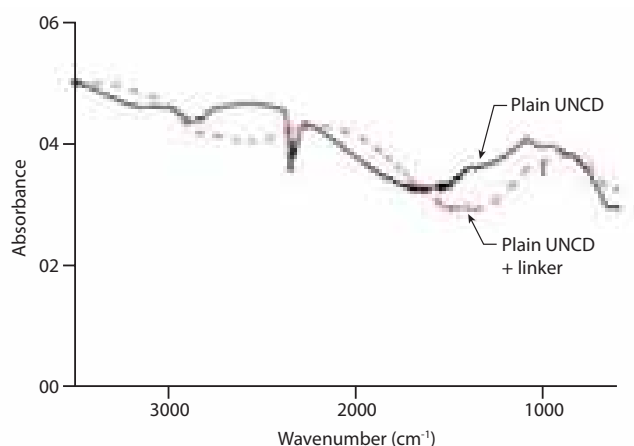


Figure 2. Infrared absorption spectroscopic analysis of the surface of a plain UNCD layer and after functionalization with the linker #4 shown in Figure 1.

Proposed Work for FY 2010

Current work shows promise in providing the basis in FY10 for identifying a good anthrax species simulator to investigate the performance of the biosensor. We will also obtain Fourier transform infrared (FTIR) spectroscopy measurements of functionalization of the UNCD by coating attenuated total reflectance (ATR) crystals with UNCD and observing the chemical modifications to the functionalized surface.

We selected anthrax to demonstrate the performance of the biosensor for the following reasons: (1) anthrax is one of six category A biological weapons, (2) it has a high potential for casualties, (3) its release might cause public panic, and (4) it requires special public-health preparedness. Anthrax exhibits activity that is dangerous but non-contagious, and it is easily spread. Because it is rich in amino acids, nucleosides, and glucose, anthrax can reproduce in blood and tissues in humans and animals. The anthrax bacteria secrete three major virulent factors: protective antigen, edema factor, and lethal factor; all of these will be investigated as the main factors to be identified by the biosensor.

We will measure the double-layer capacitance before and after bio-tethering. UNCD has a very low double-layer capacitance value ($<10 \mu\text{F}/\text{cm}^2$). Attachment of a bio-entity, such as DNA, should increase the double-layer capacitance.

Refereed Publications

Auciello, O., S. Srinivasan, J. Hiller, A.V. Sumant, and B. Kabius, "Fundamentals and Application of Materials Integration for Low-Power Piezoelectrically Actuated Ultrananocrystalline Diamond MEMS/NEMS," in *Proceedings of the International Society for Optical Engineering (SPIE)*, **7318** (2009), 7318B1-8.

Ramanathan, M., S.B. Darling, A.V. Sumant, and O. Auciello, "Nanopatterning of UNCD Thin Films via Block Copolymer Lithography," *Journal of Vacuum Science & Technology* (2010) (in press).

Shi, B., Q. Jin, L. Chen, and O. Auciello, "Fundamentals of UNCD Thin Films as Biomaterials for Developmental Biology: Embryonic Fibroblasts Growth on the Surface of UNCD Films," *Diamond and Related Materials* **18**(2-3), 596-600 (2009).

Non-Refereed Publications and Presentations

Auciello, O., A.V. Sumant, J.A. Carlisle, Y.C. Chen, X.Y. Zhong, B. Kabius, J.M. Hiller, N.H. Tai, I.N. Lin, A.R. Konicek, A.R. Krauss, D.M. Gruen, J. Libera, C. Goldsmith, D. Forehand, S. Sampath, A. Datta, C. Gudeman, D.C. Mancini, M. Burgener, J. Swonger, V.P. Adiga, R.W. Carpick, S. Pacheco, B. Shi, X. Xiao, R.J. Freda, J. Weiland, M. Humayun, B. Mech, D. Zhou, and R. Greenberg, "Status of the Science and Technology of Films and Application to Multifunctional Devices from the Macro to the Nanoscale," Plenary Talk at Diamond 2009 20th Anniversary Conference, Athens, Greece, September 6-10, 2009.

Auciello, O., B. Shi, Q. Jin, and L. Chen, "Fundamentals of UNCD Thin Films as Biomaterials for Developmental Biology: Embryonic Fibroblasts Growth on the Surface of UNCD Films," Plenary Lecture at the First Argentine School of Nanotechnology and Regenerative Medicine, Universidad Nacional de la Plata, La Plata, Buenos Aires, Argentina, July 14-17, 2009.

Auciello, O., A.V. Sumant, J.A. Carlisle, Y.C. Chen, X.Y. Zhong, B. Kabius, J.M. Hiller, N.H. Tai, I.N. Lin, A.R. Konicek, A.R. Krauss, D.M. Gruen, J. Libera, C. Goldsmith, D. Forehand, S. Sampath, A. Datta, C. Gudeman, D.C. Mancini, M. Burgener, J. Swonger, V.P. Adiga, R.W. Carpick, S. Pacheco, B. Shi, X. Xiao, R.J. Freda, J. Weiland, M. Humayun, B. Mech, D. Zhou, and R. Greenberg, "Status of the Science and Technology of UNCD Films and Application to Multifunctional Devices from the Macro to the Nanoscale," Plenary Talk at the New Diamond and Nanocarbon Conference, Traverse City, Michigan, June 7-11, 2009.

Integrating Suicide Attack Information with Radiological Material Loss Data in the Context of WMD Threat Evaluation

2009-014-NO

Robert L. Johnson, Joseph J. Adduci, and David J. LePaire

Project Description

The project builds on distinctly different but related pieces of work that have been conducted at the University of Chicago (UofC) and at Argonne. Under the direction of Dr. Robert Pape and with support from the Defense Threat Reduction Agency, researchers at the UofC have compiled the most complete inventory of suicide attacks available, the CPOST (Chicago Project on Security and Terrorism) terrorism database. Separately, with funding from the National Nuclear Security Administration (NNSA), Argonne researchers have developed and populated a joint relational database-geographic information system (GIS) for tracking incidents involving the loss of radiological and fissile material (THADIAS). THADIAS is the only worldwide relational incident tracking database of radiological incidents of its kind. For example, THADIAS data serve as the foundation for Interpol radiological incident tracking databases. The two efforts — CPOST and THADIAS — approach the issue of weapons-of-mass-destruction (WMD) threats from two different directions; if they were systematically integrated, they would provide a unique database that could be of immediate value from the perspective of considering radiological dispersion device/improvised nuclear device (RDD/IND) threats, and both efforts would establish the framework for a more generic methodology that could be applied to biological and/or chemical WMD threats.

Mission Relevance

This project is relevant to DOE's mission in national security. DOE NNSA has a number of programs aimed directly at mitigating homeland security threats from fissile/radiological WMDs. The key to many of these programs is understanding the nature of the threat as captured in design-basis threat statements, and this project helps to achieve that understanding. The degree to which the increasing occurrence of suicide attacks changes the threat identification calculus is critical to the success of homeland security activities.

FY 2009 Results and Accomplishments

Suicide attack data sets were obtained from the University of Chicago. Suicide attacks were geo-referenced for inclusion in a geographical information system. Suicide attacks were cross-referenced against locations where radiological material is known to exist and where there have been historical incidents (e.g., theft, diversion, or recovery) involving radiological material. Special focus was applied to Iraq, where there have been

a significant number of suicide attacks since 2003 and where radiological source material was present. To the degree that the data allowed, the spatial relationships between suicide attacks and the locations of source material were investigated. No significant connection was established between suicide attacks and radiological source material vulnerability.

Proposed Work for FY 2010

This project does not continue into FY10.

Rapid Elemental and Isotopic Analysis of Trace Actinides and Fission Products in Fused Materials Using Advanced Extraction Methods and Resonant Ionization Mass Spectrometry (RIMS)

2009-017-NO

Ilya A. Shkrob and Michael R. Savina

Project Description

This work focuses on isotope analysis of trace radionuclide elements in the environment for nuclear forensics applications. Nuclear forensics aims to trace fissile and radioactive materials back to their source in order to thwart terrorist activities and inform U.S. emergency response personnel. This task requires rapid isotope analysis of radionuclide elements. Current procedures sometimes require more than 24 hours for precise determinations. These long analysis times result from lengthy chemical separations of *f*-shell elements, the isotopes of which have the same mass (isobaric interferences). These elements are not distinguishable when conventional low-resolution mass spectroscopic techniques are applied to trace amounts of radionuclides. Our approach bypasses these difficulties by using resonance ionization mass spectrometry (RIMS), which is both extremely sensitive and element-specific. Argonne National Laboratory has pioneered and perfected this technique for cosmochemistry analyses. It is applied in this work to address outstanding national security concerns. With this method, the isotopic composition is determined by using multiphoton excitation that is tuned to a particular element, so only atoms of this element are ionized. The laborious analytical separations are redundant; the "separations" occur by tuning the laser frequency to particular transitions in an atom rather than by chemical means. This method greatly speeds and simplifies the preparations, since they are used only for preconcentrations of the radionuclides in a form maximally suited for RIMS analyses. The scope of this work is to develop and demonstrate such combined approaches by using ion-selective, nanoporous, ion-exchange, polymer resins and surface-modified magnetic microspheres for preconcen-

trations of the f -ions of interest. The sample is mounted in a RIMS chamber, and the isotope composition is analyzed, one element at a time. The deliverable of this project is a rapid method suitable for rapid (less than 6 hours) and accurate uranium (U) and plutonium (Pu) analyses.

Mission Relevance

This project is tied to DOE's mission in National Security. The need for rapid analytical capabilities has been articulated by the Offices of Nonproliferation Research and Development and Defense Nuclear Nonproliferation in DOE's National Nuclear Security Administration and by the Science and Technology Innovation Office of the Defense Threat Reduction Agency. In 2008, a call was issued that specifically sought "nuclear forensics technologies that rapidly provide data for conclusion to post-detonation samples which can contribute to the attribution of a nuclear/radiological event. The technology will provide rapid field and/or fixed laboratory analysis for chemical separation and isotopic measurement.... The objective is complete analysis in <24 hours." Another project aims to "detect, identify, locate and track lost or stolen nuclear weapons threats, i.e., nuclear weapons, nuclear weapon components, or special nuclear material" through the development of sensors and detectors for attribution of these materials. An analytical technique that meets these specifications will immediately find customers and beneficiaries.

FY 2009 Results and Accomplishments

We developed protocols for modifying polystyrene and glass magnetic microspheres (1–5 μm [micrometers]) by decorating them with ion-binding ligands. The typical modification involved aminopolycarboxylic, di(diphenylphosphoric)imide, and diglycolamide functionalization. Sorption capacity of 50–100 milliequivalents per gram was demonstrated with the stability constants (for binding of the cation to the grafted ligand) in excess of 10^7 liter/mol. We used these surface-modified microspheres to demonstrate rapid sequestration of more than 95% of the f -ions (such as lanthanides) from liquid samples containing a picomolar to micromolar concentration of the element, with the distribution ratios for the cation between the solution and solid phases (the ratio of the average concentrations in the solid and the liquid phases) approaching 2×10^4 . These microspheres (with the sequestered ions) can be magnetically separated either directly in the field or en route to a dedicated RIMS facility. We also demonstrated sequestration by using microparticles of impregnated nanoporous resins. In this case, the separation is by centrifugation. The microparticles were lightly gelled for cohesiveness, placed on a metal target, dried, covered with a thin layer of gold, and analyzed by using RIMS (Figure 1). Both the resins and magnetic polystyrene microparticles yielded excellent results in the test trials. The best results were obtained by using impregnated nanoporous polymer beads that were 50 μm in diameter, for which RIMS measurements proved both sensitive and robust.

The measured isotope ratios were stable and reproducible. Each individual bead analysis exhibited a precision obtained in one hour of better than 0.4% in the $^{151}\text{Eu}/^{153}\text{Eu}$ ratio, with an aggregate precision of 0.2%. Such high precision in such a short period demonstrates the feasibility of the approach.

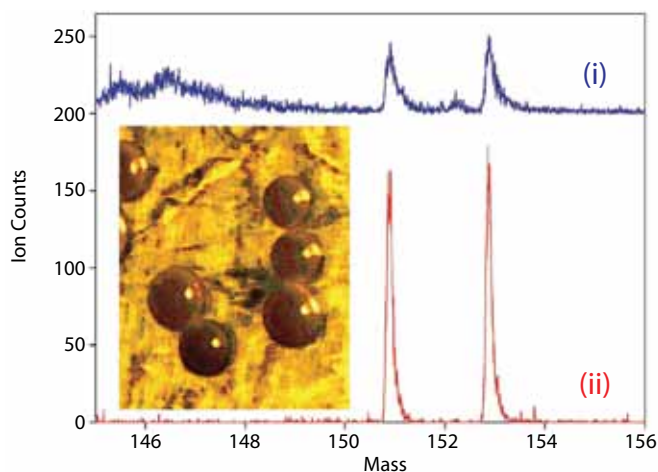


Figure 1. Element-specific RIMS detection of europium-151 and europium-153 from a single 50- μm microparticle by using (i) ion sputtering and (ii) laser desorption. Observe the clean baseline for the laser desorption. In this experiment, the isotope ratio was determined to a precision of ± 2 parts per thousand after one hour of data acquisition. (Inset) Nanoporous, transuranics-selective, ion-exchange resin particles 50 μm in diameter, loaded with europium (III) and coated with a thin layer of gold in preparation for RIMS analysis.

Proposed Work for FY 2010

We will address several issues that need be resolved before the technique is used for nuclear forensics analyses. We need to measure the absolute sensitivity of the measurements, adapt our sample preparation protocols for highly acidic solutions typical of nuclear forensics needs, speed up sample preparation and RIMS analysis, and demonstrate these analyses for U and Pu (currently, these demonstrations involve only fission products, such as the lanthanides, zirconium, and molybdenum). In FY09, we already developed and demonstrated efficient three-pulse laser ionization schemes for U and Pu that will be used for RIMS analyses.

Refereed Publications

Shkrob, I.A., M.D. Kaminski, C.J. Mertz, P. Rickert, M.S. Derzon, and K. Rahimian, "Sequestration, Fluorometric Detection, and Mass Spectroscopy Analysis of Lanthanide Ions Using Surface Modified Magnetic Microspheres," *J. Am. Chem. Soc.* **131** (2009) 15705–15710.

Shkrob, I.A., M.D. Kaminski, K. Rahimian, and M.S. Derzon, "Magnetic Extraction, Detection, and Isotope Analysis of Metal Ions Using Surface Modified Microspheres for Lab-on-a-Chip Applications," *Sep. Sci. Technol.* (2010) (in press).

Non-Refereed Publications and Presentations

Savina, M.R., and I.A. Shkrob, "Development of Rapid Sequestration and Isotopic Analysis Methods for Lanthanides and Actinides Using Resonance Ionization Mass Spectrometry," poster presentation at the 18th International Mass Spectrometry Conference, Bremen, Germany, August 31–September 4, 2009.

Savina, M.R., and I.A. Shkrob, "Sequestration and Analysis Methods for Lanthanides and Actinides Using Resonance Ionization Mass Spectrometry," presented at Asia-Pacific Symposium on Radiochemistry (APSORC-09), Napa, CA, November 30–December 4, 2009.

Tagging and Monitoring Sealed Radiological Sources

2009-028-N0

Roger G. Johnston and Jon S. Warner

Project Description

Several federal agencies are interested in being able to tag and monitor tens of thousands of sealed radiological sources because of their possible use in terrorist radiological dispersal devices (RDDs). Other tags, seals, locks, and monitoring schemes that have been proposed are impractically expensive, too large and heavy, interfere with the authorized use of the sources, and are easy for amateurs to bypass or spoof. This project involves developing and demonstrating a novel concept that avoids these problems — an "anti-evidence" method of tagging and monitoring that is potentially simpler, less expensive, and more secure than other approaches. As long as everything is fine, the microprocessor-based monitoring circuit on or adjacent to the sealed radiological source of interest will "chirp" at random, unpredictable times known only to those responsible for ensuring our nation's safety. The chirp can be an ultrashort flash from an infrared LED or a radio frequency pulse, but for the lowest cost and greatest practicality, we believe an ultra-short chirping acoustical pulse is ideal. If tampering is detected or the item being monitored is missing, the "All-OK" signals cease, providing evidence of theft or tampering.

The use of a chirping sound to signal that the sealed radiological source is still present and has not been tampered with has the additional advantages that sound goes around corners, requires little battery power, and does not suffer interference from metals and liquids, nor is it trivial to block or spoof. The sound chirps will be so short that many different sealed radio-

logical sources in the same general area can all be randomly chirping away, each one emitting a chirp once each minute or so on average, with the random chirps overlapping very infrequently.

The implementation of this chirping tag, seal, and security monitor would then look something like this: Instead of attaching a security device directly to the sealed radiological source (which presents a number of practical problems), we would design a thin, lightweight plastic case to hold each source. For many authorized radiological applications, the sealed radiological source could be used without removing it from the case. Built into the plastic case would be a coin battery and a small, inexpensive microprocessor-based electronic circuit with built-in redundancy to deal with slightly elevated failure rates due to the relatively high radiation environment near the source. This circuit does the random audible chirping and checks whether the case was opened using a photosensor and other low-cost, small commercial solid-state sensors that have not been much exploited for security applications. Evidence of opening causes the case to stop chirping.

Mission Relevance

The project is relevant to DOE's national security mission. Better tagging and monitoring of sealed radiological sources has important implications for homeland security (protecting against radiological dispersal devices), nuclear environmental safety and health, nuclear security/safeguards, nonproliferation, and treaty monitoring. There are other potential security applications as well not involving sealed radiological sources.

FY 2009 Results and Accomplishments

In FY09, we identified a high-resonant chirp transducer and analyzed possible commercial microphones for monitoring the chirping. We designed, fabricated, programmed, debugged, and tested a microprocessor-based circuit that generates random chirps using the high-resonant chirp transducer (see Figure 1). We began testing the chirp circuit with real-time fast Fourier transform analysis, developed software to capture the chirps and extract the data, and began developing software that will allow us to test various chirp recognition algorithms in FY10. Figure 2 is an intensity versus time plot of the acoustic chirp the preliminary unit emits. Detection range exceeds 300 feet.



Figure 1. Both sides of the preliminary acoustic chirper tag and real-time monitor developed in FY09, which has not been fully miniaturized.



Figure 2. Chirp waveform generated by the device shown in Figure 1, as recorded by a microphone.

Proposed Work for FY 2010

In FY10, we will make a final choice of the microphone and design and test possible chirp recognition algorithms (including in the presence of background noise) toward the ultimate goal of a fully working system in FY11.

Non-Refereed Publications and Presentations

Warner, J.S., and R.G. Johnston, "287 Security Blunders You Should Avoid," presented the ASIS (American Society for Industrial Security) International Annual Meeting, Anaheim, CA, Sept. 21–24, 2009.

Photoacoustic Technique for Remote Detection of Special Nuclear Materials

2009-059-N0

Hual-Te Chien and Shuh-Haw Sheen

Project Description

The goal of this project is to develop and evaluate a nonconventional technique for detecting shielded special nuclear materials (SNM). Instead of directly detecting nuclear radiation, the photoacoustic spectroscopy (PAS) technique focuses on detecting radiation-induced gases, such as ozone and nitrogen oxides, in the ambient air surrounding the shielded SNM. The project includes (1) evaluation of the required sensitivity of alternative signatures and (2) development and evaluation of a laboratory remote PAS system.

Mission Relevance

The project is relevant to DOE's national security mission. Because nuclear materials can cause mass destruction, their proliferation and unauthorized movement are great threats to our national security. The success of this project will lead to further development of a portable or standoff remote sensing instrument for search and surveillance of SNM in broad areas. This technique may also be used for remote detection of explosives, chemicals, and biological agents. The technique may even be used for environmental monitoring and food inspection.

FY 2009 Results and Accomplishments

We have done a literature search and theoretical modeling on the concentrations of ozone and nitrogen oxides induced by different radioactive sources of various intensities for several exposure times. For a single radioactive source, the ozone concentration is proportional to the electrons produced by the radioactive source in the volume of the containing space.

It has been demonstrated that the PAS technique can be used for remote detection of chemicals, explosives, emissions, and biological agents. The PAS technique uses a pulsed tunable laser (for example, a CO₂ laser) to excite the target molecules that are in either gas or condensed phase and then employs an acoustic sensor to detect the acoustic waves generated from the relaxation process of the excited molecules.

We studied the sensitivity of ozone and nitrogen oxides detection by using the PAS technique. Our remote-detection PAS system consists of a carbon dioxide (CO₂) laser, a mechanical chopper, acoustic resonators, generated ozone/nitrogen oxides, and a data acquisition and analysis system. The wavelength of CO₂ laser is between 9.3 and 11 μm . The lasing transition at a specific wavelength (for example, 9.6 micrometers [μm]) is a simultaneous change of these vibrational and rotational quantum states. Based on the changing of their energy state, those transitions are grouped into two branches: *P*-branch and *R*-branch transitions. Within each branch, there are various dominant transitions. The wavelengths associated with the some transitions are, for example P(16)-9.52 μm , P(18)-9.54 μm , and P(28)-9.615 μm .

Distinct ozone absorption lines are in the region of the 9P branch (9.44 to ~9.78 μm) of the CO₂ laser. Figure 1 shows the time-history image of instant and consistent ozone detection when the laser shutter is opened and closed at two selected 9P lines, 9.6 microns P(16) and P(20). It also shows that the P(16) line has stronger absorption than the P(20) line, which also agrees with the literature. The resonator is designed to amplify the PA signal at the chopper frequency, which is set at 1.17 kHz. The result also shows that the resonator acts as a bandpass filter, with a bandwidth of 50 Hz. Figure 1 also shows fast response and recovery of the system. Therefore, one of

the advantages of this technique — unlike most chemical sensors and spectrometers — is that the system does not need to be purged or cleaned and it recovers instantly.

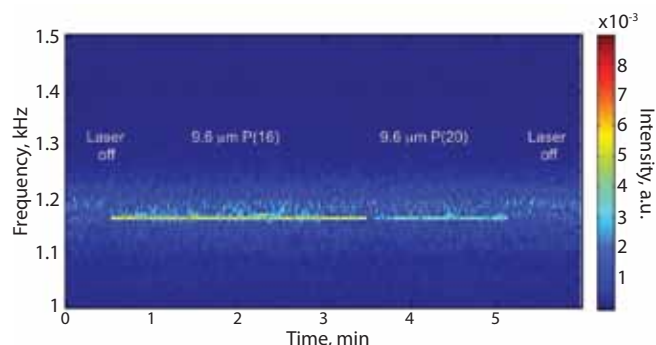


Figure 1. PAS signal intensity of ozone detection at lines of 9.6 μm P(16) and P(20).

We also designed and tested an adjustable resonator incorporated with a sliding tube so that it could be sensitive to a wider frequency range, such as 1.0 to 5.0 kHz, rather than a particular frequency. Results show that the resonator is effective at producing amplification for a wider frequency range. Figure 2 shows that the resonator, operating at 1.17 kHz, effectively amplified the PAS signal with various signal-to-noise ratios. However, further investigations can yield improvements in the physical characteristics of the resonator that would enhance amplification and filtering of the acoustic signals with regard to various target gases.

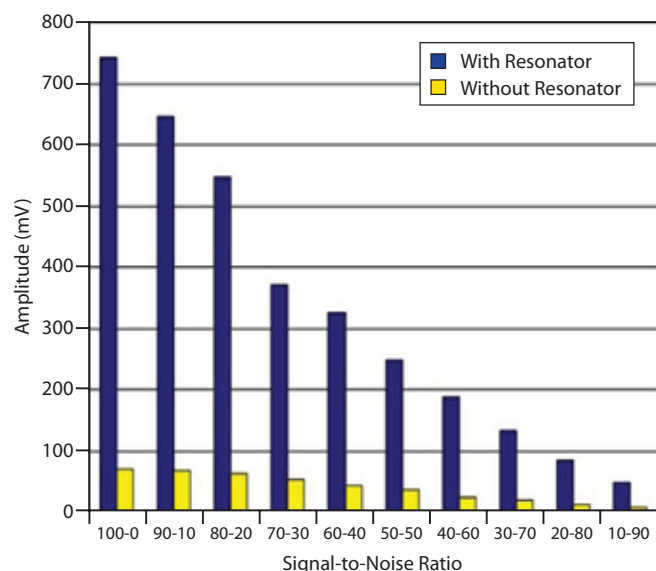


Figure 2. Acoustic amplitude measured with and without resonator under various signal-to-noise ratios.

After further study and validation as a result of this project, our patent application, entitled “Photoacoustic Spectroscopy System and Technique for Remote Sensing of Explosives and Toxic Chemicals,” filed in 2008, passed the U.S. patent review. A joint proposal with the University of Chicago to use the same PAS technique to study the skin penetration rate of chemicals was approved for 2010 funding by the Defense Threat Reduction Agency. Five other proposals have been submitted to various U.S. agencies.

Proposed Work for FY 2010

We will set up a dual-laser PAS system, which will consist of CO_2 and mid-infrared lasers for multi-gas detection. We will conduct theoretical modeling and further investigations of the physical characteristics of the dual-resonator and adjustable resonator to improve their sensitivity, range, and frequency bandwidth. We will also continue our feasibility study of the positive identification of SNM and our efforts to improve detection sensitivity and range and increase system integration.

Fusion Cell Nucleus

2009-117-NO

David K. Brannegan, Ronald E. Fisher, Daniel J. Miller, and James P. Peerenboom

Project Description

The establishment of a network of “fusion centers” to facilitate nationwide information sharing is a top priority of federal, state, and local partners. Fusion centers are designed to serve as focal points for the collection, analysis, and dissemination of homeland security- and crime-related information and intelligence. To date, fusion center collection efforts have been extremely successful; however, subsequent analysis of collected resources has not achieved necessary requirements. This dual-track project seeks to enhance fusion center analytic capabilities by (1) addressing the processing limitations of fusion centers in “crossing” large sets of unrelated data and (2) reducing the subjectivity of fusion center tools by adding strong analytic capabilities to existing geographic information system (GIS) platforms. Enabling fusion centers to overcome processing limitations while maximizing the analytic potential of existing GIS tools will ensure that the national network of fusion centers meets baseline analytic requirements in support of the U.S. intelligence community and the first preventers and first responders that they serve.

Mission Relevance

Effective analytic capabilities in fusion centers are critical to U.S. intelligence community efforts to detect, prevent, disrupt, preempt, and mitigate the effects of terrorism against the territory, people, and interests of the United States. As a core departmental component of the U.S. intelligence community, this project supports the DOE national security mission and is directly relevant to the activities of the DOE Office of Intelligence and Counterintelligence. Fusion centers are consumers of and contributors to DOE intelligence analyses and associated technical, research, and operational efforts. This project will enable rapid development of new, cutting-edge capabilities that will support the integrated activities of all levels and sectors of government and the private sector involved in the national information-sharing environment. In addition, this project seamlessly integrates into Argonne's growing fusion-center portfolio in support of the U.S. Department of Homeland Security (DHS) and other potential sponsors, such as the Department of Justice, Department of Defense, and the Office of the Director of National Intelligence. Finally, all 72 state and local fusion centers will benefit from the results and potential follow-on activities regarding this effort.

FY 2009 Results and Accomplishments

During FY09, we completed a thorough strategic planning process that included a number of core research tasks. A detailed review of data sets that feed current fusion-center processes was conducted to ascertain the common sources of information and intelligence across the national information-sharing environment. Fusion center operations were also reviewed to determine primary functional models that govern collection, analysis, and dissemination processes. Gap and effectiveness analyses of existing analytic tools and techniques employed by fusion centers (with particular emphasis on GIS analytic capacities) were conducted to generate an exhaustive list of available capabilities.

The project also initiated a focused methodology development phase and subsequently met all major milestones. This project phase focused on the establishment of an analytic methodology based on existing threat, vulnerability, and consequence data ascertained through an integrated set of site-specific survey mechanisms regarding critical infrastructure and key resources (CIKR). A defensible process by which to assign values to specific assets based on vulnerability and consequence data for various threat scenarios was developed and is currently being finalized by a team of decision and information science experts.

The project also made strong progress regarding the development of technical approaches to address the processing limitations of fusion center analytics. Tiled indexing approaches were developed, tested, validated, and applied to linear and non-linear clustered relationships in disparate data sets through the use of arrayed computing approaches in graphics processing units. The tiled indexing techniques have yielded initial positive results in the crossing of large data sets while avoiding the power, cooling, and/or location limitations that restrict the effectiveness of current fusion-center approaches.

Proposed Work for FY 2010

Project work throughout FY10 will focus on implementing the analytic methodology and technical approaches developed in FY09 into operational tools used within fusion centers. Plans are in place to conduct an initial effort to test and validate methodology, software, and hardware with assistance from an expert panel and select federal, state, and local partners. Relationships have been established with multiple fusion-center leaders from throughout the country that will be leveraged in FY10 to provide guidance regarding applicability of analytic components. Efforts will commence to deploy the analytic tools to fusion centers nationwide and solidify Argonne as a central hub for fusion-center CIKR analytics in support of daily fusion-center activities. The DHS and other potential sponsors will be actively engaged to obtain support for the deployment of project capabilities.

Non-Refereed Publications and Presentations

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Feasibility of Multiplexed Antibody-Based Sensors

2009-227-NO

Fred J. Stevens and Rosemarie Wilton

Project Description

It is generally recognized that sensors are needed for national security to detect numerous threats, including explosives, chemicals, toxins, and microbial and viral pathogens. Antibodies are a unique family of proteins that have evolved in animals specifically to recognize and bind to other molecules. They are generated by the immune system and are critical for maintaining health. Their recognition properties are the basis for their use in the multibillion-dollar immunodiagnostic and immunotherapeutic industries. In principle, these recognition properties make antibodies (or fragments of antibodies) ideal for use in biosensors to detect targets from bio-warfare and terrorism threats to environmental contaminants. Indeed, antibodies against many, if not most, relevant targets (including TNT [trinitrotoluene], botulinum toxin, and PCBs [polychlorinated biphenyls]) exist. However, the successful incorporation of such antibodies into field-deployable, multiplexed biosensors has not been realized. Several technical challenges must be overcome. The first challenge is to develop antibodies that retain functionality outside a laboratory environment. Second, with regard to a multiplex sensor, the panel of antibodies must have similar strengths and rates of binding such that all assays operate under a uniform protocol.

Argonne's Biosciences Division recently demonstrated that significant improvements in antibody stability can be achieved with a relatively small number of amino acid replacements. Moreover, we have developed a strategy to optimize the stability of a target antibody by comparing the amino acid sequence of the target antibody with antibody variable domains in the protein sequence database. This work directly affects the first technical challenge, because it is now possible to rapidly and reliably improve the stability of an antibody to a level where functionality is maintained in harsh environments outside the laboratory. Stabilized antibody domains will have a direct impact on the second challenge, permitting flexibility in modifying the antigen-binding regions to create antibodies with uniform binding characteristics, even if some of those modifications are inherently destabilizing.

Mission Relevance

This project is relevant to DOE's missions in national security and environmental quality. A field-deployable, multiplexed sensor system for threats associated with terrorism or warfare is of direct benefit to homeland and national security, with potential applications in airports, subway systems, outdoor

environments, and the battlefield. Antibodies that recognize environmental contaminants will benefit DOE with regard to detection and remediation and the selective removal of contaminants from water and soil. Likewise, a large array of stable antibodies that recognize microbial proteins will complement DOE's investment in metagenomics by enabling a new field of metaproteomics to quantitatively analyze enzymatic activity in the environment. The ability to improve the stability of antibodies will facilitate the development of therapeutic antibodies and could thus benefit programs sponsored by the National Institutes of Health.

FY 2009 Results and Accomplishments

We searched the literature and identified three antibodies that bind to the ligand fluorescein with varying affinity. On the basis of published information on amino acid sequences, we designed and synthesized bacterial expression vectors to produce the heavy chain (VH) and light chain (VL) variable domain components of each antibody. Expression vectors for the production of the corresponding single-chain FVs (scFV) were also fabricated. An scFV consists of a VH and VL domain connected via a flexible polypeptide linker; it represents the smallest unit of the antibody molecule that still maintains binding activity.

We identified a list of potentially stabilizing amino acid replacements for each VH and VL domain by comparisons with antibody variable domain sequences in the protein sequence database. Site-directed mutagenesis was performed on the VL domain of one of the scFVs (4-4-20). A total of 39 single amino acid variants were fabricated. To date, seven of these variants have been expressed in *E. coli* and purified.

We previously developed a simple screening protocol for identifying amino acid variations that stabilize antibodies. The method relies on first measuring the effect of each variation on the thermal stability of the VH or VL domain by using a high-throughput, fluorescence-based thermal screen. (For several reasons outside the scope of this report, it is not practical to screen for stabilizing variations directly in the scFV.) The effect of the seven amino acid substitutions on the stability of the 4-4-20 VL was determined by the fluorescence-based thermal screen. Three of the seven variants had better thermal stability than the wild type protein.

To date, the three stabilizing mutations have not been transferred back into the scFV framework, so the effect of the stabilizing mutations on scFV stability and fluorescein binding capacity has not been assessed.

Proposed Work for FY 2010.

This project does not continue into FY10.

**PARTICLE AND NUCLEAR
ASTROPHYSICS COSMOLOGY**

Transition-Edge Sensors

2007-100-R2

Valentyn Novosad, Aaron M. Datesman, John E. Pearson, Gensheng Wang, and Volodymyr G. Yefremenko

Project Description

The existence of cosmic microwave background (CMB) radiation is one of the cornerstones of the current Hot Big Bang model — its spectrum, temperature anisotropy, and polarization carry information about the fundamental properties of the universe. High-sensitivity detectors are the key enabling component in observations of CMB. Current bolometric arrays have already achieved background-limited performance. Achieving the sensitivity required to detect and characterize the faint CMB polarization signals will only be possible by increasing the number of detectors and using a high-throughput telescope, such as the 10-meter South Pole Telescope (SPT). The goal of the project, therefore, is to improve transition-edge sensor (TES) characteristics and develop state-of-the-art detector array technology for conducting precise measurements of the polarization anisotropy of the CMB radiation at the SPT.

Mission Relevance

This project is tied to DOE's mission in science, particularly to its mission of "performing world-class research in high-energy physics, using synchrotron radiation, providing detectors, instrumentation, and support for national and international research programs in elementary particle physics." Detectors are the enabling technology that helps push measurements to higher levels of precision and lead to new, innovative experiments. Obtaining accurate measurements of the CMB polarization is a critical step in extending our knowledge of both the early universe and fundamental physics at the highest energies. The same type of detector technology (but with a different radiation absorber) can also be applied to soft and hard x-ray detectors that have excellent energy resolution and fast array readout.

FY 2009 Accomplishments and Results

In FY09, significant project advances were made in four principal areas: design, technology tools, theory, and testing.

Design

Design advancements in FY09 have been made in several areas and at multiple scales, from the overall level of the SPT focal plane down to the design of individual absorber-coupled TES detector dies. At the highest level, technological guidance driven by scientific goals and observational strategies has now been firmly established. This guidance has allowed us to finalize detector design targets. A waveguide mounting scheme for our dual-polarization configuration has now been

designed, has undergone initial testing, and has been assessed for functionality and suitability. Methods for integrating this mounting scheme with feedhorns, readout circuitry, and the dual-frequency focal plane array have been developed, interrogated, and refined.

We have implemented new detector designs that meet project targets for thermal conductance, TES resistance, and operating temperature, along with an effective scheme for the face-to-face mounting of individual dies at a required spacing of ~50 micrometers or less. Plans to fabricate an entire production run of ~200 detector dies that meet design targets have been developed and interrogated and were found to be robust. Mounting and wiring schemes are illustrated in Figure 1(a,b).

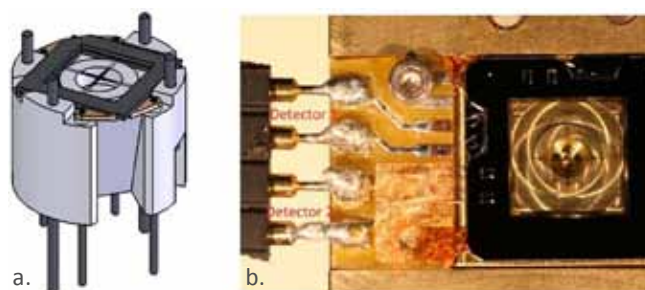


Figure 1. Dual-polarization detector (a) design for feedhorn-coupled waveguide mount and (b) wired for cryogenic testing.

Technology Tools

During FY09, a 6-inch deposition system from AJA International, a manufacturer dedicated to superconducting thin films, was installed and brought on line. Full-time access to this capability provides an enormous boost to the project. The new system has demonstrated better than 1% thickness uniformity over a 4-inch wafer, along with the ability to deposit superconducting thin films in a confocal geometry that are both highly uniform and of excellent quality. By utilizing this system, we have demonstrated the ability to turn out approximately 25 or more detector dies per week for several consecutive weeks. The multiplexed optical cryostat for high-throughput testing was largely completed by the end of the project period.

Theory

Theoretical efforts have been intensified and have yielded excellent results. Because of continuing refinements, thermal modeling results for the absorber-coupled TES detector accord well with experiment and have been employed to refine the detector design without necessitating expensive testing. In addition, the application of a boundary-limited phonon scattering model to cryogenic results measured for our suspended silicon nitride structures led to the first empirical determination of the phonon mean free path in this technologically important material.

Testing

In FY09, very significant advances were made in the optical, thermal, and electrical testing of preliminary detectors, indicating that the project has now transitioned from the preliminary stage into a more rapid region of the deployment curve. Testing has included measurements of the optical time constant and optical response, the cross-polarization, beam maps with co- and cross-polar response, and thermal readout efficiency. In every case, testing results are promising and are quickly converging to design goals.

Proposed Work for FY 2010

This project does not continue into FY10.

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Simulations and Hardware Development for Astrophysics

2007-180-R2

Stephen E. Kuhlmann

Project Description

This project includes simulations and hardware development for optical astronomy experiments investigating dark matter and dark energy, the "missing" 95% of the universe that is undetected and not understood. One key to understanding the nature of dark energy is to explore the range of supernova explosions by using many hundreds of simulations with varying parameters that change the brightness, colors, and time development of the supernovae light curves. These simulations are being performed for three leading supernova experiments — the Dark Energy Survey (DES), the Sloan Digital Sky Survey (SDSS), and the Large Synoptic Survey Telescope (LSST).

Three different hardware development projects are under way: (1) a new portable charge-coupled device (CCD) test laboratory was commissioned in FY09 and took four runs of x-ray diffusion data at Argonne's Advanced Photon Source (APS); (2) mechanical engineering R&D for DES was finished in FY09 and seeded significant DOE funding of design and fabrication work at Argonne; and (3) Argonne is playing a leading role in CCD-camera development for the PreCam calibration project for DES.

Mission Relevance

This project supports the DOE science mission and the DOE Office of Science's mission to understand the fundamental nature of matter and interactions. Gaining understanding of dark matter and dark energy is expected to have a profound impact on the fields of high-energy physics and astrophysics.

Recommendations made in 2006 by the DOE-appointed Dark Energy Task Force and the Particle Astrophysics Scientific Assessment Group indicate that astrophysics research by optical astronomy will be strongly supported over the next decade. The recommendations included the full approval of the DES, as well as research and development for next-generation experiments, underscoring DOE's commitment to astrophysics and to solving the dark matter/dark energy mysteries.

FY 2009 Results and Accomplishments

In FY09, the research team (1) produced valuable CCD data with x-rays at the APS; (2) simulated and analyzed thousands of supernova explosions with varying parameters for three optical astronomy surveys (DES, SDSS, and LSST); (3) performed important engineering tasks for the DES camera; and (4) developed a new cryogenic CCD camera by using DES electronics for the DES calibration project, Precam.

CCDs: The APS x-ray detector allowed us to collimate x-rays into a spot smaller than the size of a DES pixel. This capability has enabled many specialized studies of CCDs with x-rays that cannot be duplicated at Fermi National Accelerator Laboratory (Fermilab). The first use of this capability is a study of the "glowing edge" of the CCD, with comparisons to engineering models from Lawrence Berkeley National Laboratory (LBNL). The glowing edge is characterized by greatly enhanced detector response due to distorted electric fields. In addition, the distorted fields cause a shifted measured centroid compared to the true source location. The results of our measurements agree qualitatively with those of the engineering models, but the models are not precise enough to use in DES CCD simulations. Our results on shifted centroids are expected to have a direct impact on DES CCD simulations, and a draft publication is being finalized.

A second result from the CCD x-ray studies is a large (5-pixel) diffusion effect in front-illuminated CCDs which is incompatible with the engineering models. Since DES is using back-illuminated CCDs this is not expected to affect DES science, but the result is of considerable interest to the CCD engineers at LBNL because they enable them to better understand the devices. These measurements are also included in the draft publication.

Supernova science: Our LDRD-funded post-doc Joe Bernstein is a core developer of the sophisticated supernova simulation and analysis package called SNANA (SuperNova ANALysis). Because of this capability we are leading the development of the detailed survey strategy for DES, and a draft paper is being finalized. This study involves hundreds of simulations that illuminate how well DES can constrain dark energy models and how these constraints depend on survey strategies. Our SNANA simulation/analysis capability also led us to assume a leadership position in the LSST supernova group; we contributed two major sections to the *LSST Science Book*.

Mechanical engineering: Argonne mechanical engineers, designers, and technicians have played major roles in DES design and fabrication. This effort has included staff from the High Energy Physics (HEP) and Nuclear Engineering groups. One important aspect of the Argonne effort has been our ability to perform the jobs from start to finish (i.e., from design to procurement to fabrication, assembly, and testing) at Argonne. We have fabricated and tested a 6-ton installation platform for a 1-ton secondary mirror that has to be aligned to within 300 μm . Argonne also designed and procured the 3-m steel rings for the telescope simulator, the optical filter changer installation mechanism, the electronics cooling, the cell for the 5th lens, a test imager vessel, a flat window and its cell, and instrument controls. Our involvement has led to DOE funding more than \$1M of mechanical parts and Argonne labor for DES.

DES calibrations: The Argonne group has been leading in an effort that will significantly improve and speed up DES calibrations: the Precam project proposes to use a small telescope to create a catalog of standard stars that will occupy almost every DES image. In FY09, our lead engineer designed the Precam camera, which is very similar to the two previous cameras we designed and currently use for x-ray studies.

Proposed Work for FY 2010

This project does not continue into FY10.

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Study of the Fundamental Properties of Buoyancy-Driven Turbulent Nuclear Burning in the Context of Type Ia Supernovae

2008-130-R1

Raymond A. Bair, Robert J. Latham, Ewing L. Lusk, Michael E. Papka, Katherine M. Riley, and James W. Truran

Project Description

This project aims to (1) optimize the FLASH astrophysics code to run efficiently on the Intrepid IBM Blue Gene/P computer and (2) refine the parallel processing tools needed to analyze datasets from Blue Gene/P simulations, many of which are expected to exceed 100 terabytes. Astrophysics computations are being carried out as part of a series of groundbreaking simulations of the fundamental properties of buoyancy-driven turbulent nuclear burning in Type Ia supernovae (SN Ia). This study has the potential to produce a major paradigm shift in the understanding of SN Ia.

Mission Relevance

The project is relevant to the DOE's science mission. Observations using SN Ia as "standard candles" led to the discovery of "dark energy." Understanding dark energy is widely regarded as the most important problem in all of physics. The project is also relevant to the goals of DOE's Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program.

FY 2009 Results and Accomplishments

SN Ia are powerful stellar explosions that are usually homogeneous. A proposed mechanism is the Gravitationally Confined Detonation (GCD) model, in which ash created during subsonic nuclear combustion ejects from a star, flows around the surface, and collides with itself at the opposite point of breakout, sparking a detonation (see Figure 1). Using computer time allocations from the INCITE program, we ran more than 25 additional GCD models on Intrepid in 2009. These models pushed the GCD model into regimes of extreme stellar

pre-expansion and demonstrate that the model can produce a detonation in those regimes. This set of simulations revealed correlations within the GCD model that suggest the nature of the homogeneity of SN Ia. This project contributed to two new FLASH code releases.

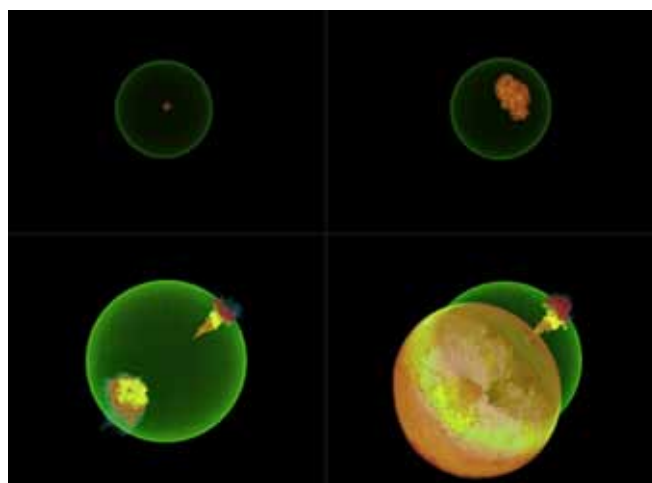


Figure 1. Simulation of the deflagration and detonation phases of a SN Ia. Ignition occurs at 30 points centered 80 km from the center of the star. The stellar surface is depicted as green, and hot material is shown in flame-like colors.

High-resolution studies of the how buoyancy instabilities enhance the flame surface and burning rate for thermonuclear flames were extended to a new regime in which the buoyancy-generated turbulence interacts strongly with the flame surface. When complete in FY10, we will be able to quantify the scale dependence of flame surface structure induced by buoyancy-generated turbulence.

Computations at unprecedented scales, like those in this project, often stress computer software and hardware in ways that reveal scaling issues. In FY09, we focused on input/output (I/O) bottlenecks that limited overall run time scalability. I/O improvements reduced the 35% I/O overhead to around 22%, taking 1–2 hours off a typical 12-hour science run.

Proposed Work for FY 2010

In FY10, we will complete experiments to characterize the I/O behavior of the FLASH3 code with respect to the I/O libraries, data layout, and parallel file systems used. We will also complete the redesign and reimplementation of the FLASH I/O system and will document best practices for portable and efficient parallel I/O implementations.

Continuing simulations will determine the sensitivity of the properties of SN Ia explosions to initial conditions and provide input data to radiation transfer calculations of the light curves and spectra of SN Ia, enabling us to validate the four current models of SN Ia.

Refereed Publications

Meakin, C.A., I. Seitenzahl, D.M. Townsley, G.C. Jordan IV, J.W. Truran, and D.Q. Lamb, "Study of the Detonation Phase in the Gravitationally Confined Detonation Model of Type Ia Supernovae," *The Astrophysical Journal*, **693** (2009), 1188–1208.

Seitenzahl, I.R., C.A. Meakin, D.Q. Lamb, and J.W. Truran, "Initiation of Detonations in the Gravitationally Confined Detonation Model of Type Ia Supernovae," *The Astrophysical Journal*, **700** (2009), 642–653.

Seitenzahl, I.R., C.A. Meakin, D.M. Townsley, D.Q. Lamb, and J.W. Truran, "Spontaneous Initiation of Detonations in White Dwarf Environments: Determination of Critical Sizes," *The Astrophysical Journal*, **696** (2009), 515–527.

Nuclear Astrophysics

2008-147-R1

James W. Truran, Roy J. Holt, Kenneth M. Nollett, Karl E. Rehm, Craig D. Roberts, and Guy Savard

Project Description

More than ever before, astronomical discoveries are driving the frontiers of fundamental physics, and our knowledge of fundamental physics is driving progress in understanding the universe and its contents. This interplay is reflected in the research activities of this project: (1) the development of experimental techniques essential to the determination of a significantly improved (i.e., more accurate) rate for the critical $^{12}\text{C}(\alpha,\gamma)^{16}\text{O}$ reaction for astrophysical studies and (2) the exploration of the mechanism of the rapid nuclear capture process (r-process) responsible for the synthesis of heavy elements through the actinide region in supernovae.

Mission Relevance

The project is relevant to DOE's missions in basic science and national security. The development of a resource for exotic beam experiments is the U.S. nuclear physics community's highest priority in basic science. Its design and operation will also provide technologies that are important to national security. The resource will enable the terrestrial measurement of reaction rates, masses, and lifetimes that are expected to play an important role in studies of the nuclear processes that provide the energetics of supernova and associated nucleosynthesis. We will test and develop aspects of the relevant theory and expand expertise in techniques of large-scale numerical computation. We will also continue development of an experiment focused on the determination of the astrophysically critical $^{12}\text{C}(\alpha,\gamma)^{16}\text{O}$ reaction rate.

FY 2009 Results and Accomplishments

Our research has been focused theoretically on understanding the r-process mechanism of the synthesis of heavy elements and experimentally on the $^{12}\text{C}(\alpha,\gamma)^{16}\text{O}$ reaction.

Considerable progress has been made for the planned study of the $^{12}\text{C}(\alpha,\gamma)^{16}\text{O}$ reaction. The experiment will study the inverse reaction $^{16}\text{O}(\gamma,\alpha)^{12}\text{C}$ — that is, the breakup of ^{16}O into $^{12}\text{C} + \alpha$ initiated by high-energy gamma rays from the free electron laser at the High Intensity Gamma-Ray Source at Duke University. The outgoing charged particles will be stopped in a liquid kept under supercritical pressure and temperature. The energy loss of these particles causes the creation of one bubble, which is detected within 10–20 ms. We have chosen water at supercritical conditions as the target material. Extensive tests have been performed, which are summarized below:

1. A small test setup filled with the refrigerant $\text{C}_2\text{H}_2\text{F}_4$ was fabricated tested with neutron sources and cosmic rays. This vessel is viewed by two fast TV cameras for bubble detection (see Figure 1). The use of the refrigerant $\text{C}_2\text{H}_2\text{F}_4$ allowed us to study bubble formation at room temperature.

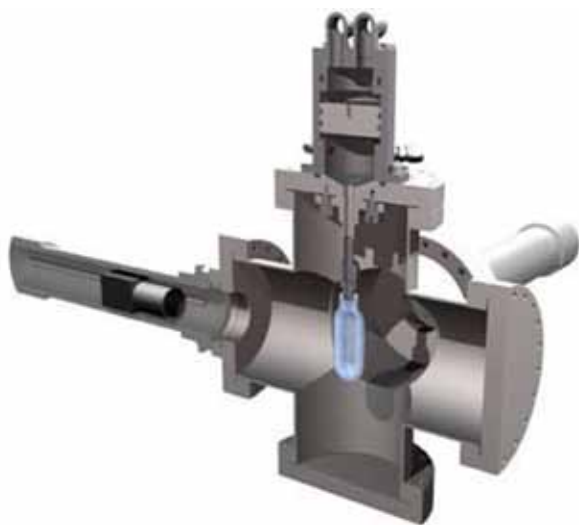


Figure 1. Schematic view of the test setup.

2. Software for detecting bubbles that are quenched through a rapid pressure increase has been developed (Figure 2).

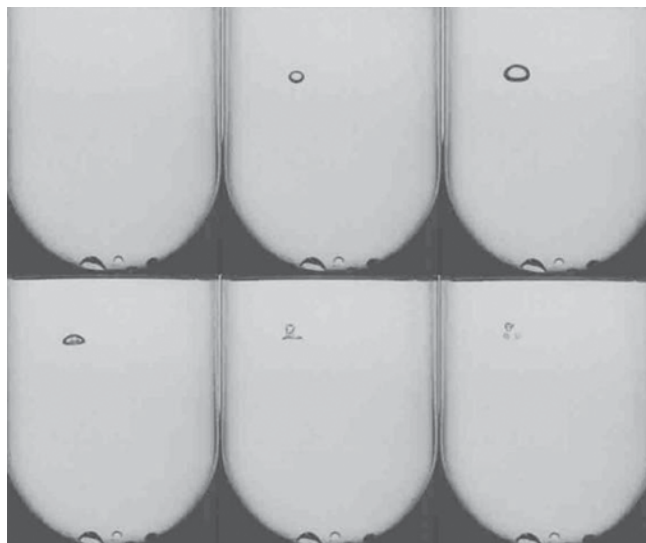


Figure 2. Sequence (pictures taken in 10-ms time intervals) showing the development and subsequent quenching of a cosmic ray-induced bubble.

3. In the next step, $\text{C}_2\text{H}_2\text{F}_4$ will be replaced by water; for which we are presently modifying our test setup.
4. A proof-of-principle test experiment is planned for the spring of 2010.

Proposed Work for FY 2010

We will continue to seek a comprehensive picture of the nuclear evolution of matter in galaxies resulting from the incorporation of the best available nuclear data regarding the lifetimes and masses of heavy nuclei for use in theoretical simulations of the advanced stages of stellar evolution and the outbursts of both thermonuclear (Type Ia) and core collapse (Type II) supernova explosions.

Refereed Publications

Fallis, J., J.A. Clark, K.S. Sharma, G. Savard, F. Buchinger, S. Caldwell, J.E. Crawford, C.M. Deibel, J.L. Fisker, S. Gulick, A.A. Hecht, D. Lascar, J.K.P. Lee, A.F. Levand, G. Li, B.F. Lundgren, A. Parikh, S. Russell, M. van de Vorst, M. Scholte, N.D. Scielzo, R.E. Segel, H. Sharma, S. Sinha, M. Sternberg, T. Sun, I. Tanihata, J. van Schelt, J.C. Wang, Y. Wang, C. Wrede, and Z. Zhou, "Determination of the Proton Separation Energy of Rh-93 from Mass Measurements," *Phys. Rev. C* **78** (2008), 22801.

Farouqi, K., K.-L. Kratz, B. Pfeiffer, L.I. Mashonkina, J.J. Cowan, F.-K. Thielemann, F.-K., and J.W. Truran, "Nucleosynthesis Modes in the High-Entropy-Wind of Type II Supernovae: Comparison of Calculations with Halo-Star Observations," *Astrophysical Journal* **694** (2009), L49–L53.

Glasner, S.A., and J.W. Truran, "CNO Breakout and Nucleosynthesis in Classical Novae," *Astrophysical Journal* **692L** (2009), 58–61.

Meakin, C.A., I. Seitenzahl, D. Townsley, G.C. Jordan, IV, J.W. Truran, and D.Q. Lamb, "Study of the Detonation Phase in the Gravitationally Confined Detonation Model of Type Ia Supernovae," *Astrophysical Journal* **693** (2009), 1188–1208.

Non-Refereed Publications and Presentations

Rehm, K.E., "The Influence of Nuclear Structure and Reactions in Astrophysics," AIP (The American Institute of Physics) Conference Proceedings **1165** (2009), 399.

Tang, X., K.E. Rehm, I. Ahmad, C.R. Brune, A. Champagne, J.P. Greene, A.A. Hecht, D. Henderson, R.V.F. Janssens, C.L. Jiang, L. Jisonna, D. Kahl, E.F. Moore, M. Notani, R.C. Pardo, N. Patel, M. Paul, G. Savard, J.P. Schiffer, R.E. Segel, S. Sinha, B. Shumard, and A.H. Wuosmaa, "The SE1 Factor of the $^{12}\text{C}(\alpha,\gamma)^{16}\text{O}$ Reaction and the ^{16}N β -delayed α Decay," AIP Conference Proceedings **972** (2008), 261–269.

Very High Energy Gamma-Rays: Present and Future

2008-159-R1

Karen Byrum, John Anderson, Gary R. Drake, Victor Guarino, Andrew Krepps, Andrew W. Smith, and Robert G. Wagner

Project Description

This project is focused on two goals. The first is to search for the dark matter particle via possible decay modes involving very high energy (VHE) gamma-rays. Gamma-rays produced in the decays of galactic halo concentrations of weakly interacting massive dark matter particles (WIMPs) can possibly be detected by observations of Imaging Atmospheric Cherenkov Telescope arrays (IACTs, e.g., VERITAS). (It is hypothesized that WIMPs constitute the dark matter that to date has only been inferred from its gravitational interaction with "normal" baryonic matter.) The second goal is the eventual development of a next-generation gamma-ray telescope array that achieves sensitivity levels that are an order of magnitude better than current instruments, while also operating at an energy threshold in the 20–50-GeV range, compared to the current typical value of 100 GeV. Telescope R&D has been pursued through the design and fabrication of a very fast pattern-recognition trigger and through the mechanical design of both a conventional Davies-Cotton (DC) and a novel Schwarzschild-Couder (SC) telescope structure.

Mission Relevance

This project supports DOE's science mission in its High Energy Physics program in non-accelerator-based physics at the cosmic frontier. Specifically, the project proposes to use the detection of VHE gamma-rays from astrophysical sources to explore particle and astroparticle physics to search for the mysterious component of matter that constitutes nearly 25% of the energy density of our universe (i.e., dark matter). This project is also developing cutting-edge technology to advance the sensitivity of the telescope arrays used to perform gamma-ray astrophysics. In addition, the project fosters the development of scientific and technical expertise in applying the technology to both gamma-ray astrophysics and, in the case of the pattern-recognition trigger, to accelerator-based particle physics.

FY 2009 Results and Accomplishments

Part 1: Analysis of VHE Gamma-Rays

During the past two years, VERITAS has observed the local spiral galaxy, M33, and four low-surface brightness dwarf spheroidal (dSph) galaxies: Ursa Minor, Draco, Boötes 1, and Willman I (Figure 1). We have performed the primary analysis of the dSph galaxy data and has also analyzed the M33 data. No significant gamma-ray signal was observed from any of the galaxies.

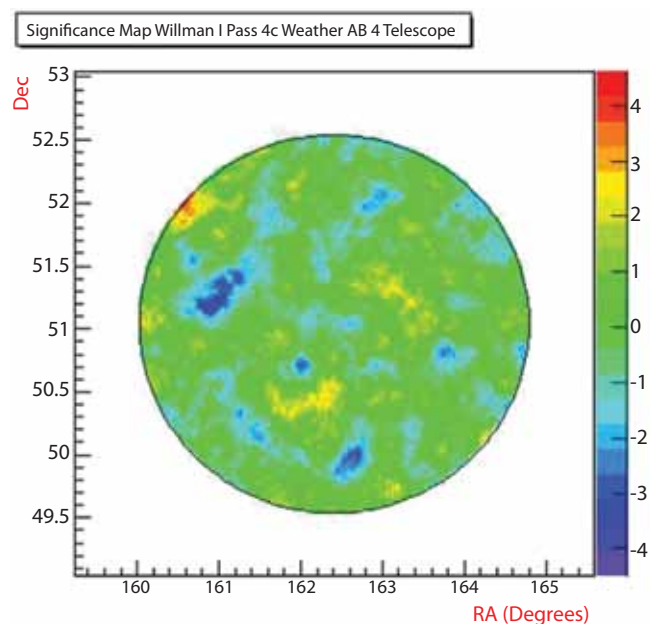
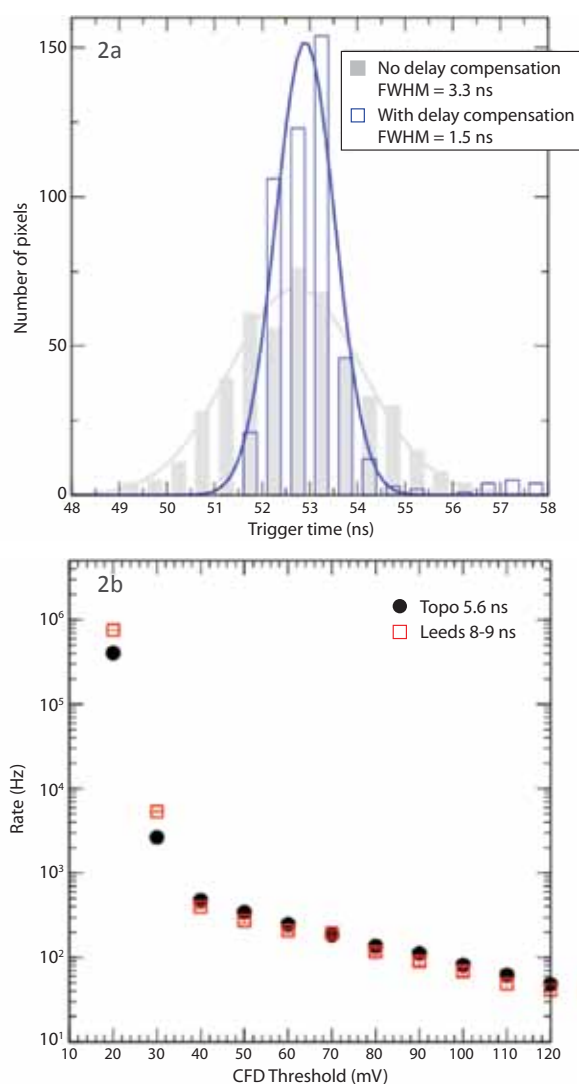


Figure 1. The significance map from the analysis of 2008 observations of the Willman I dwarf spheroidal galaxy. The number of standard deviations from the estimated background flux is plotted by using a "temperature scale" that runs from purple (indicating four standard deviations below the estimated background) to red, which is four standard deviations above the background. The patterning on the plot is consistent with Gaussian fluctuations about a constant background and centered on Willman 1. A real signal would be indicated by the region of high positive standard deviation at the central location.

Part 2: Fast Pattern-Recognition Trigger

Our concept uses parallax displacement of Cherenkov light images to develop a trigger that exploits the imaging differences between gamma-ray and hadron-induced air showers by utilizing the different viewpoints in an IACT array. These fluctuations translate into a large spread of shower core reconstruction in the telescope plane. The key to our approach is to incorporate pattern recognition into a Level 2 Trigger by using the simple discriminated hits from Level 1 as input. When the Level 3 Trigger accepts an event, a signal is sent back to the front-end electronics of all cameras participating in the trigger, and the event is read out by the data acquisition system. Selected highlights from the second year's work follow.



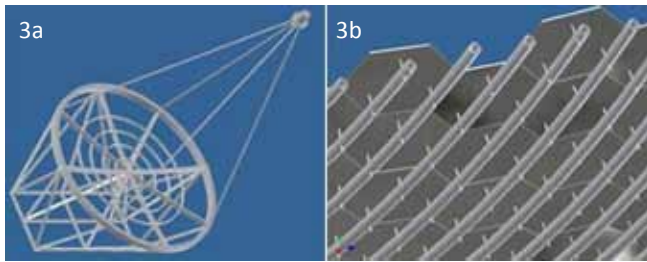
Figures 2a and 2b. Figure 2a is the distribution of the signal arrival time for all pixels on one of the VERITAS telescopes. The improvement in narrowing the pixel signal arrival time due to the programmable adjustment capability of our Level 1.5 module is shown. Figure 2b is the VERITAS Level 2 cosmic ray rate as a function of the VERITAS Level 1 signal threshold. The flat part of the spectrum (above 40 mV) shows signals (cosmic rays); the exponential rising edge is background (mostly due to night sky random starlight).

We built several board modules, including an I/O module; Level 1.5 (L1.5) processor boards, which use a Xilinx Vertex 5 field-programmable gate array (FPGA), one of the fastest available; and a Level 2 processor module. The processing includes forming a programmable time window and evaluating the hits. Figures 2a and b, shown on the left, show results from our first field measurements. Figure 2a plots the laser timing alignment, where the gray Gaussian is the distribution from the VERITAS Level 1, and the dark blue Gaussian is that after adjustment in the L1.5 modules. Figure 2b shows the VERITAS Level 2 cosmic ray rate as a function of the VERITAS Level 1 signal threshold. The flat part of the spectrum (above 40 mV) shows real signal events (i.e., cosmic rays, which include gamma-rays); the exponential rising edge is background (mostly random night sky starlight). In our initial test, we were able to reduce random night sky background by about 20% while realizing greater than 100% efficiency in retaining the cosmic ray signal. We believe our trigger is more efficient than that used in the current figure.

Part 3: Future Telescope Design

During the past year, our role in mechanical telescope design has been substantially expanded in two projects under consideration for a next-generation, ground-based gamma-ray experiment: (1) the Atmospheric Gamma-Ray Imaging System (AGIS), which is a mostly U.S.-based project pursuing a novel (i.e., SC), telescope design that has never been built, and (2) the Cherenkov Telescope Array (CTA), a mostly European-based project pursuing a more classical (i.e., DC) telescope design. Most of our second-year efforts have been focused on the mechanical design and analysis of this DC telescope and on the design of an azimuth drive system for both DC and SC telescopes. Selected highlights follow.

Figure 3a shows a 12-m telescope design that focuses on studying the engineering aspects. The mirror support structure consists of concentric rings that provide stiffness and support for the mirrors; the optical surveillance system pivots at the 3- and 9-o'clock positions, and gears at the same locations drive the elevation motion. Figure 3b shows one method for providing support to the attachment points for the mirrors. Figure 4 shows initial calculations of the structure analysis, which were used as input into a simple 3D finite element analysis model.



Figures 3a and 3b. The left figure shows a 12-m DC telescope optical support structure design. The right figure shows one method for providing support to the attachment points for the mirrors.

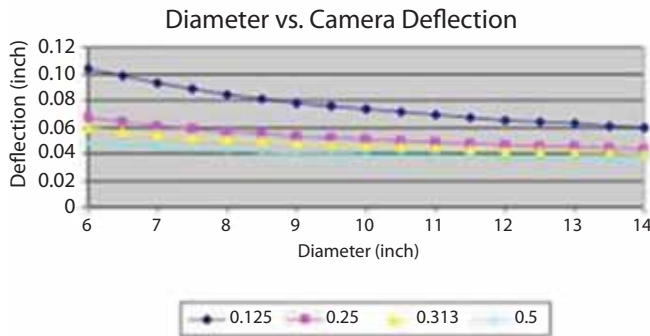


Figure 4. Initial calculations of the structure analysis, which were used to evaluate the deformation of the camera only in the simple truss structure for multiple focal length/diameter values.

We have studied several telescope motion systems, specifically, elevation and azimuth drive systems. Figure 5a shows a model of the bearings and gear for an elevation drive system. Figure 5b is V. Guarino's design for a low-cost, fast-rotating telescope azimuth drive motion system. Based on the concept of large industrial turntables, a straight gear is rolled accurately to the required radius, potentially providing a gear drive that is robust and stiff.



Figure 5. The left figure shows a model of the bearings and gear for an elevation drive system. The right figure is a design for a low-cost, fast-rotating telescope, azimuth drive motion system.

Proposed Work for FY 2010

Part 1: Analysis of VHE Gamma-Rays

The VERITAS array will continue to observe dark matter targets, including dwarf galaxies, during FY10. We have done the analysis of these data thus far and will take responsibility for publishing the results. We will also perform the secondary confirming analysis for non-dwarf dark matter targets: local large galaxies and globular clusters.

Part 2: Fast Pattern-Recognition Trigger

During FY10, we intend to complete both the model pattern-recognition trigger system itself (including all firmware design) and field testing of the system at a VERITAS array. We expect to use this model system as the basis for a proposed upgrade to the VERITAS trigger starting in FY11.

Part 3: Future Telescope Design

During FY10, we intend to complete a final design of a 12-m DC telescope, which may be chosen as the standard CTA instrument. The plan is to continue this design effort through mid FY10. A final decision on choice of design is expected during the early spring of FY10. If our design is selected, we will build a model with DESY.

While the SC telescope originally was designed as a 9-m primary mirror instrument and met all of the deformation specifications, we now need to scale up the design to an 11.5-m size, which provides significantly better capability and matches current camera designs under development at Stanford Linear Accelerator Center and the University of Chicago. We will continue work to complete an 11.5-m SC design and remain positioned for leading roles on either or both of the future array telescope mechanical fabrication efforts (i.e., AGIS or CTA).

Non-Refereed Publications and Presentations

Anderson, J., K. Byrum, J. Dawson, G. Drake, B. Haberichter, D. Horan, F. Krennrich, A. Kreps, A. Madhavan, M. Schroedter, and A. Smith, "A New High-Speed Pattern Recognition Trigger for Ground-Based Telescope Arrays Used In Gamma Ray Astronomy," presentation at the IEEE (Institute of Electrical and Electronics Engineers) Nuclear Science Symposium (and paper submitted to IEEE Nuclear Science Symposium Conference Proceedings), Dresden, Germany, October 20–24, 2008.

Buckley, J., E.A. Baltz, G. Bertone, K. Byrum, S. Fegan, F. Ferrer, P. Gondolo, J. Hall, D. Hooper, D. Horan, S. Koushiappas, H. Krawczynski, S. LeBohec, S. Profumo, J. Silk, T. Tait, V. Vasiliiev, R.G. Wagner, S. Wakely, M. Wood, and G. Zaharijas, "Section on Prospects for Dark Matter Detection of the White Paper on the Status and Future of Ground-Based TeV Gamma-Ray Astronomy," *Astrophysics (astro-ph)*, arXiv:0812.0795 December 2008.

Buckley, J., K. Byrum, B. Dingus, A. Falcone, P. Kaaret, H. Krawczynski, M. Pohl, V. Vassiliev, and D.A. Williams, "The Status and Future of Ground-based TeV Gamma-ray Astronomy," a White Paper prepared for the Division of Astrophysics of the American Physical Society, *Astrophysics (astro-ph)*, arXiv:0810:0444, October 2008.

Byrum, K., "Array Trigger Costs," presentation at AGIS Costing Review, Ames, Iowa, March 6, 2009.

Byrum, K., J. Buckley, S. Bugayov, B. Dingus, S. Fegan, S. Funk, E. Hays, J. Holder, D. Horan, A. Konopelko, H. Krawczynski, F. Krennrich, S. Lebohec, G. Sinnis, A. Smith, V. Vassiliev, and S. Wakely, "Technology Section of the White Paper on the Status and Future of Ground-based TeV Gamma-ray Astronomy," *Astrophysics (astro-ph)*, arXiv:0810:4367 October (2008).

Guarino, V., "ANL Mechanical Engineering Capabilities and DC and SC Telescope Designs," CTA Collaboration Meeting, Padova, Italy, November 3–5, 2008.

Guarino, V., "Design of a 12m Telescope by ANL/DESY Group," CTA Collaboration Meeting, Krakow, Poland, May 11–13, 2009.

Guarino, V., K. Byrum, J. Buckley, S. Digel, S. Funk, D. Hanna, F. Krennrich, A. Falcone, S. Fegan, J. Finley, P. Kaaret, A. Konopelko, H. Krawczynski, R. Romani, V. Vassiliev, R. Wagner, T. Weekes, and M. Woods, "The Advanced Gamma-ray Imaging System (AGIS): Telescope Mechanical and Optical System Designs," poster at the APS Meeting, Poster Session I, Denver, CO, May 2–5, 2009.

Schroedter, M., J. Anderson, K. Byrum, G. Drake, C. Duke, J. Holder, A. Imran, A. Madhavan, F. Krennrich, A. Kreps, and A. Smith, "A Topological Trigger System for Imaging Atmospheric-Cherenkov Telescopes," *Astrophysics (astro-ph)*, arXiv:0908:0179, August 2009.

Wagner, R.G., K. Byrum, M. Sanchez, A. Vaniachine, O. Siegmund, N. Otte, E. Ramberg, J. Hall, and J. Buckley, "The Next Generation of Photo-Detectors for Particle Astrophysics," *Astrophysics (astro-ph)*, arXiv:0904:3565 April 2009.

Solar and Astrophysical MHD

2008-188-R1

Paul F. Fischer, Fausto Cattaneo, and Aleksandr Obabko

Project Description

The purpose of this work is to investigate some basic properties of astrophysical and solar magnetohydrodynamics (MHD) by using petascale platforms. The work involves both theoretical and computational components, with the former providing guidance for identifying problems that will elucidate the essential mechanisms of observable MHD phenomena, such as the solar dynamo. The solar dynamo is still poorly understood, yet it is a central driver for many observable astrophysical phenomena that affect life on earth, including the sun spot cycle and the formation of coronal ejections. In addition to solar/stellar dynamos, MHD is believed to play a critical role in generating some of the most energetic phenomena in the universe: namely, the energy releases from the in-fall of matter onto compact objects, such as black holes. Current theories for the phenomenal rate of energy release center on magneto-rotational instability (MRI) providing the trigger to destabilize what would otherwise be a stable orbit of matter around these objects. MHD is also of relevance to terrestrial physics. Liquid metal film cooling has been proposed for targets in high-energy accelerators and as the first-wall for tokamaks.

Mission Relevance

The project supports the science mission of DOE's Office of High Energy Physics by expanding astrophysics research. Other agencies that will be interested in the results of the project include the National Science Foundation (NSF) and the National Aeronautics and Space Administration (NASA).

FY 2009 Results and Accomplishments

We identified some outstanding challenges in shearing-box computations, which are commonly used to investigate small-scale turbulence central to magneto-rotational instabilities and self-sustained dynamos. In particular, we showed that the aspect ratio of the computational domain can have a profound effect on the degree of intermittency in angular momentum transport. For unit-aspect ratio domains, our computations showed strong intermittency, as found in previous studies. In boxes with larger aspect ratios, however, the intermittent behavior disappears, and angular momentum transport is inhibited.

The results of this study call into question the viability of the shearing box as a surrogate for a global model of magneto-rotational turbulence simulations in astrophysical settings. In addition to addressing the intermittency question, we have been using our large-scale simulation results to investigate fundamental scaling laws in MHD turbulence. The exact ana-

lytic relations of Politano and Pouquet (see *Geophys. Res. Lett.* **25** [1998] 273 and *Phys. Rev. E* **57** [1998] R21) are often invoked to suggest that the spectrum of MHD turbulence follows the $-5/3$ Kolmogorov scaling; however, recent observations and high-resolution numerical simulations indicate a $-3/2$ spectrum. These observations can be reconciled with the Politano-Pouquet relationship if one accounts for scale-dependent dynamic alignment between the velocity and magnetic fields. We used large-scale MHD turbulence data computed on the Argonne Leadership Computing Facility (ALCF) to qualitatively demonstrate the correctness of this interpretation, which yields further insight into properties of MHD turbulence.

We also continued developing our macro-scale MHD code (in the context of the Argonne hydrodynamics code, Nek5000). It will allow us to simulate global instabilities in spherical shells. We developed a new two-fluid MHD formulation for Nek5000 that will accommodate general boundary conditions for the magnetic field. To be specific, this new formulation allows imposition of far-field boundary conditions that are more realistic than the standard Neumann or Dirichlet types supported in the past. The new MHD formulation will be validated in 2010 and tested at scale on the ALCF Blue Gene (BG)/P by using time provided under the NEK5000 project.

Proposed Work for FY 2010

This work will focus on continued large-scale simulations of MHD turbulence. In addition to our spectral code, we anticipate large simulations in spherical geometries based on the newly developed formulation in Nek5000. In the first half of FY10, we will validate the new extended-boundary formulation for MHD. Once it is validated with proper boundary conditions, we will be able to investigate MHD turbulence in more complex domains than are accessible with the spectral code.

Refereed Publications

Boldyrev, S., J. Mason, and F. Cattaneo, "Dynamic Alignment and Exact Scaling Laws in Magnetohydrodynamic Turbulence," *Astrophys. J. Lett.* **699**(1) (2009), L39.

Giannakis, D., R. Rosner, and P. Fischer, 2009, "Instabilities in Free-Surface Hartmann Flow at Low Magnetic Prandtl Numbers," *J. Fluid Mech.* **638** (2009), 217.

Mignone, A, A. Ferrari, G. Bodo, P. Rossi, and F. Cattaneo, "Aspect Ratio Dependence in Magnetorotational Instability Shearing Box Simulations" pp. 77–82 in *Protostellar Jets in Context*, by K. Tsinganos, T. Ray, and M. Stute, Astrophysics and Space Science Proceedings Series, Springer, Berlin, Germany, 2009.

Non-Refereed Publications and Presentations

Fischer, P., "Scaling the Spectral Element Method to One Million Processors," presented at the International Conference on Spectral and High Order Methods (ICOSAHOM 09), June 22–26, 2009, Trondheim, Norway.

Explosive Nucleosynthesis of Heavy Elements

2009-035-NO

James W. Truran and Craig D. Roberts

Project Description

The focus of this research in theoretical nuclear astrophysics concerns (1) the mechanisms of heavy element synthesis iron-to-uranium, (2) the nature of the explosive stellar environments in which nucleosynthesis occurs, (3) the impact of the nuclear energetics on the explosive events, and (4) the resulting chemical evolution of galaxies. The research will result in nuclear theory inputs for specific astrophysical problems and refined theoretical methods that will be of use far into the future.

Mission Relevance

This project is tied to DOE's mission in science. The proposed research will result in both nuclear theory inputs for specific astrophysical problems and refined theoretical methods that will be of use far into the future. Such a resource will enable the terrestrial measurement of reaction rates, masses, and lifetimes that are expected to play an important role in studies of the nuclear processes that provide the energetics of supernova and associated nucleosynthesis. We will develop and test aspects of the relevant theory and expand expertise in techniques of large-scale numerical computation. Our studies of Type Ia supernovae (SNe Ia) can be expected to impact the reliability of their use as distance indicators and probes of dark energy. The results will have a major impact on experimental physics programs and will be of interest to both the DOE Office of Nuclear Physics and the Nuclear Physics Division of the National Science Foundation.

FY 2009 Results and Accomplishments

Research has achieved significant progress in several areas:

We have significantly increased our understanding of flame propagation in the deflagration phase of SNe Ia by using 3D whole-star simulations and the gravitationally confined detonation (GCD) model. We continue to study this problem and the nucleosynthesis "post-processing" of the temperature/density trajectories recovered from hydrodynamic models of

SNe Ia in order to provide more accurate determinations of the composition of the ejecta and to identify the expected range of peak SNe Ia brightnesses resulting from our models.

We have undertaken a detailed investigation of the nucleosynthesis processes that are understood to be responsible for the origin of the heavy elements. Theoretical calculations of the operation of the rapid process of neutron capture synthesis in the “high entropy winds” of Type II supernovae have identified and constrained conditions that are required to reproduce the extraordinary robustness of the observed rapid-process abundance patterns in the most metal-deficient stars in our galaxy’s halo. We have also investigated the “neutrino-p” process in which outgoing neutrinos interacting with proton-rich nuclei have been shown to produce abundance levels of nuclei through the strontium-yttrium-zirconium regime that are comparable to those observed in metal-deficient galactic halo stars.

We have explored the behaviors of nova runaways resulting from matter accretion at low rates onto massive white dwarfs of low central temperatures and have pursued multidimensional studies of the final stages of the evolution to thermonuclear runaway of classical novae. Two separate major topics concerning the equation of state for astrophysical applications have been investigated, yielding promising results.

Proposed Work for FY 2010

We will continue to seek a comprehensive picture of the history of nucleosynthesis in supernovae and of nuclear energetics and the associated nucleosynthesis history of matter in galaxies, dominated by input from both Type Ia and Type II supernovae. This will be used to address broader questions, such as the observed trends in galactic enrichment in heavy elements, as reflected in the abundance history of galaxies. Our immediate emphasis will be on constraining models for SNe Ia and understanding their luminosity histories and on identifying the site of rapid-process neutron capture synthesis in the early galaxy. These results will also serve both to identify critical nuclear parameters to be determined with future nuclear experiments and to better constrain stellar evolution and supernova models. We will continue working toward an equation of state appropriate for compact astrophysical objects and the identification of unambiguous signatures of quark matter in their cores.

Refereed Publications

Klähn, T., C.D. Roberts, L. Chang, H. Chen, and Y.-X. Liu, “Cold Quarks in Medium: An Equation of State,” submitted to *Phys. Rev. C* (2009).

Meakin, C.A., I.R. Seitenzahl, D.M. Townsley, G.C. Jordan, J.W. Truran, and D.Q. Lamb, “Study of the Detonation Phase in the Gravitationally Confined Detonation Model of Type Ia Supernovae,” *Astrophys. J.* **693** (2009), 1188–1209.

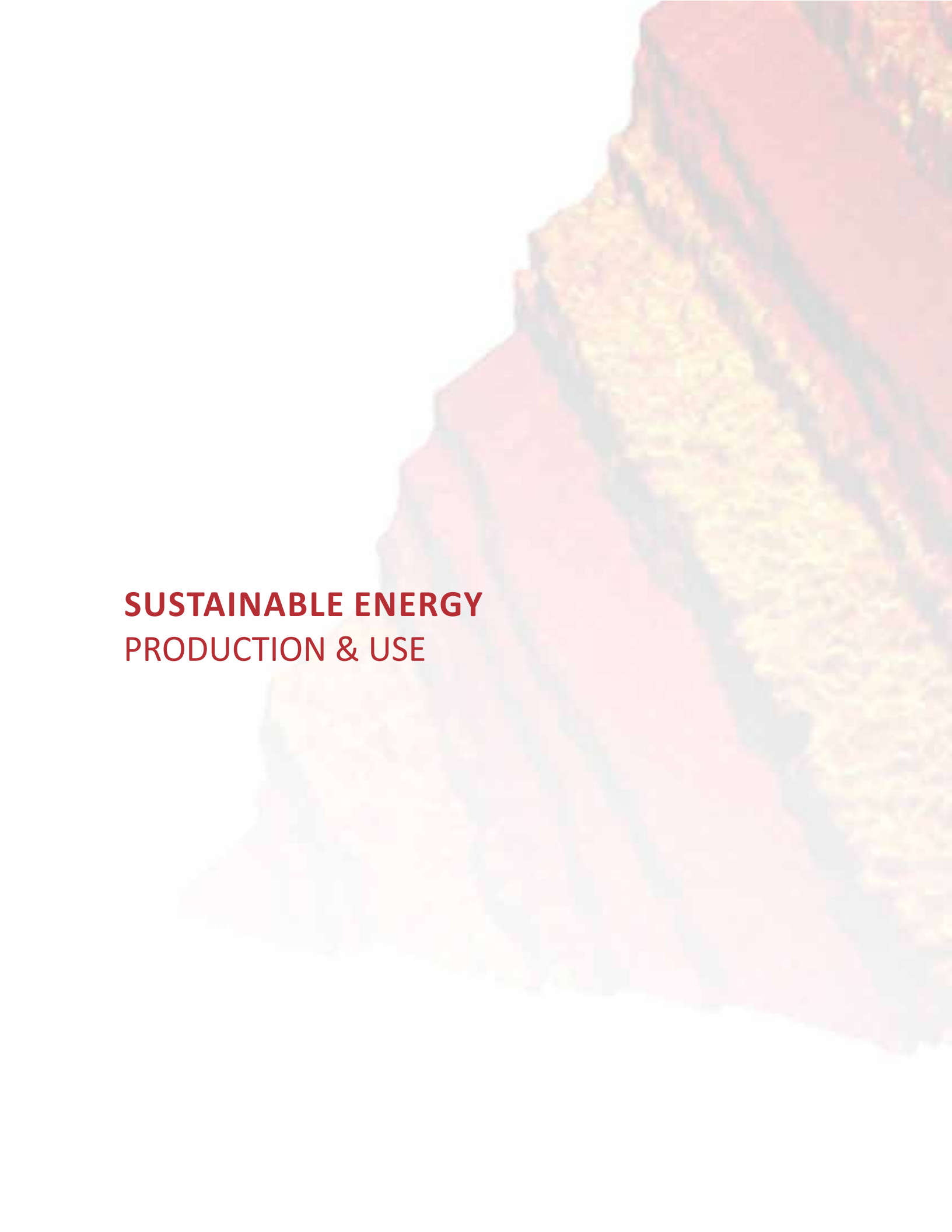
Seitenzahl, I.R., C.A. Meakin, D.M. Townsley, D.Q. Lamb, and J.W. Truran, “Spontaneous Initiation of Detonations in White Dwarf Environments: Determination of Critical Sizes,” *Astrophys. J.* **696** (2009), 515–528.

Seitenzahl, I.R., C.A. Meakin, D.Q. Lamb, and J.W. Truran, “Initiation of the Detonation in the Gravitationally Confined Detonation Model of Type Ia Supernovae,” *Astrophys. J.* **700** (2009), 642–653.

Typel, S., G. Röpke, T. Klähn, D. Blaschke, and H.H. Wolter, “Composition and Thermodynamics of Nuclear Matter with Light Clusters,” submitted to *Phys. Rev. C* (2009).

Non-Refereed Publications and Presentations

Klähn, T., C.D. Roberts, D.B. Blaschke, and F. Sandin, “Neutron Stars and the High Density Equation of State,” *AIP Conf. Proc.* **1128** (2009), 175–185.



SUSTAINABLE ENERGY PRODUCTION & USE

Solid-State Chemistry for Advanced Thermoelectric Materials

2007-186-R2

Mercouri G. Kanatzidis

Project Description

A goal of this project was to design, model, synthesize, and characterize a wide variety of novel solid-state materials for thermoelectric applications. In particular, the target systems for the third year were (1) cubic nanostructured chalcogenides that (a) exhibit spinodal decomposition as a mechanism of nanostructure formation or (b) contain nanocrystals of second phases introduced via matrix encapsulation, (2) low-dimensional crystalline materials characterized by a highly anisotropic complex structure and solid solutions with multiple constituent elements, and (3) intermetallic alloys that exhibit semiconducting or semi-metallic properties.

Mission Relevance

This project is relevant to DOE's mission in science. In support of this mission, we focused on achieving highly functioning thermoelectric materials for practical applications in energy production, conversion, and conservation by attempting to lower the thermal conductivity of the materials and simultaneously increase electrical conductivity and thermoelectric power. Extensive investigation of physical and chemical principles at a fundamental level is essential to understanding how advanced thermoelectric materials should be designed. As expected, the results of this project are general in nature, broadly applicable to a variety of thermoelectric materials systems as well as to energy conversion systems. The novel materials synthesis techniques we developed as a result of this project will also help basic and applied materials science communities in creating new classes of materials with targeted properties and functionalities.

FY 2009 Results and Accomplishments

Among all members of the $\text{AgPb}_m\text{MQ}_{2+m}$ class of materials that we previously investigated, we selected $\text{Ag}_{1-x}\text{Pb}_m\text{SbSe}_{2+m}$ and $\text{Ag}_{1+x}\text{Pb}_m\text{SbSe}_{2+m}$ ($m = 11, 15, 20$) for the doping study to further improve their thermoelectric properties. The applied doping levels (x) were 0.03, 0.1, and 0.2. Enhanced electrical conductivity with constant thermal conductivities was achieved, regardless of doping level, thus giving rise to a net increase of ZT , the figure of merit for the efficiency of thermoelectric materials.

For $\text{Yb}_5\text{Al}_2\text{Sb}_6$ (discovered in FY09), we attempted substitution of Yb cations by Sr or Mg to lower the thermal conductivity. A significant reduction in thermal conductivity was achieved — to values of 2.5 and 0.8 W/m·K (Watt/meter-Kelvin) for $\text{SrYb}_4\text{Al}_2\text{Sb}_6$ and $\text{Mg}_{0.1}\text{Yb}_{4.9}\text{Al}_2\text{Sb}_6$, respectively, compared to the 3.8 W/m·K thermal conductivity of the parent, $\text{Yb}_5\text{Al}_2\text{Sb}_6$.

A new compound, CaFe_4As_3 , with a three-dimensional framework made of Fe/As ribbons, was synthesized (Figure 1A–D). This result is an exciting discovery, indicating that the Fe/As network is adaptable and suggesting a broad family of complex Fe/As materials. Electrical resistivity shows typical metallic behavior with significant anisotropy. Strong anisotropy is also found in the magnetization of CaFe_4As_3 . The unit cell volume shows abrupt changes as a function of temperature, with hysteretic transitions observed at ~ 23 K and ~ 90 K. We found that the observed magnetic transitions are accompanied by subtle structural distortions, which have a profound effect on the magnetic exchange interactions.

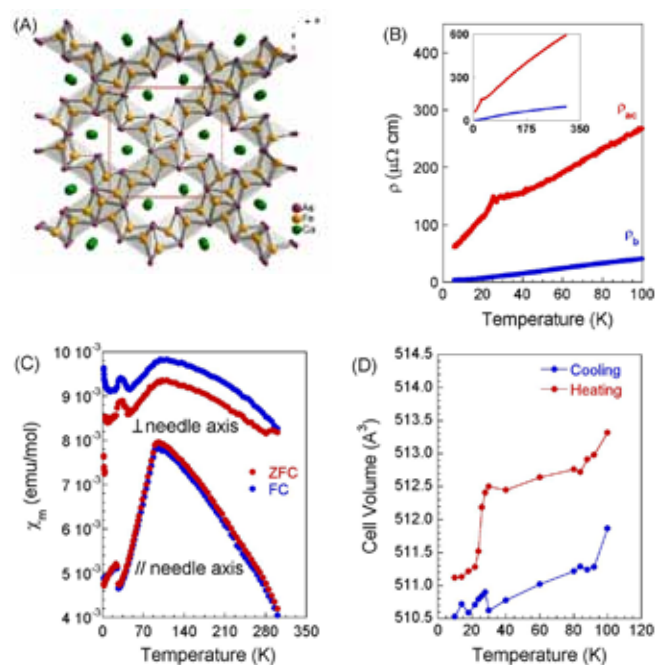


Figure 1. (A) The structure of CaFe_4As_3 , (B) single-crystal electrical resistivity measured perpendicular (red) and parallel (black) to the b -axis at 5–100 K (the inset shows data up to 300 K), (C) anisotropic magnetic susceptibility data at 2000 Oe, and (D) the unit cell volume measured upon heating and cooling from 10 to 100 K (Note that data collections between 10 and 100 K upon heating and cooling were performed separately, and before data collection, the crystal was quenched from RT to 5 K and 100 K for heating branch and cooling branch, respectively. At each data point, an equilibration time of 5 min [after stabilization within 0.1 K] was used before the data acquisition for both heating and cooling. None of the temperature points were collected with the same temperature history/treatment; therefore, they do not have to overlap.)

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Cook, B.A., M.J. Kramer, J.L. Harringa, M.-K. Han, D.-Y. Chung, and M.G. Kanatzidis, "Analysis of Nanostructuring in High Figure-of-Merit $\text{Ag}_{1-x}\text{Pb}_m\text{SbTe}_{2+m}$ Thermoelectric Materials," *Adv. Funct. Mater.* **19** (2009), 1254.

Todorov, I., D.Y. Chung, C.D. Malliakas, Q. Li, T. Bakas, A. Douvalis, G. Trimarchi, K. Gray, J.F. Mitchell, A.J. Freeman, and M.G. Kanatzidis, "CaFe₄As₃: A Metallic Iron Arsenide with Anisotropic Magnetic and Charge-Transport Properties," *J. Am. Chem. Soc.* **131** (2009), 5405.

Todorov, I., D.Y. Chung, L. Ye, A.J. Freeman, and M. Kanatzidis, "Synthesis, Structure and Charge Transport Properties of Yb₅Al₂Sb₆: A Zintl Phase with Incomplete Electron Transfer," *Inorg. Chem.* **48** (2009), 4768.

Hahn, S.E., Y. Lee, N. Ni, P.C. Canfield, A.I. Goldman, R.J. McQueeney, B.N. Harmon, A. Alatas, B.M. Leu, E.E. Alp, D.Y. Chung, I.S. Todorov, and M.G. Kanatzidis, "Influence of Magnetism on Phonons in CaFe₂As₂ as Seen via Inelastic X-ray Scattering," *Phys. Rev. B* **79** (2009), 220511.

Hoang, K., A. Tomic, S. Tessmer, S.D. Mahanti, Th. Kyratsi, D.Y. Chung, and M.G. Kanatzidis, "The Role of K/Bi Disorder in the Electronic Structure of $\beta\text{-K}_2\text{Bi}_8\text{Se}_{13}$," *Phys. Rev. B* **80** (2009), 125112.

Sootsman, J., D.Y. Chung, and M.G. Kanatzidis, "New and Old Concepts in Thermoelectric Materials," *Angew. Chem.* **48** (2009), 8616.

Non-Refereed Publications and Presentations

Freeman, A.J., G. Trimarchi, M. Kanatzidis, and I. Todorov, D.Y. Chung, "Emergence of complex magnetism in three-dimensional, yet quasi-layered, iron pnictides: CaFe₄As₃," presented at the 2009 APS March Meeting, Pittsburgh, PA, March 16–20, 2009.

Hahn, S., A. Alatas, B. Leu, Y. Lee, N. Ni, D.Y. Chung, I. Todorov, M. Kanatzidis, E. Alp, P. Canfield, A. Goldman, and R.B. Harmon, "CaFe₂As₂ Phonons via Inelastic X-ray Scattering and First Principles Calculations," presented at the 2009 APS March Meeting, Pittsburgh, PA, March 16–20, 2009.

Osborn, R., S. Rosenkranz, E.A. Goremychkin, D.Y. Chung, I.S. Todorov, H. Claus, A.D. Christianson, M.D. Lumsden, C.D. Malliakas, M.G. Kanatzidis, R.I. Bewley, and T. Guidi, "Resonant spin excitation in Ba_{1-x}K_xFe₂As₂," presented at the 2009 APS March Meeting, Pittsburgh, PA, March 16–20, 2009.

Rosenkranz, S., R. Osborn, E.A. Goremychkin, A.D. Christianson, M.D. Lumsden, D.Y. Chung, I.S. Todorov, H. Claus, C.D. Malliakas, M.G. Kanatzidis, R.I. Bewley, and T. Guidi, "Resonant spin excitation in Ba_{1-x}K_xFe₂As₂," presented at the International Conference on Neutron Scattering 2009, Knoxville, TN, May 3–7, 2009.

Rosenkranz, S., R. Osborn, E. Goremychkin, I.S. Todorov, D.Y. Chung, H. Claus, J.A. Schlueter, C.D. Malliakas, and M.G. Kanatzidis, "Pressure dependence of the inelastic neutron scattering response of CaFe₂As₂," presented at the 2009 APS March Meeting, Pittsburgh, PA, March 16–20, 2009.

Todorov, I., D.Y. Chung, H. Claus, K. Gray, Q. Li, J. Mitchell, T. Bakas, and M. Kanatzidis, "Exploring the Fe/As Ternary System: Synthesis, Structure, Magnetic, and Charge Transport Properties of CaFe₄As₃ and Na_xFe₂As₂," presented at the ICAM Workshop on Fe-pnictide and Related Superconductors, University of Maryland at College Park, MD, November 16–17, 2008.

Todorov, I., D.Y. Chung, C.D. Malliakas, H. Claus, K. Gray, and M.G. Kanatzidis, "Superconductivity of NaFeAs Reviewed," presented at the 2009 The North American Solid State Chemistry Conference, Ohio State University, Columbus, OH, June 17–20, 2009.

Innovations in Advanced Simulation and Experimental Code Validation for Nuclear Energy Applications

2008-118-R1

Kenneth E. Kasza, Paul F. Fischer, Stephen W. Lomperski, and William D. Pointer

Project Description

The project will greatly advance nuclear reactor research and design by establishing the validity of high-fidelity thermal fluids and computer simulation tools. The simulation tools, when developed, could be used directly for reactor design or for qualifying/tuning lower fidelity models/tools. The long-range goal is to greatly reduce the need for experimental performance quantification of new reactor designs. The improved phenomenological research capabilities and advanced simulation tools being developed will significantly contribute to the design of high-performance, safe, and reliable nuclear reactors, ultimately impacting thermal fluid performance of all individual components (including the core, plenums, heat exchangers, steam generators, pumps, and piping); reactor emergency cooling, which depends on multi-component interactions; structural integrity issues related to detrimental thermal distributions; and heat sink design.

Mission Relevance

This project supports DOE's energy mission. The experimental and computational expertise in thermal fluid science and reactor design being developed are key elements in DOE's efforts to develop safe, reliable, and economical advanced reactors, including liquid metal reactors. Other advanced reactor systems such as gas- and lead-cooled systems are key components of the Generation IV Nuclear Energy Systems Program.

FY 2009 Results and Accomplishments

In FY08, we selected above-core parallel jet mixing as our initial focus, designed an air-based parallel jet mixing apparatus, and initiated procurement of critical state-of-art measurement instrumentation. Also two computational fluid dynamics codes, STAR-CD and NEK5000, were configured to simulate mixing phenomena and used to guide the design of the apparatus. Additionally, two turbulence models were implemented: RANS (Reynolds-averaged Navier-Stokes) and LES (large eddy simulation). We received a DOE competitive INCITE grant to use Argonne's BlueGene/P computer.

In FY09, the parallel jet mixing apparatus was completed (Figure 1), and equipment checkout and tune-up were initiated. Simulations (Figure 2) with STAR-CD and NEK5000 were performed to compare features of both codes and to explore the influence of various parameters on jet behavior.

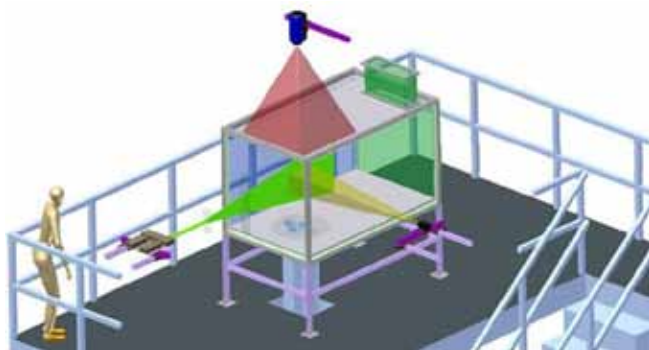


Figure 1. Argonne's gas jet mixing apparatus called MAX: utilizes PIV Nd:YLF laser (left), infrared camera (top), PIV camera (right), and hexagonal flow channels below glass mixing chamber.

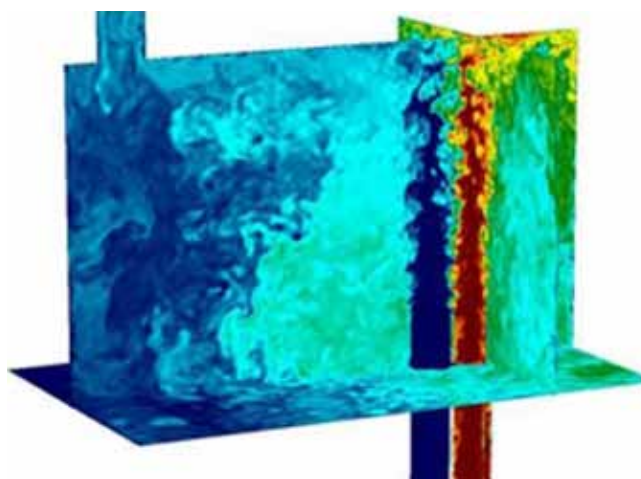


Figure 2. NEK5000 Simulated temperature field of two parallel jets mixing: cold (blue) and hot (red).

Proposed Work for FY 2010

In FY10, we will conduct a series of jet mixing tests and corresponding simulations with STAR-CD and NEK5000 that will result in a report on achieved simulation fidelity and the adequacy of existing experimental techniques for measuring jet mixing velocity and important turbulence parameters. We will also establish a strongly integrated team of experimental and simulation experts who have a clear understanding of the longer-range experimental equipment and facilities needed for supporting additional advanced simulation code development/validation studies aimed at investigating a broader range of phenomena, such as thermal buoyancy-mediated flows in a wide range of reactor components beyond the core upper plenum and for other reactor coolant fluids.

Refereed Publications

Pointer, W.D., S. Lomperski, P. Fischer, and A. Obabko, "Proposed Experiment for Validation of CFD Methods for Advanced SFR Design: Upper Plenum Thermal Striping and Stratification," *Proceedings of the 17th International Conference on Nuclear Engineering, ICONE17*, Brussels, Belgium, July 12–16, 2009.

Characterization of Ignition, Combustion, and Emissions for Advanced Engines and Fuels

2008-121-R1

Stephen T. Pratt, R. Raj Sekar, Bipin Bihari, Stephen A. Ciatti, Sreenath B. Gupta, Lawrence B. Harding, Stephen J. Klippenstein, Sundar Krishnan, Kyeong O. Lee, Douglas E. Longman, Glen G. Macdonald, Joe V. Michael, and Robert S. Tranter

Project Description

The ultimate goal of this project is to develop a fundamental understanding of, and predictive models for, the combustion of petroleum-based and alternative fuels. To address this challenge, we have assembled a vertically integrated team of Argonne researchers spanning in expertise fundamental combustion chemistry to applied engines and emissions research. The goal is to demonstrate the advantages of this approach by developing mechanisms and models for novel ignition schemes in several advanced engine/fuel combinations, as well as by investigating some aspects of particulate formation in the combustion of these fuels. Fundamental knowledge of chemical ignition mechanisms will be vital for optimizing the efficiency and pollutant emissions in these systems. The approach combines experimental studies of the kinetics of fundamental reactions, theoretical studies of these reactions, the development of chemical mechanisms and models for the ignition processes, and direct experimental testing of the models by using Argonne's Rapid Compression Machine (RCM) and test engines.

Mission Relevance

The research provides solutions to issues related to the performance of advanced engines and alternative fuels. Improvements in both engine efficiency and emissions are expected. As a result, this project has direct relevance to the DOE missions of providing energy security while minimizing environmental impacts. This research is also expected to be of substantial benefit to both stationary and transportation engine manufacturers and potential producers of biofuels.

FY 2009 Results and Accomplishments

RCM studies were performed by using mixtures of methane with a number of heavier hydrocarbon additives to test whether these additives could improve the ignition properties of this fuel. Of the additives studied, dimethyl ether appeared to have the most beneficial attributes, by enhancing both ignition and the rate of combustion. Theoretical studies on the pyrolysis of alkanes to generate radicals were key to the ignition enhancement. A rapid sampling valve was ordered, fabricated, and delivered, and will be installed in the near future.

Work on the kinetics of the OH + alkanes reactions was completed last year, and reports on this work were published. This effort was extended to the reactions of OH with cyclic alkanes, and this work was published as well. Work on understanding the thermal decomposition of ethanol was also completed and prepared for publication. Finally, joint experimental and theoretical work was performed on the thermal decomposition of cyclohexane and 1-hexene. This work is aimed at understanding the early stages of ignition and combustion.

Proposed Work for FY 2010

Work on the RCM will expand to allow the use of liquid fuels and to characterize the effect of liquid fuel additives on the ignition properties of methane and natural gas. The rapid sampling valve will be incorporated into the RCM to allow studies of the time dependence of stable species within the combustion cell. Experimental shock-tube studies will continue on the thermal decomposition of dimethyl ether and toluene. Theoretical studies will continue on the thermal decomposition of fuel molecules and radicals generated by hydrogen loss from fuel molecules. Theoretical studies will also continue on the oxidation of alkyl radicals, including the kinetics of the addition of the second oxygen molecule (O_2) in the oxidation of the propyl radical. This poorly understood reaction is a model for the addition of the second O_2 in the oxidation of larger alkyl radicals, and it is expected to be a key reaction in low-temperature combustion. Finally, we will continue to explore approaches to bridge work that spans both fundamental and applied research.

Refereed Publications

Kiefer, J.H., K.S. Gupte, L.B. Harding, and S.J. Klippenstein, "Shock Tube and Theory Investigation of Cyclohexane and 1-Hexene Decomposition," *J. Phys. Chem. A* (2009), in press.

Sivaramakrishnan, R., and J.V. Michael, "Shock Tube Measurements of High Temperature Rate Constants for OH with Cycloalkanes and Methyl-cycloalkanes," *Combust. and Flame* **156** (2009), 1126–1134.

Sivaramakrishnan, R., and J.V. Michael, "Rate Constants for OH with Selected Large Alkanes: Shock Tube Measurements and an Improved Group Scheme," *J. Phys. Chem. A* **113** (2009), 5047–5060.

Non-Refereed Publications and Presentations

Gupta, S.B., B. Bihari, and M.V. Johnson, "Additive Effects on Ignition and Combustion Characteristics of Natural Gas," presented at the 2009 Fall Technical Meeting of the Eastern States Section of the Combustion Institute, University of Maryland, College Park, MD, October 18–21, 2009.

Michael, J.V., and R. Sivaramakrishnan, “Rate Constants for OH with Selected Large Alkanes: Shock Tube Measurements and an Improved Group Scheme,” presented at the 6th U. S. National Combustion Meeting, Combustion Institute, University of Michigan, Ann Arbor, MI, May 17–21, 2009.

Integrating Radiatively Important Aerosols into a New ANL Socioeconomic/Global Change Modeling Framework

2008-135-R1

David G. Streets, Ian T. Foster, Donald A. Hanson, Robert L. Jacob, Veerabhadra (Rao) Kotamarthi, and Fang Yan

Project Description

This project will develop an aerosol emissions analytical capability and integrate it into the Argonne Socio-Economic-Environmental (SEE) model being developed. Tasks include assembling the capability of forecasting future aerosol emissions, integrating radiative forcing estimates of aerosols, and assessing mitigation opportunities (such as modern biofuels). This project will also develop historical estimates of primary aerosols back to 1850, which will enable the first-ever simulation of the influence of aerosols on the global temperature trend during the 20th century.

Mission Relevance

The project is relevant to DOE’s environmental mission. In modeling the interactions between human activities and global climate change, it is essential that aerosols be integrated in an effective way. The U.S. Global Change Research Program has identified modeling, quantifying, and evaluating fundamental aerosol-related processes to be of highest priority. This objective has been taken up by DOE’s Office of Biological and Environmental Research. The project also provides data to verify observations from a new generation of NASA satellites.

FY 2009 Results and Accomplishments

In the second year of the project, we developed an aerosol modeling capability that can be integrated with the SEE model. Development of the on-road vehicle segment of the model was completed, as was an assessment of the model’s sensitivities. We use the Speciated Pollutant Emissions Wizard (SPEW) model to project aerosol emissions in future years because SPEW provides flexibility and transparency in the production of global inventories. It tabulates values of emission characteristics from the literature, including particulate matter emission factors and black carbon and organic carbon fractions keyed to a fuel/technology combination. Because the SEE model was still under development during Year 2, we

developed forecasts out to 2050 for four future pathways of human development — the so-called marker scenarios of the Intergovernmental Panel on Climate Change — and used these surrogate datasets as a test bed to develop and refine our predictive aerosol module.

Some of the relationships represented in SPEW (such as vehicle retirement age, superemitter generation fraction, and lag years between different emission standards) are only loosely constrained by observations. Therefore, we have quantified the uncertainties inherent in our emission projections. Current models already contain intrinsic assumptions; here, we represent the levels of confidence in projections by making these assumptions explicit and demonstrating how the uncertainties affect the projected emissions. If the model results are too uncertain for their intended use, explicit representation of uncertainty parameters allows us to identify the dominant contributors and recommend studies to constrain them. The importance of this treatment of model uncertainty cannot be overemphasized. Our results show forecasting power in portraying the sensitivity of future aerosol emissions to vehicle retirement rate, scrappage rate, superemitter generation, and introduction of a new vehicle emission standard. We have already begun to link this module to SEE so that dynamic aerosol emission forecasts result. We have also begun to develop similar approaches for off-road vehicles and industrial plants, both of which are major sources of aerosol emissions. Many different kinds of inter-module linkages are being explored — such as using the land-use component of SEE and its forecasts of agricultural cropland to drive our estimates of emissions from agricultural vehicles (e.g., tractors).

Proposed Work for FY 2010

During FY10, we will complete the fabrication of our aerosol module and fully integrate it with the SEE model. Characterization of the transportation sector will be completed, and its linkage to the SEE model will be tested to ensure that it produces reasonable results. We will also complete the fabrication of the stationary source component of the model, which mainly relates to industrial fuel combustion in the developing world. In addition, we will focus on providing greater definition within the U.S. region, by coupling to high-resolution geospatial and socioeconomic data distributions over the North American continent, while retaining inputs at global and world-regional scales for atmospheric and climate modeling purposes. Finally, we will make use of the technology-specific structure of our aerosol module to look at the overall changes in global and regional aerosol releases consequent upon new policy initiatives to increase the use of modern biofuels, such as bioethanol, biodiesel, and bioelectricity. The conventional technologies delivering these services at present are already characterized in the model. The effects of replacement by modern biofuels will be simulated once the emissions of the new fuels are available.

Non-Refereed Presentation

Yan, F., and T. Bond, "Future Emissions from Vehicle Fleets," presented at the Air and Waste Management Association 101st Annual Conference and Exhibition, Portland, OR, June 24–27, 2008.

Oxidative Decomposition of Cellulosic Materials

2008-146-R1

Christopher L. Marshall, Peter J. Chupas, Larry A. Curtiss, Weiling Deng, Jeffrey W. Elam, Jeffrey P. Greeley, Julius Jellinek, Michael J. Pellin, Peter C. Stair, Stefan Vajda, and Randall E. Winans

Project Description

Sub-nanoscale catalytically active phases, particularly metal nanoparticles and metal oxide clusters, supported on high-surface-area oxides are one of the most important classes of heterogeneous catalysts. The overall objective of the project is to improve our fundamental understanding of these supported heterogeneous catalysts and their catalytic chemistries. The goals of this integrated experimental/theoretical research project are to (1) synthesize new materials based on atomic layer deposition (ALD) and direct size-selected metal and metal oxide catalyst deposition in order to produce atomically uniform catalytic metal oxide clusters and monolayers supported on high-surface-area and flat substrates; (2) evaluate the catalytic activity, selectivity patterns, and reaction kinetics and mechanisms; (3) characterize the chemical and structural properties of these uniformly supported catalysts at each stage of their life cycle; and (4) computationally model the new catalysts to understand the relationships among the atomic composition/structure of the clusters/nanoparticles and their catalytic chemistries, including reaction mechanisms and kinetics.

Mission Relevance

The project is relevant to DOE's missions in energy, the environment, and basic science. This is the first catalytic project at Argonne investigating the oxidative breakdown of cellulose to monomeric sugars and, as such, is relevant to the bioprocessing interests of DOE's Office of Energy Efficiency and Renewable Energy. The project is undertaking a novel approach (oxidative hydrolysis) that could provide both new catalysts and new fundamental knowledge about the oxidation chemistry of this important feedstock.

FY 2009 Results and Accomplishments

The target reaction involves cleaving the C-O-C bond in cellulosic materials. Decomposition of 1-methoxy-2-methyl-2-propanol (MMP) was chosen as the gas phase model reaction (Figure 1). All 20 catalytic membrane samples (platinum [Pt], palladium [Pd], vanadia [VO_x], and cobalt oxide [Co₃O₄] supported on aluminum oxide [Al₂O₃]- or zinc oxide [ZnO]-coated anodic aluminum oxide membranes) synthesized in FY08 by both ALD and cluster deposition (CD) techniques were tested regarding this reaction. We found that the Co₃O₄ clusters (prepared by CD) were more active in breaking the C-O-C bond than larger nano-size Co₃O₄ (prepared by ALD). ALD-VO_x affected reaction activity and selectivity by inhibiting coke formation. ALD-Pt oxidized to a stronger extent, which promoted carbon dioxide [CO₂] formation. Powder catalysts with various acidities were also tested in both direct hydrolysis and oxidative hydrolysis of MMP, showing that MMP hydrolysis was more pronounced on acidic oxides than on basic oxides. Furthermore, acidic oxides were more active in oxidative hydrolysis than in direct hydrolysis.

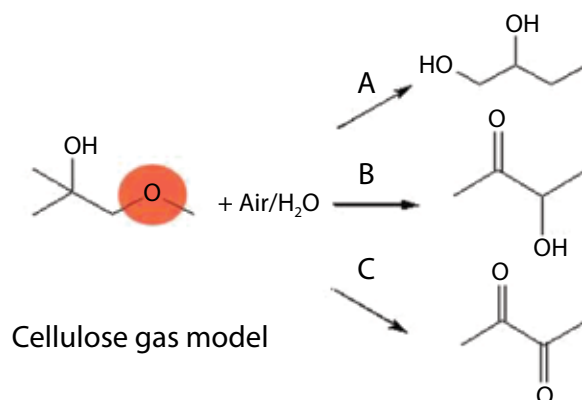
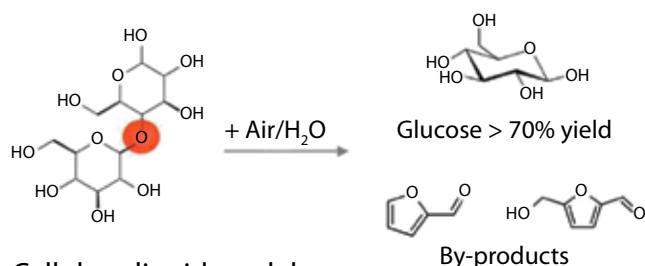


Figure 1. Gas phase probe molecule and products for cellulose breakdown (shaded red oxygen atoms are the ones we are trying to activate).

Another model reaction uses cellobiose to investigate C-O-C bond cleavage in a more realistic feed condition (liquid phase hydrolysis) (Figure 2). Hydrolysis was enhanced by the stronger acidity of solution in an inert gas medium, while air-assisted hydrolysis under neutral solution was able to achieve a glucose yield of more than 70%. With air present, the decomposition rate of glucose was faster than its formation from cellobiose decomposition in lower pH. The acidic environment created by supercritical CO₂ (without generating acid waste at the end of reactions) increased cellobiose conversion but dramatically decreased the selectivity to glucose, resulting in the loss of glucose yield. Pt, Pd, VO_x, and gold supported on alumina catalysts were tested in both oxidative hydrolysis and direct hydrolysis reactions.



Cellulose liquid model

Figure 2. Reactant cellobiose, a two-carbon cellulose fragment, and the desired reaction product (glucose) and undesirable side products (shaded red oxygen atoms are the ones we are trying to activate)

Proposed Work for FY 2010

The project will continue with support from the DOE Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.

Refereed Publications

Deng, W., and C.L. Marshall, "Oxidative Hydrolysis of Cellobiose to Glucose," *Catalysis Today*, submitted for publication.

Non-Refereed Publications and Presentations

Deng, W., S. Lee, S. Vajda, J.A. Libera, J.W. Elam, and C.L. Marshall, "C-O-C Bond Cleavage in Oxidative Hydrolysis of Cellulosic Materials," Chicago Catalysis Club Spring Symposium, Naperville, IL, May 18, 2009.

Deng, W., S. Lee, S. Vajda, J.A. Libera, J.W. Elam, and C.L. Marshall, "Glycosidic Bond Cleavage in Oxidative Hydrolysis of Cellulosic Materials," American Institute of Chemical Engineer Midwest Regional Conference, Chicago, IL, October 5–6, 2009.

Publication

Deng, W., S. Lee, S. Vajda, J.A. Libera, J.W. Elam, and C.L. Marshall, "Oxidative Hydrolysis of Cellulosic Materials," *Proceedings of the 21st North American Catalysis Society National Meeting*, San Francisco, CA, June 7–12, 2009.

Advanced Simulation of Separations

2008-150-R1

David A. Nowak, Mihai Anitescu, Candido Pereira, Monica C. Regalbutto, Branko Ruscic, Andrew Siegel, and Kent E. Wardle

Project Description

The initial goal of our project is to provide a firmer foundation for applying advanced simulation techniques to nuclear separations. The work focuses on three areas in which significant advances are needed to take full advantage of modern

computational capabilities. First, thermodynamic data for many radionuclides are limited. The Active Thermochemical Tables (ATcT) approach can be expanded to include actinides and fission products, thus broadening the thermochemistry parameter space and intrinsically boosting reliability. ATcT derives accurate, reliable, and internally consistent thermochemical values for stable, reactive, and transient chemical species. Second, safeguards are needed to prevent the diversion of nuclear material. This approach sets up an algorithm to model the propagation of small-scale perturbations for a simple chemical process and evaluates diversion strategies through a stochastic optimization with constraints. Third, dynamic process simulations of the process equipment and operations are needed. Time-varying systems must be understood at the unit-operations level through better models of fluid flows and interfacial chemistries and through integration of multiple operations.

Mission Relevance

This project is tied to DOE's missions in science, energy, and national security. We expect that the tasks under this project will address fundamental basic science problems of interest to the Office of Science and application problems of interest to the Office of Nuclear Energy (NE) or the National Nuclear Security Administration. DOE-NE's Fuel Cycle Research and Development (FCRD) program is developing campaigns in aqueous separation safeguards and also simulations as part of the Nuclear Energy Advanced Modeling and Simulations (NEAMS) project. The approach, models, and software developed in this project should be directly relevant to developing and safeguarding advanced spent fuel treatment technologies.

FY 2009 Results and Accomplishments

We successfully tested the ability of ATcT to correctly handle condensed phases relevant to actinide thermochemistry by using representative solid/liquid/aqueous species intertwined with gas-phase species in the current Core Thermochemical Network (TN). As part of this effort, an Actinide Thermochemical Network (AxTN) that describes key species pertinent to actinide systems is being constructed. We have gathered and critically examined several hundred original papers and reports and distilled the relevant information into a series of condensed summaries. The intent is that the AxTN be fully superimposable on the current Core TN, thus obviating the need to re-describe common nonactinide chemical species that already exist in the Core TN. So far, the condensed reports that form the basis for AxTN contain analyses of more than 150 relevant measurements and fully define at least 27 key species.

After an initial model-based product diversion assessment for a steam-methane reforming model was developed with input from ATcT, we determined the approach to be applied

to the class of process models used to represent separations. More recent work has centered on formulating and testing the “maximum likelihood” approach for recovering the best information from all sources available for a chemical process. After information from multiple inputs is incorporated, this effort should yield the best estimate of the diverted output. Overall, this portion of the project is at a stage at which a moderate number of scenarios for reactions of the type that describe separations chemistry can be assessed. The previous year’s results for a simple steam-methane reforming model, similar in structure to that of models that describe separations processes, were validated and published. This formulation was extended to optimal management of integrated energy systems, including intermittent sources.

In separations modeling, the focus was on full-scale testing of the open source computational fluid dynamics (CFD) code, OpenFOAM, on a number of different computational platforms in order to demonstrate modeling capability for turbulent, multiphase fluid dynamics in an annular centrifugal contactor. As an initial step, simulations of the contactor mixing zone using free-surface volume of fluids (VOF) and turbulence large eddy simulation (LES) were completed and compared to existing experimental velocity measurements for this configuration. The results were in good agreement with data and previous simulations using a commercial code. Additional simulation of the heavy phase underflow section of the rotor that combined free-surface modeling with a moving reference frame (MRF) produced flow phenomena previously predicted by using a commercial CFD code. We laid the foundation for further work with multiple liquid phases, explored parallel scaling of the code, and made modifications to enable coupled mixing zone/separation zone simulations. A three-phase liquid-liquid-air mixing simulation was conducted for a highly refined mesh using 2,000 processors of the SiCortex machine in Argonne’s Mathematics and Computer Science (MCS) Division. Analysis of the data from this run is under way, but the general results demonstrate the limits of the current modeling methodology (interface capturing using VOF) and the need to develop advanced mixing models. In addition, the first coupled mixing-zone/separation-zone model of the contactor run by using VOF and MRF showed the start-up and filling of the contactor with a single liquid phase and air.

Proposed Work for FY 2010

We will continue building and testing the core AxTN and expand and enrich it for selected actinide thermochemistry. As the test AxTN grows, we will conduct a statistical analysis of the new determinations included in the enriched AxTN and compare results with existing traditional evaluations where applicable. AxTN will be developed to a point where the capabilities of ATCT to deliver reliable actinide thermochemistry can be demonstrated and its superiority to traditional sequential approaches can be shown.

As part of diversion analysis, an abstract template will be defined such that the equilibrium reactions can be securely computed in a portable extensible toolkit for scientific computing (PETSC), to serve as an option for a function/gradient interface. Parallelization of the posterior sampling code will be completed, as will implementation of advanced sequential importance sampling for reducing the variance. Another goal is to port the assessment code on the Blue Gene (BG)/P.

The third leg of this project will continue to establish a basis for a dynamic process simulation with an emphasis on using OpenFOAM to develop codes to examine the fluid dynamics of centrifugal contactors. We plan to conduct combined zone mixer/centrifuge simulations for the centrifugal contactor for three phases (two liquid phases and air). In addition, to demonstrate how such modeling can provide insight into existing flow issues, we will conduct various targeted simulations to explore design modifications to the heavy phase underflow and weir cap region of the contactor to mitigate unstable flow patterns that were previously identified. We will also evaluate methods for dynamic liquid-liquid simulation, establishing a plan for implementation into the open source code framework. Finally, initial scaling studies for running OpenFOAM on BG/P will be carried out for large and very large engineering problems.

Refereed Publications

Zeng, X., M. Anitescu, C. Pereira, and M. Regalbuto, “A Framework for Chemical Plant Safety Assessment Under Uncertainty,” *Studies in Informatics and Control* **18**(1) (2009), 5–20.

Non-Refereed Publications and Presentations

Wardle, K.E., “Application of Open-Source CFD to Simulation of the Flow in Solvent Extraction Equipment,” 16th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 18–22, 2009.

End-to-End Biofuels Analysis: Building Capability in HPC Socio-Economic-Environmental Modeling

2008-160-R1

Ian T. Foster, Michael Q. Wang, Michael J. Wilde, Richard D. Doctor, Steven M. Goldberg, Donald A. Hanson, Robert L. Jacob, Veerabhadra (Rao) Kotamarthi, Sven Leyffer, Charles M. Macal, and Todd S. Munson

Project Description

This project seeks to develop new tools for analyzing biofuels from production to use. We will create a system comprising climate models; macroeconomic models of biofuel raw-material

production, fuel generation, and distribution; sector models of transportation and of energy use and generation; and models of coal-biomass co-firing in power plants and liquefaction or gasification of biomass into diesel fuel substitutes.

Mission Relevance

This project is relevant to DOE's missions in environment and energy. DOE is concerned with bioenergy as an alternative energy source that is environmentally friendly and economically competitive. The Office of Science has expressed interest in high-performance socioeconomic modeling; this topic was one of six application chapters in the DOE planning report for exascale computing.

FY2009 Results and Accomplishments

We released version 0.1 of our economics models and completed two case studies, one on the propagation of errors from the input calibration data set by using 10K random draws and another studying carbon leakage under various global scenarios of climate change mitigation policy that includes carbon budgets for each industry. We developed numerical methods for solving linear and nonlinear mathematical programs with equilibrium constraints, which are required for studying models with strategic players, such as OPEC (Organization of Petroleum Exporting Countries). We formulated a model for studying optimal transitions from high- to low-carbon technologies. We finished the 600-year initialization run for the crop model in the Community Land Model (CLM), and we completed a study of water requirements for corn-ethanol refineries.

Proposed Work for FY 2010

Biofuel Economics

We will improve the sectoral representation in our economics model, adding corn, sugarcane, and soy-based biofuels data and disaggregating the electricity sector into conventional, nuclear, wind, solar, hydro, and geothermal, among others. We will enhance our model with such features as overlapping consumer generations and nonseparable utility functions. Using this model, we will study the socioeconomic implications of a biofuel-based economy. We will also study water use at the plant level and evaluate emerging technologies impacting the climate-economics evaluation. In addition, we will complete our design for cellulose-to-ethanol refinement.

Biofuel Physical Processes

We will complete development of a landuse/landcover (LU/LC) change model and generate predictions for the next 20–30 years. We will explore the coupling of this model with the economic model. We will use the CLM crop model to perform sensitivity runs. These simulations will focus on changes in stored soil organic carbon for each LU/LC scenario under varying land management practices.

Uncertainty in Models

We will apply our statistical approach to quantify uncertainty and the propagation of uncertainty from one model to another. We will formulate computational problems that include distributions for key unknown parameters; these massive combinatorial problems lend themselves to parallel computing, and we will be able to quantify the uncertainty in the output. By taking multiple climate samples, we can produce economic model ensembles.

Refereed Publications

Wilde, M., I. Foster, K. Iskra, P. Beckman, Z. Zhang, A. Espinosa, M. Hategan, B. Clifford, and I. Raicu, "Parallel Scripting for Applications at the Petascale and Beyond," *IEEE (Institute of Electrical and Electronics Engineers) Computer* **42**(11) (2009) 50–60.

Non-Refereed Publications and Presentations:

Elliott, J., "CIM-EARTH," presented at the University of Chicago, October 2, 2009.

Foster, I., "CIM-EARTH: A Community Integrated Model of Energy and Resources Trajectories for Humankind," keynote presentation, International Conference on e-Social Science, Cologne, Germany, June 25, 2009.

Hanson, D., Y. Kryukov, S. Leyffer, and T. Munson, "Optimal Control Model of Technology Penetration," MCS Preprint ANL/MCS-P1544-0908, Revised June 2009.

Leyffer, S., and T. Munson, "A Globally Convergent Method for MPECs," MCS Preprint ANL/MCS-P1457-0907, Revised April 2009.

Macal, C., "An Agent-Based Model for the Long-Run Global Petroleum Market," in *Proceedings of the 2009 North American Association for Computational Social and Organizational Science Conference*, Tempe, Arizona, October 22–24, 2009.

Munson, T., "CIM-EARTH: Community Integrated Model of Economic and Resource Trajectories for Humankind," presented at Exxon Mobil visit to Argonne National Laboratory, December 2009.

Next-Generation Fuel Cell Electrocatalysts: An Integrated Experiment/Theoretical Approach to Structure-Property-Function Relationships in Electrocatalysis

2008-172-R1

Deborah J. Myers and Julius Jellinek

Project Description

This project focused on the development of improved anode and cathode electrocatalysts — noble-metal-based metal bimetallics — for polymer electrolyte fuel cells operating on conventional and alternative renewable fuels (e.g., ethanol). The cathode reaction — the oxygen reduction reaction (ORR) — is the dominant cause of efficiency loss in hydrogen-air fuel cells and a major contributor to losses in alcohol-air fuel cells, necessitating a high loading of the costly platinum-based electrocatalyst. Although liquid renewable fuels, such as methanol and ethanol, have distinct distribution and storage advantages over hydrogen for portable applications, the efficiency of alcohol fuel cells is severely limited by the sluggish kinetics of alcohol oxidation. A major goal of this project is to establish a basis for the selection of nanoparticle catalyst size and composition (choice of primary and secondary metals and their relative concentrations), resulting in technology-enabling increases in electrocatalytic activity. The theoretical effort was combined with an experimental effort focused on synthesizing nanoparticles of controlled size and composition and determining the relationships among nanoparticle composition, ability to form oxygenated intermediates, and ORR and alcohol oxidation activity.

Mission Relevance

This project is relevant to DOE's mission in energy security and the environment by enhancing energy efficiency and increasing the viability of renewable energy technologies. Polymer electrolyte fuel cells offer efficient conversion of renewable fuels (e.g., ethanol) or renewable energy-derived fuels (e.g., methanol and hydrogen) to provide power for numerous stationary and portable applications. However, widespread implementation of this promising technology requires improvements in the activity and conversion efficiency of electrocatalysts for the cathode and anode reactions.

FY 2009 Results and Accomplishments

In FY09, for the experimental portion of the project, we (1) synthesized a series of palladium (Pd), rhodium (Rh), and platinum (Pt) alloy catalysts by using co-impregnation and colloidal techniques and (2) characterized their particle size, phase structure, and electrochemical activities for methanol and

ethanol oxidation and oxygen reduction. We studied the effect of noble-metal-to-base-metal ratio, post-deposition heat treatment atmosphere, and temperature on these properties. We found that alloying Pt and Pd with oxophilic metals (such as ruthenium [Ru], osmium [Os], cobalt [Co], and copper [Cu]) greatly enhances methanol and ethanol oxidation activity. The electrochemical activities of these catalysts for the following reactions were found to decrease in the order shown below.

Methanol oxidation: PtRu > PtOs > Pt₃Co > Pt >> Co₃Rh > Cu₃Pd > PdCu > Pd

Ethanol oxidation: PtRu > PtOs > Pt₃Co > Rh₃Co > Pt >> Cu₃Pd > PdCu >> PdNi > Pd

Oxygen reduction: Pt₃Co > Pt > Cu₃Pd > PdCu > PdNi > Pd >> Co₃Rh

As illustrated by the results for the Rh-Co bimetallic system (Figure 1), we found the following general trends: (1) increasing methanol oxidation activity with increasing base-metal-to-noble-metal ratio in the nanoparticles and (2) increasing ethanol oxidation activity with decreasing base-metal-to-noble-metal ratio. The first trend indicates that the methanol oxidation activity is limited by the oxidant coverage on the nanoparticle surface, because the base metals are more oxophilic than the noble metals. The ethanol oxidation activity trend indicates that the ethanol oxidation reaction is limited not by availability of oxidant but by the adsorption and dissociation of the ethanol molecule. The optimum base-metal-to-noble-metal ratio for the oxygen reduction reaction was highly dependent on the type of noble metal and base metal and was highest for the most stable alloys, because of the highly corrosive conditions necessary for the oxygen reduction reaction (i.e., high potentials and low pH).

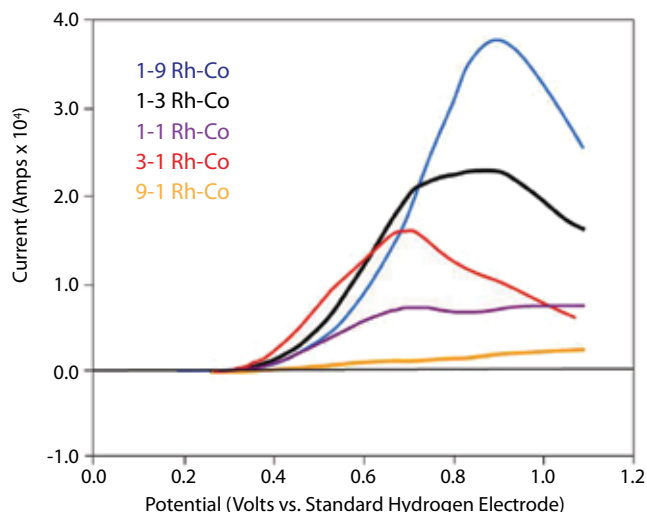


Figure 1. Ethanol oxidation current for Rh-Co bimetallic nanoparticle catalysts as a function of rhodium-to-cobalt atomic ratio (9-1 to 1-9).

In FY09, the theoretical/computational studies focused on determination of the structures of Pd_n clusters and characterization of their energetic, electronic, dielectric, and chemical reactivity properties. We used state-of-the-art density functional theory in the computations. The size range covered was $n=2-25$. We considered a number of isomeric forms for each cluster size and established the energy ordering of the isomers. The structure of the lowest energy for each cluster size was then subjected to further characterization. The attributes computed and analyzed included total and individual atomic dipole moments and polarizabilities. We evaluated trends in the total cluster dipole moments and polarizabilities (per atom) as a function of cluster size and analyzed the behavior of the individual atomic dipole moments and polarizabilities as a function of the site location of the atoms within the cluster structure. We then introduced and tested the notion of the atomic polarizability as a local, site-specific reactivity descriptor. Use of this descriptor allows researchers to predict the most reactive site of a cluster and establish a hierarchical classification of its different reaction centers. We demonstrated this for the reactions of Pd_n with H_2O (see Figure 2), the source of the alcohol oxidant on the direct alcohol fuel cell anode electrocatalyst. Our analysis of the results led us to the following conclusions: (1) as the polarizability of an atom becomes larger in the cluster, the binding of H_2O to it becomes stronger; (2) top binding is preferred to two-center (edge) binding, which in turn is preferred to three-center (face) binding; and (3) in the case of multiple-center binding, multiplets of atoms with higher polarizability form stronger bonds with H_2O . These findings are general, and they can be used to predict and to understand the hierarchy of bonding arrangements of H_2O on Pd_n clusters of any size and structure. Moreover, we have indications that their validity also extends to clusters of other metals.



Figure 2. Computed energetically, this illustration shows the most preferred adsorption arrangements of H_2O on Pd_4 and Pd_7 clusters. The adsorption sites are those with the highest polarizability.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Jackson, K., L. Ma, M. Yang, and J. Jellinek, "Atomistic Dipole Moments and Polarizabilities of Na_n Clusters, $N=2-20$," *Journal of Chemical Physics* **129** (2008), 144309/1–10.

X-Ray Studies of Catalysts

2008-193-R1

Jeffrey T. Miller

Project Description

The goals are to develop new techniques and applications for using x-ray spectroscopy and to study catalytic systems, with an emphasis on catalysts operating under realistic conditions with regard to temperature, pressure, and gas composition. The Advanced Photon Source at Argonne will be used to make *in situ* x-ray measurements to gain insights into mechanistic reaction processes that other spectroscopic techniques cannot readily provide. Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Spectroscopy (XANES) are two techniques for obtaining structural and electronic details on catalysts under wide range of operating conditions and environments.

Mission Relevance

This project will support the energy and science missions of DOE's Office of Basic Energy Sciences. This research will benefit both the materials synthesis and characterization communities and the catalytic community. Catalytic technology is essential for ensuring our economic prosperity and promoting energy security and environmental responsibility. Given that the world demand for energy is expected to double by 2050, the need to develop new catalysts and catalytic processes that promote sustainable energy production is great. Catalysts, because they control the rates at which chemical bonds are formed and broken, are used to increase the yields of desired products over those of undesired products in chemical reactions. One of the most significant research challenges is to synthesize and characterize catalytic particles that are tailored at the nano-scale to optimize performance.

FY 2009 Results and Accomplishments

Hydrogen is produced through the water-gas shift (WGS) reaction: carbon monoxide plus water equal carbon dioxide plus hydrogen ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$). Currently, copper (Cu) is the most active commercial catalyst available for speeding up this reaction, but much more active catalysts are needed for the widespread application of fuel cells, biomass upgrading, and other new energy technologies. We know that new catalyst compositions with palladium, platinum, and gold (Pd, Pt, and Au) are more active than Cu by up to several orders of magni-

tude, but we do not know much about what properties lead to this high activity.

A high-pressure, plug-flow reactor that can simultaneously measure accurate kinetic rates and x-ray absorption spectroscopy (XAS) spectra was developed and applied to the study of WGS catalysts. The catalyst is located in the center of the tubular reactor, and the x-ray beam is directed through the wall of the reactor while the gases flow down through the catalyst bed. The reaction products and conversion are determined at the reactor outlet by gas chromatography or mass spectrometry.

During the past year, this reactor demonstrated the dynamic nature of the bimetallic, nanoparticle structure during the WGS reaction. At low temperatures, 2-nm, Pd-rich particles, the activity of which is equivalent to that of supported, monometallic Pd, are formed. At higher temperatures, a 5-nm Pd-Zn alloy with a reaction rate about 30 times faster than that of Pd alone is formed. Under reaction conditions, changes in the gas composition lead to significant changes in the surface composition; evidence for this is the changes in the linear-to-bridge ratio of CO, as measured by infrared spectroscopy. Small changes in the EXAFS under similar conditions indicate that the bulk structure only changes slightly. Thus, during reaction, only the surface atoms are modified, which creates a more active bimetallic catalytic surface.

The kinetics-EXAFS reactor was used to develop a new analysis technique for determining the coverage of reactants on catalyst surfaces under reaction conditions. Figure 1 shows the changes in XANES spectra, or Δ XANES, (XANES with adsorbed gas minus that in helium [He]) on a 1-nm Pt catalyst with different adsorbates.

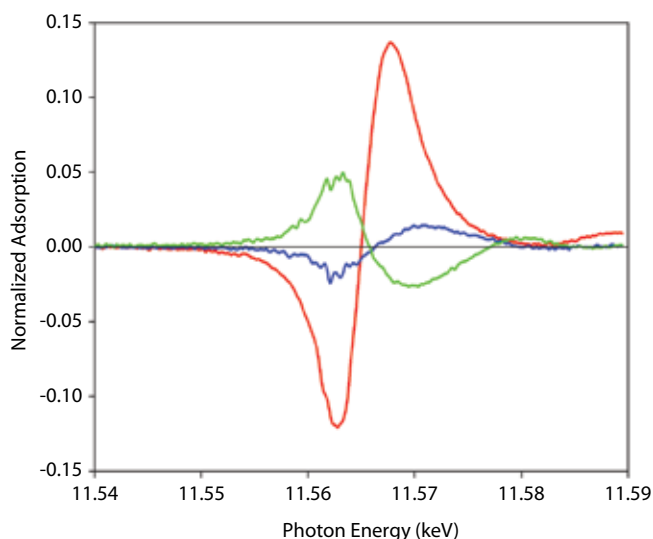


Figure 1. Pt L_3 XANES with adsorbed CO (red), H_2 (blue), and H_2O (green) at 280°C.

By fitting the D XANES spectra under reaction, one can determine the surface composition of reactants and products. For Pt catalysts, the dominant species is CO, and its surface coverage is high. H_2O and H_2 coverages are much lower. By comparison, the changes in the XANES spectra of Au nanoparticles (data not shown) indicate that surface coverages of CO, H_2O , and H_2 are very low. The fact that, for example, the reaction rate of Au is much higher than that of Pt at low temperature appears to result from weak adsorption and low surface coverage of CO, leading to exposure of active surface sites, rather than from a higher intrinsic kinetic activity. These results imply that the key to higher activity in WGS catalysts is to develop nanoparticles in which CO is weakly chemisorbed. The role of adsorption on kinetic rates is also important in a number of other environmental and energy-related reactions.

Proposed Work for FY 2010

We will develop an *in situ* grazing incidence XAS cell for the structural analysis of supported, nanoparticle model catalysts on planar supports. A number of novel subnanometer metal and alloy catalysts that can be prepared on planar supports are difficult to prepare on high-surface-area powders. Determining the structure and electronic properties of these compositions can initially lead to an understanding of new catalytic phenomena and chemical reactivity and ultimately lead to the large-scale synthesis of new high-performance catalytic materials.

Refereed Publications

Fingland, B.R., F.H. Ribeiro, and J.T. Miller, "Simultaneous Measurement of X-Ray Absorption Spectra and Kinetics: A Fixed-Bed, Plug-Flow Operando Reactor," *Catal. Lett.* **131** (2009), 1–6.

Fox, E.B., S. Velu, M.H. Engelhard, Y.-H. Chin, J.T. Miller, A.J. Kropf, and C. Song, "Roles of Cu and Pd in CeO_2 Supported Cu-Pd Bimetallic Catalyst for the Oxygen-Assisted Water-Gas Shift Reaction," *J. Catal.* **260** (2008), 358–370.

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Ruddy, D.A., J. Jarupatrakorn, R.M. Rioux, J.T. Miller, M.J. McMurdo, J.L. McBee, K.A. Tupper, and T.D. Tilley, "Site-Isolated Pt-SBA15 Materials from Tris(*tert*-butoxy)siloxy Complexes of Pt(II) and Pt(IV)," *Chem. Mater.* **20** (2009), 6517–6527.

Schuyten, S., S. Guerrero, J.T. Miller, and E.E. Wolf, "Characterization and Oxidation States of Cu and Pd in Pd-CuO/ZnO/ZrO $_2$ Catalysts for Hydrogen Production by Methanol Partial Oxidation," *Appl. Catal. A: Gen.* **352** (2009), 133–144.

Tew, M.W., J.T. Miller, and J.A. van Bokhoven, "Particle Size Effect on Hydride Formation and Surface Hydrogen Adsorption on Nano-sized Palladium Catalysts: L3 Edge vs. K Edge X-Ray Absorption Spectroscopy," *J. Phys. Chem. C* **113** (2009), 15140–15147.

Wong, M.S., J.J. Alvarez, Y.-L. Fang, N. Akcin, M.O. Nutt, J.T. Miller, and K.N. Heck, "Cleaner Water Using Bimetallic Nanoparticle Catalysts," *J. Chem. Technol. Biotechnol.* **84** (2009), 158–166.

Integrated Biofuel/Engine Design

2009-097-NO

Douglas E. Longman, Philip D. Laible, YuPo J. Lin, Stephen T. Pratt, Seth W. Snyder, and Michael Q. Wang

Project Description

The need exists to integrate the efficient production of biofuels with the design of internal combustion engines that have high efficiency and ultra-low emissions. Historically, combustion regimes and thus overall engine designs have been dictated by a given set of fuel properties. By designing the fuel properties in coordination with engine research following a multi-disciplinary team approach, we are seeking to realize the full potential of the energy source (fuel) and conversion device (engine). Fuel design during engine development may hold the key to unlocking promising new combustion regimes, such as low-temperature combustion in diesel engines. Low-temperature combustion has been shown to simultaneously reduce both oxides of nitrogen and particulate matter while increasing fuel conversion efficiency. Fuel properties directly affect this combustion regime.

Mission Relevance

This project is relevant to DOE's missions in energy and the environment. It directly responds to the advanced biofuel mandates defined in the Energy Independence and Security Act of 2007. The primary benefit to DOE is the potential for replacing foreign petroleum with renewable fuel while increasing fuel conversion efficiency and reducing engine emissions. The associated increase in efficiency and reduction in emissions would have a global impact by providing sustainable energy. The integrated development of fuels and engines could also create a new paradigm for the engine/transportation industry by providing a methodology to produce (concurrently) a fuel and engine with well-refined characteristics. Success in this project will lay the groundwork for integrated pathways to design fuels and engines that reach their maximum potential. Beneficiaries include fuel manufacturers and other renewable energy companies.

FY 2009 Results and Accomplishments

The integrated team approach for the fuel and engine design process was first explored by researching the use of butanol (C_4H_9OH) in a spark-ignited engine. This known, but not commercially used, biofuel was chosen to get our "feet wet" at using an integrated team approach. The design process covered fuel production analysis, combustion analysis, life-cycle analysis, and engine evaluation to illustrate the feasibility and potential success of our approach.

Additionally, in the theoretical validation of chemical-kinetic reaction mechanisms for biofuels, we implemented a novel project for the validation of chemical-kinetic mechanisms based on feedback among various first-principle theoretical methods. Our initial implementation of this method, performed with Rex Skodje (University of Colorado) and Alison Tomlin (University of Leeds, UK), involved the combustion of methanol, which served as a model for more complex and interesting biofuels like ethanol and butanol. Global sensitivity analysis of the mechanism indicated that the predicted ignition times were most sensitive to the reaction $CH_3OH + HO_2 = CH_2OH + H_2O_2$. By means of state-of-the-art theory, we then derived an improved calculation of the rate constant for this reaction, with the new rate constant differing by an order of magnitude from the values used by current modelers. With the improved rate constant for this reaction, the time to ignition of methanol/air mixtures was determined to be much longer than for the previous mechanism. The application of this approach to butanol is also under study.

We next investigated the creation of a unique fuel that could be efficiently made biologically, phytol ($C_{20}H_{40}O$). We identified the most promising approach for phytol generation, which involves introducing plant genes into *Rhodobacter*, facilitating a one-step, enzyme-catalyzed cleavage of a prominent membrane-localized cofactor into phytol and another by-product. Additionally, we found that all mutant strains showed dramatic and anticipated changes in pigmentation (Figure 1). This result was expected as our approach interrupts many of the biosynthetic pathways used in the generation of highly colored, light-harvesting machinery. Most but not all strains retained the ability to grow photosynthetically. Plant genes expressed in *Rhodobacter* are active. Success with *in vitro* assays utilizing purified forms of *Rhodobacter*-produced plant enzymes revealed additional post-culture strategies for production of advanced next-generation biofuels. Our major accomplishment in this area was to generate more than 10 new strains of photosynthetic bacteria, species *Rhodobacter*, in a series of steps aimed at the (over)production of phytol through culture of these organisms. Characterization efforts are well under way, and simple separation methods have been developed to quantify levels of C15–C20 alcohols produced by these cells.

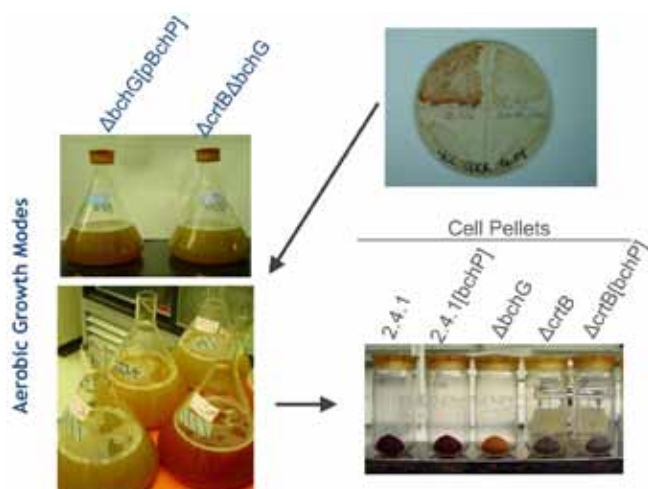


Figure 1. Engineered strains of photosynthetic bacteria (*Rhodospirillum rubrum*) used in strategies for production of next-generation biofuels. Differences in pigmentation of engineered strains ($\Delta bchG$, $\Delta crtB$, $\Delta crtB\Delta bchG$, $\Delta bchG[pbchP]$, $\Delta crtB[pbchP]$, 2.4.1[pbchP]), as compared to each other and to the unmodified organism (2.4.1), are clearly seen for colonies on agar plates (upper right) and for aerobic cell cultures (left). These changes are accentuated in cell pellets derived from large-scale cultures (bottom right).

We did find the physical characteristics of phytol to be non-ideal as a single-component transportation fuel, primarily due to its high viscosity. However, phytol did show promise as a blending component with some potentially shorter chain C15 hydrocarbons, since theoretical analysis showed the combustion properties to be good for compression-ignition engines.

This project has been presented to DOE-EERE's Office of Biomass as a model for advanced biofuel development and has served to assist in defining its future research goals. Two patents generated from this work are in process: "Integrated System for the Production and Separation of Biodiesel and Method Thereof" and "Engineered Photosynthetic Bacteria and Methods of Manufacture of Advanced Biofuels."

Proposed Work for FY 2010

We will continue our integrated interactive approach with phytol by the continued pursuit of its efficient production and the study of its physical and combustion properties. We are on track to generate quantities required for testing fuel properties and purity levels in the first part of calendar year 2010. This biofuel will then be evaluated with our Caterpillar single-cylinder diesel engine, which is being modified to include variable valve timing to facilitate effective compression ratio changes.

Advanced Cathode Materials for High-Performance Lithium-Ion Batteries

2009-115-N0

Jie Li, Khalil Amine, Zonghai Chen, Jeffrey W. Elam, Yan Qin, Yung Y. Liu, Michael J. Pellin, and Dapeng Wang

Project Description

Potentially, the best lithium-ion-battery cathode material for future plug-in hybrid electric vehicles is Li-Mn-O because of its higher working voltages and lower cost than other materials. However, it suffers from electrochemical instability: the Mn^{3+} ions dissolve into the electrolyte, and the reduced metallic Mn blocks the channels of the graphite anode, leading to quick degradation in battery performance. Exploiting a film coating to passivate cathode particles may enable its commercial application. Until recently, progress has been limited by the trade-off between surface protection and induced higher electrical impedance for coated layers grown on the cathode by current technologies.

With the unique feature of two-step and self-terminated reactions, the atomic layer deposition (ALD) method is particularly suited to synthesizing ultra-thin, highly conformal protective coatings with the film thickness controllable at the atom scale. As such, ALD can satisfy both the demands of surface protection and charge transport. This project is aimed at demonstrating that significant improvements in battery performance are possible by applying ultra-thin ALD nano-films to the granular cathode materials and then developing an advanced processing technology.

Mission Relevance

This project supports DOE's mission in energy security. We anticipate this project will contribute to DOE's Industrial Technology Program in the area of nano-manufacturing by developing advanced ALD-coating technology in a fluidized-bed reactor (ALD is one of five key areas identified) and to DOE's battery R&D program by manufacturing advanced cathode materials on a large scale.

FY 2009 Results and Accomplishments

In a fixed-bed reactor, ALD was used to prepare Al_2O_3 on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder. The Al_2O_3 thickness on these samples was varied from 0.25 nm to 10 nm (Figure 1) by controlling the number of depositions: 2, 8, 15, 40, and 80. Cells using these ALD-coated cathode materials showed significant improvements in both capacitance retention over 200 cycles (see Figure 2) and impedance control after 200 cycles (Figure 3). Performance tests in which other coating cathode materials were used, including ZrO_2 and V_2O_5 , also exhibited various degrees of improvements in cell performance.

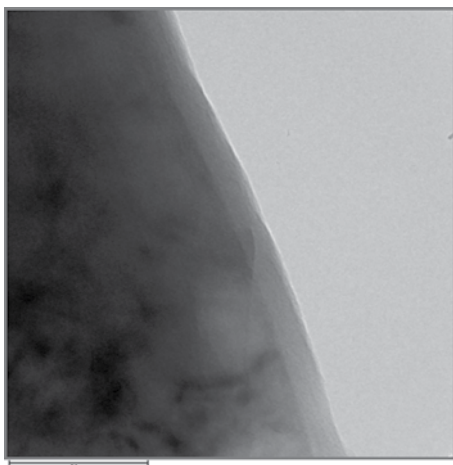


Figure 1. Transmission electron micrograph of ALD-coated Al_2O_3 thin film. Image shows a highly uniform film, 10 nm in thickness (size bar: 50 nm).

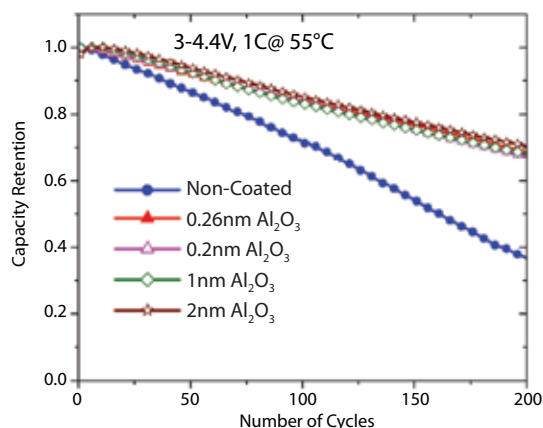


Figure 2. Capacity retention of cell with ALD Al_2O_3 coating on the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode, demonstrating better cycling performance than a non-coated electrode.

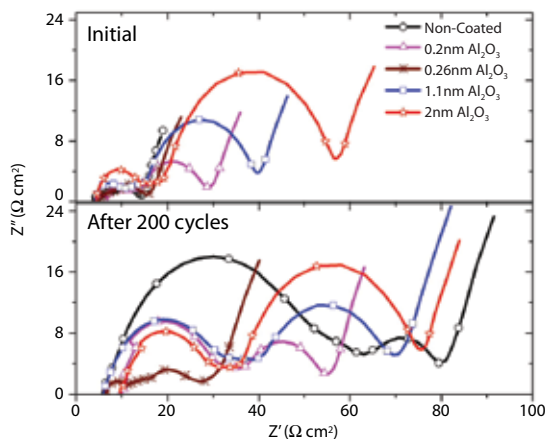


Figure 3. Impact of ALD Al_2O_3 coating on cell AC impedance. The increase of impedance for the coated cathode is much slower (colored lines) than that without coating (black line), where Z' and Z'' are real and imaginary components of the AC impedance, respectively, and a larger radius of the curve indicates a higher AC impedance.

In addition, a new gas fluidized-bed reactor, operating under a vacuum of 1~10 torr, was built for ALD powder coating. In contrast to a conventional fluidized-bed reactor, a nonlinear controlling technology was implemented in this new reactor by adaptively superimposing an oscillatory second flow on the main fluidizing gas to suppress flow instabilities, such as powder clustering and channeling flow. We discovered that a $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathode with a 10- μm (micrometer) -diameter powder size can be uniformly fluidized in our coherently controlled gas-fluidized bed (CCGFB), which otherwise functions as a channeling flow. Dispersing the primary cathode particles uniformly in a gas flow creates the necessary condition that will eventually enable a conformal ALD coating on each primary cathode particle at a large commercial scale.

Proposed Work for FY 2010

In FY10, we will deposit ultra-thin film coatings on the surfaces of Li-Mn-O cathode powders in our newly fabricated ALD-CCGFB reactor and characterize them both structurally and electronically. We expect to achieve further enhancement by using the ALD-coated cathode particles in a fluidized-bed reactor because each particle can come in intimate contact with the gas flow and thus be fully coated. In addition, we will investigate the influence of film properties, including layer thickness, morphology, and material types on cell performance to optimize the material design for cathode powders. Moreover, the size/porosity effect of primary cathode particles on cell performance will be studied by using our existing resources. Through this research, we expect to further enhance cell performance as a result of drastically enlarged interface area and a superionic effect when the building block shrinks to a small dimension at the nanometer scale.

Advancing the Frontiers of Computational Design of New Materials

2009-180-NO

Larry A. Curtiss, Ian T. Foster, Jeffrey P. Greeley, Kalyanasundaram Kumaran, and Peter Zapol

Project Description

The objective of this project is to develop the capability needed to design materials with desired properties. The development work is targeted toward the design of new catalytic materials, a forefront research area for energy applications. Success in this first step will make it possible to extend the capability to many other types of materials.

Mission Relevance

This project is tied to DOE's missions in energy, national security, and basic science. The development of capabilities to design a new material with targeted properties would have far-reaching implications. Given the high cost of experiments, computational materials design can improve the efficiency of the search process for new materials and have a major impact on science and engineering. New materials are crucial to many energy-related technologies and to the DOE mission of energy security. A portfolio of such "materials by design" might include efficient catalysts to convert a hydrogen-rich molecule (such as methanol) to hydrogen for fuel cells, new molecular or compound semiconductors that efficiently absorb sunlight across the full solar spectrum, or hierarchical organic-inorganic assemblies that provide the spin-coherent host as a basis for quantum computing. The capabilities developed during this project will be relevant to the Energy Frontier Research Center (EFRC) and solar energy projects.

FY 2009 Results and Accomplishments

Considerable data have been generated with regard to our initial target catalytic reactions. For the electrocatalysis reaction involving H_2O_2 formation, this involved optimization of metal surfaces and data for the reaction steps. We are using plane-wave density functional theory calculations to characterize the interactions of molecules, atoms, and reaction intermediates on flat and stepped transition metal surfaces including the elements Cu, Ag, Au, Pt, Pd, Co, Fe, Rh, Ru, Ir, Os, and Ni. We have profiled the bulk energy as a function of lattice constant. The calculated bulk properties agree well with experiment. The stepped and flat surfaces of Cu, Ru, Co, and Fe ($\sim 12 \text{ \AA}$ thick slabs) have been optimized. The preliminary free energy landscape for H_2O_2 on Cu(111) and Co(0001) is shown in Figure 1.

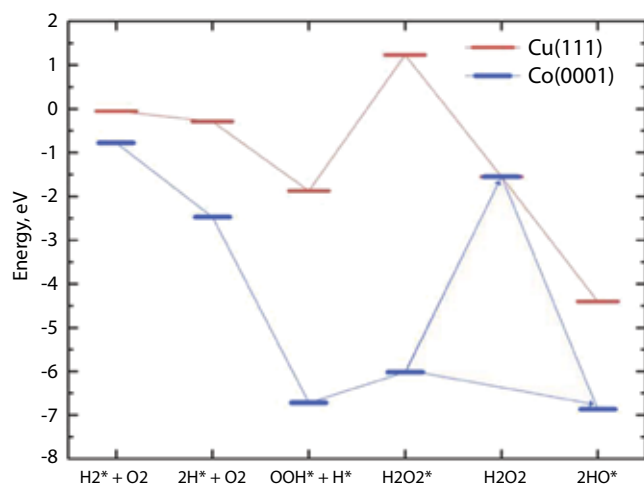


Figure 1. Free energy surface showing relative energies for reactions for formation of H_2O_2 on Cu(111) and Co(0001). The energies are relative to adsorbed H_2 on Cu(111) and gas phase O_2 .

For heterogeneous catalysis, generated data have included C-H bond activation in methane on small transition metal clusters both in the gas phase and on surfaces; we are using methane as a model system to investigate adsorbate energies and activation barriers. Correlations have been obtained between the adsorbate energies and the activation barriers to provide descriptors that can be used to find optimal catalyst candidates for experimental testing. We are also carrying out investigations into reaction pathways to develop an understanding of the reaction mechanisms of experimentally observed catalytic reactions.

In the component of the project on database development, we have successfully developed the first phase of the database software. It is based on MySQL with a web browser interface that makes searches very easy. Software has been written for extracting data from electronic structure calculations. The data that are being generated are being collected and entered into the database.

We are making good progress on the optimization of the GPAW (grid-based projector-augmented wave) code for electronic structure calculations on the Blue Gene/P supercomputer, with the help of Argonne Leadership Computing Facility staff. Several scientists from the Danish Technical University have spent time at Argonne working on optimizing the code. For example, the scaling that has been obtained for a gold nanoparticle of 102 atoms is shown in Figure 2.

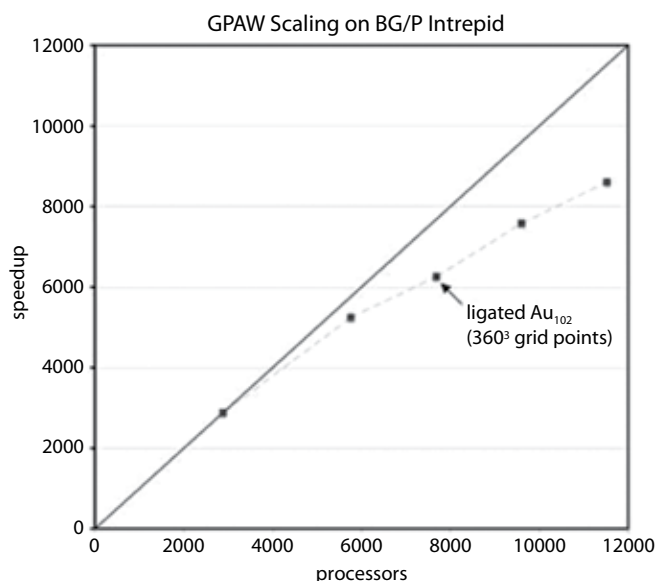


Figure 2. Example of scaling of the GPAW code being developed for the Blue Gene/P for a gold nanoparticle of 102 atoms.

In terms of outreach, we have established a working relationship with Jens Norskov from the Danish Technical University on database and GPAW code development. We are also organizing a materials design workshop that will be used to establish a catalytic materials design network that will enhance our capabilities. Several researchers have expressed interest in using the database capabilities that we are developing.

Proposed Work for FY 2010

We will continue to develop a powerful computational materials design capability at Argonne targeted toward the design of new catalytic materials. Our research will focus on:

- Generating complete data for electrocatalysis (H_2O_2 formation) and C-H bond activation in CH_4 and the derivation of descriptors.
- Developing screening algorithms.
- Initiating screening for catalysts with desired properties.
- Initiating data generation for carbon dioxide reduction and oxygen addition.
- Completing optimization of the code for electronic structure calculations and initiating large-scale computations on the Blue Gene/P.
- Developing the second phase of database software, including visualization and initiate data analysis capabilities and tools.



SYSTEMS & COMPUTATIONAL BIOLOGY

Development of Unique Environmental Basic Research Capabilities for Sustainable Bioenergy Research

2007-107-R2

R. Michael Miller, Julie D. Jastrow, and Roser M. Matamala

Project Description

The primary goal of this project is to establish an experimental resource for evaluating plants for their potential not only as a biofuel feedstock but for carbon sequestration. With our group's nearly quarter-century research history conducted at the Fermilab (Fermi National Accelerator Laboratory) site, the establishment of experimental research plots there enables us to leverage a significant amount of information about plants, microbes, and soils obtained through our previous investigations of prairie restorations. The focus is the identification of plant and microbial processes that can improve the sustainability of low-input (fertilizer) production of biofuel crops while increasing a crop's ability to sequester carbon into longer-turnover soil carbon pools. The development of the resource will allow for field-scale research addressing mechanisms of carbon sequestration by using the prairie as a model system. The research will also have applications in the areas of ecosystem restoration, conservation biology, and sustainable agriculture.

Mission Relevance

The project supports DOE missions in energy and the environment. Recently, prairie restorations have been a primary focus of the DOE's Office of Biological and Environmental Research (OBER) carbon sequestration program, primarily via the Carbon Sequestration in Terrestrial Ecosystems (CSiTE) program. The experimental design will facilitate the validation of carbon sequestration models, which is especially critical in establishing the true value of traded carbon credits. The project has the potential to generate unique capabilities in basic environmental research related to the development of sustainable, carbon-negative biomass feedstocks.

FY 2009 Results and Accomplishments

Biomass from the first (2008) growing season was left in the field because there was too little material to harvest or to remove by burning. In spring 2009, all large plots were treated with a broadleaf-specific herbicide to control weeds, and two nitrogen fertilization treatments (0 and 60 kg N ha⁻¹) were superimposed over the vegetative treatments. Weeds in the small plots were removed by hand. Second-year growth of switchgrass and other potential bioenergy species was much greater and more uniform than during the first growing season, although some weed-dominated patches still existed. Switchgrass cultivar growth during the second growing season

showed a clear relationship with latitude of cultivar origin. Date of flowering was earliest for the most northerly cultivar and latest for the most southerly cultivar. Similarly, aboveground biomass production was lowest for the more northerly cultivar, but the overall highest level of production was found for the upland cultivar originating in southern Illinois rather than for the lowland cultivar originating in Oklahoma. However, preliminary investigations suggest that belowground biomass does not follow aboveground production and that cultivar differences exist in the ratio of root-to-shoot production. The more northerly cultivar had considerably more belowground biomass in the surface 15 cm of soil than the other two cultivars, particularly in the fertilized plots. While much of this difference was in rhizome production, root mass was also higher for the more northerly cultivar than for the others.

Cutting and baling of the vegetation from each plot was accomplished through a contract with a local farmer. Aboveground harvested yields ranged from 1,400 kg ha⁻¹ dry mass for the poorest yielding plot of the most northerly cultivar to 6,300 kg ha⁻¹ dry mass for the best-yielding plot of the upland cultivar from southern Illinois. We also identified four groups interested in working with us to use the harvested bales from the plots for research on feedstock quality in various bioenergy engineering projects. Packer Engineering in Naperville will test the three switchgrass cultivars, the mixture of all three cultivars, and the switchgrass-big bluestem mixture in its pilot gasification plant. The Biological Systems Department at Idaho National Laboratory will evaluate and compare the chemical and physical properties of the three switchgrass cultivars for their efficacy in biorefinery applications. Engineers in Argonne's Energy Systems Division are also interested in testing feedstocks from the site in new bioenergy facilities being built this year in collaboration with Packer Engineering. Lastly, a small business in Wisconsin that manufactures palletizing equipment and biomass-burning heating products is planning to test whether or not the various mixed-vegetation treatments can be used to reduce or eliminate the need to add binding materials to switchgrass feedstocks in the pelletizing process.

From a research perspective at the field site, Argonne scientists are currently partnered in the multi-laboratory CSiTE consortium with Oak Ridge National Laboratory and Pacific Northwest National Laboratory, which is funded by BER to investigate carbon sequestration. Research efforts by this group have begun to use materials from the site to compare cultivar differences in decomposability and soil carbon sequestration potentials in laboratory investigations and will conduct large-scale field investigations beginning next field season. As a part of this project, we have already established an eddy flux tower on the site and, during the past year and a half, have measured net ecosystem exchange of CO₂ and soil respiration across the plots. In addition, baseline measurements of soil

properties were conducted. We are also working with Justin Borevitz and Geoff Morris of the University of Chicago, who established 160 experimental mini-plots within the field site for investigating the genetic diversity effects on biofuel feedstock production.

Proposed Work for FY 2010

This project does not continue into FY10.

Presentations and Non-Refereed Publications

Miller, R.M., "The Challenge of Sustainability and Carbon Sequestration in Biofuel Feedstock Development," invited speaker, Workshop on Biotechnology and Biofuels, sponsored by the Department of Biotechnology of the Government of India, October 12–16, 2007, New Delhi, India.

Miller, R.M. "Carbon and Geologic Carbon Sequestration," invited speaker, presented at the Economic Valuation of Ecosystems Conference, Program on Global Environment, University of Chicago, May 29, 2009.

Miller, R.M., "A History of Grassland Research at Fermilab," invited speaker, Grassland Restoration Network, The Nature Conservancy, University of Wisconsin Arboretum, August 26, 2008.

Morris, G.P., P. Grabowski, J.O. Borevitz, R. Michael Miller, and J.D. Jastrow, "Effects of Ecotypic Diversity on Establishment of Reconstructed Native Grasslands and Outputs of Ecosystem Services," presented at the Annual Meeting of the Society of Ecological Restoration, April 8, 2009, Madison, WI.

An Ultra-Sensitive Detection Assay

2007-133-R2

Liaohai Chen, Qiaoling Jin, and John T. Bahns

Project Description

The goals of the project are to synthesize new imaging tracers, to create new sensing platforms, and to develop the corresponding assays for DNA, RNA, protein, and cell identification and quantification at single-molecule and single-cell levels both *in vitro* and *in vivo*. For image tracing, we are developing a novel polymeric-micelle-based imaging probe with great sensitivity and specificity. For sensing, we are developing oligonucleotide (oligo)-based sensing probes that allow the visualization of DNA binding proteins (regulation factors) in living cells and the analysis of multiple gene targets at a single-cell level. These assays enable genomics and protein functional

analysis of a single cell as well as its interactions with other cells in a cell community (such as niche cells or mutated cells in tissues or environmental samples).

Mission Relevance

This project is directly related to DOE missions in improving energy security and strengthening scientific discovery and innovation. The research aims at establishing rapid, sensitive, and convenient bioassays for imaging, detecting, and quantifying DNA, RNA, protein molecules, and/or specific cells at a single molecule/ cell level in a complex cell community. This technology is applicable to bioenergy, carbon sequestration, and bioremediation.

FY 2009 Results and Accomplishments

In FY09, we focused on (1) establishing DNA-based sensing techniques for *in vivo* DNA-binding protein visualization and quantification at a single-cell level and (2) developing a second generation of polymeric-micelle-based image tracing by omitting the dye-releasing step and demonstrating *in vivo* application.

For the first effort, we optimized an oligo beacon sensor to follow the function of the transcription factor Octamer-4 (Oct4) *in vivo*. DNA binding proteins such as transcriptional factors play essential roles in determining cell functions. A non-destructive tool to monitor the expression of these master genes in a quantitatively and timely manner *in vivo* is essential to better understanding cell functions and cell reaction to environmental changes. Classically, the detection of these transcriptional factors was achieved by fixing and staining cells. To recover the biomarker positive cells and to observe their culture behaviors, "staining" transcriptional factor biomarkers of viable cells is highly desired. In FY09, we focused on the development of oligo beacon probes to tackle the challenge. The probe was designed for measuring the Oct4 level *in situ* and in real time. As a control, a nonspecific Oct4 probe was also synthesized. Our results indicated that the transfection of the Oct4 probe into stem cells was very efficient. More than 90% cells were observed to be red after transfection (Figure 1A, top row), while cells transfected with non-specific probe gave only background fluorescence (Figure 1A, middle row). To further investigate whether the Oct4-specific probe can indicate the Oct4 level *in vivo*, we induced differentiation by growing stem cells in retinoic acid (RA) followed by dual immuno-labeling with Oct4 and stage-specific embryonic antigen 1 (SSEA1). As shown in Figure 1B, the center part of colonies underwent apparent differentiation. When the Oct4 probe was introduced to differentiated cells induced by RA, we discovered that the edge cells had comparable fluorescence as undifferentiated colonies, but the center part showed much less fluorescence (Figure 1A, bottom row), matching the observation obtained by immunostaining. This gentle, nonde-

structive probe was thus demonstrated to be extremely useful in monitoring the undifferentiated status *in vivo*. In addition, the transfected cells can be kept for further growth after separation based on the labeling intensity, thus providing a tool to study the diversity of stem cell colonies. A proposal for new research based on these results was submitted to the National Institutes of Health.

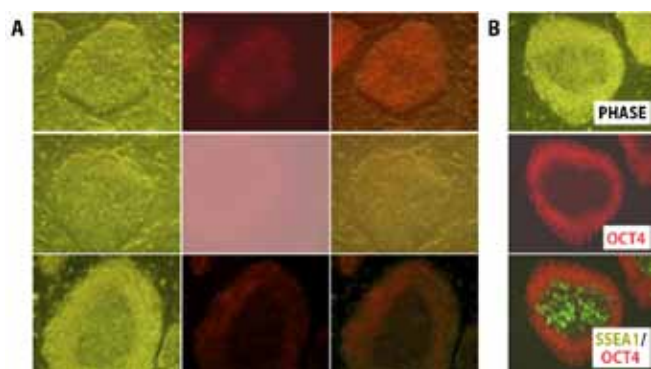


Figure 1. (A) Oct4-specific probe was transfected into undifferentiated cells (top row), or differentiated cells were induced by RA (bottom row). The nonspecific probe was used as a control for nonspecific uptake (middle row). (B) Dual labeling of Oct4 and SSEA1 revealed that the center part of RA-treated colonies were differentiated.

In the effort to develop a second generation of polymeric micelle-based imaging, we identified a new infrared dye molecule — squaraine-cholesterol derivative, which did not exhibit self-quenching upon micelle encapsulation. Given the emission wavelength of 750 nm, squaraine-dye-encapsulated polymeric micelles are the ideal optical imaging probes for *in vivo* studies. Working with Dr. Chin-Tu Chen at the University of Chicago, we have started *in vivo* experiments. A proposal based on these results was submitted to the DOE Office of Biological and Environmental Research.

Proposed Work for FY 2010

This project does not continue into FY10.

Systems Biology for Enhanced Bioconversion

2007-161-R2

Kevin White and Folker Meyer

Project Description

In this project, we applied second-generation DNA sequencing technology to the study of problems relevant to DOE missions. These exploratory genome-driven capabilities were used to analyze complex microbial communities in environmental

samples, with the goal of obtaining information about the interwoven processes in environmental remediation and the control of carbon uptake by terrestrial ecosystems. By taking advantage of second-generation DNA sequencing technology and integrating it with powerful informatics analysis, we have been able to generate the scale of sequence data that parallel the number of genes underlying these processes. More importantly, we have modeled process dynamics by coupling these analyses with additional physical and chemical characterizations of environmental samples. Combining molecular (DNA)-based inventories of the genetic potential for an environmental system and the physical readouts will allow us to derive the basic underlying biological parameters that drive larger-scale phenomena.

Mission Relevance

This project is directly relevant to DOE's carbon sequestration program and thus to DOE's energy and environment missions. The capabilities developed in this project will make it possible to characterize the metabolic processes of key microbial populations, from which the parameters for microbe-facilitated sequestration of carbon can be determined. Creating economically competitive, safe, and practical mechanisms for carbon sequestration is essential to reducing greenhouse gases to levels that will address climate change processes.

FY 2009 Results and Accomplishments

We have added single-gene-based community reconstruction to the existing community reconstruction methods. To further the resolution of microbial community composition from environmental sample sets, we used inventories of conserved gene markers, such as the gene encoding for the 16S ribosomal ribonucleic acid (16S rRNA) molecule. Although the identification of low abundance populations within these communities is possible with the throughput of second-generation DNA sequencing technology, the real advantage is the increased throughput for sample analysis. This increase is achieved by using a polymerase chain reaction primer approach that essentially provides sample bar coding by means of a sequence tag. The analysis of massive amounts of single-gene sequence data requires analysis capabilities that are distinct from those required for shotgun metagenome analysis, such as that provided by the MG-RAST (Metagenomics Rapid Annotation using Subsystems Technology) server.

We have established a preliminary data generation and analysis pipeline for in-house single-gene (e.g., 16S rRNA) sequence analysis and community composition reconstruction. Deconvoluting the output data and integrating these data readouts with physical and chemical characterizations of the datasets ("meta-data") have led us to uncover trends in the shift of large groups of organisms between different terrestrial ecosystems. In collaboration with the group of Dr. R. Knight at the

University of Colorado, we have also analyzed the 16S rRNA-based data overlaid on the functional gene data sets produced from shotgun metagenomics. This is the first time that correlations between these data types have been performed with this number of datasets from a single environmental study.

Proposed Work for FY 2010

This project does not continue into FY10.

Metagenomics and Discovery for Biofuels

2007-162-R2

Kevin White and Folker Meyer

Project Description

In this project, we applied second-generation DNA sequencing technology to the study of problems relevant to DOE missions. These exploratory genome-driven capabilities were used to conduct metagenomic sequencing of complex microbial communities from environmental samples in order to obtain information about the types of genes and their relative abundances. Biological systems play a key role in such processes as environmental remediation and the control of carbon uptake by terrestrial ecosystems. For the last decade, many of these processes have remained beyond the reach of analysis with first-generation DNA sequencing technology. With the advent of second-generation DNA sequencing technology and its integration with powerful informatics analysis capability, we can now start to explore the functions of these environments systematically by using a cultivation-independent approach: metagenomics. By sequencing the metagenomes directly from environmentally derived samples, we were able to simultaneously study the microbial populations (“what is out there?”) and their metabolic activity (“what are they doing?”). In this manner, we are able to contribute to a greater understanding of the microbial component of several processes, including carbon sequestration in a prairieland ecosystem (e.g., the Fermilab National Environmental Research Park site) and contaminant stabilization in a subsurface environment (e.g., the reduction of uranium at DOE’s Uranium Mill Tailings Remedial Action site).

Mission Relevance

This project is directly relevant to DOE’s carbon sequestration program and thus to its energy and environment missions. The capabilities developed in this project will help make it possible to characterize the metabolic processes of key microbial populations, from which the parameters for microbe-facilitated sequestration of carbon can be determined. Creating economically competitive, safe, and practical methods for carbon

sequestration is essential for reduction of greenhouse gases to levels that will address climate change processes.

FY 2009 Results and Accomplishments

Analysis of metagenome data sets from several carbon sequestration and management-related sampling sites was expanded to a continental scale by obtaining samples from more than 20 states in the continental United States. The ability to partition metagenomes within the context of the ecosystem from which they were collected indicates that unique functional gene sets were obtained from the microbial communities therein. Furthermore, we compared data sets generated using different second-generation DNA sequencing chemistries (e.g., 454 LR70 versus XLR70) and found minimal distortion in terms of the gene types and relative abundances generated from one sequencing chemistry versus the other. Presently, these data sets are being mined for candidate gene sequences for the generation of novel protein structures from the environment.

Because we are presently not able to produce an appreciable assembly of DNA sequences from topsoil samples, we are investigating the utility of Illumina’s Solexa GAII DNA sequencing platform to achieve the necessary level of oversampling (or sequencing depth) for increasing the likelihood of sequence assembly. The first set of Solexa data was generated from a sample taken from a subsurface environment originally stemming from the DOE UMTRA site. The scale of generated data was approximately 25 times more than produced by the 454 XLR70 DNA sequencing chemistry.

In addition to increasing the sequencing depth possible with second-generation DNA sequencing platforms, we have also developed a library construction protocol for de novo transcriptome sequencing. This library was developed initially for eukaryotic systems and has been adopted for the production of metatranscriptome libraries from environmental systems. Using this approach for focusing on the actively expressed portion of functional genes from an environmental sample, we can decrease the overall sequence “search space” and focus the sequence recovery on those genes relevant to microbial community function.

Additionally, in keeping pace with the number of project data sets produced as well as the increased scale of data generated, a laboratory information management system was developed for data handling. This improved web-based platform has a user interface to assist in sample tracking, but more important, a query system for performing comparative analyses between samples and projects.

Proposed Work for FY 2010

This project does not continue into FY10.

A Framework for Scalable Statistical Genomics

2007-164-R2

Folker Meyer, Ian T. Foster, and Michael J. Wilde

Project Description

Several software systems provide bioinformatics tools for analyzing bacterial genome datasets. However, the growing number of datasets and the increasing diversity of research areas in which these datasets are used have created new requirements for the analysis software. In response to these requirements, we are developing a comprehensive framework for analysis of large numbers of bacterial genomes and metagenomes. This project supports the new MG-RAST (Meta Genome Rapid Annotation using Subsystem Assembly) system, which enables researchers to analyze and view large numbers of genomic or metagenomic datasets by using high-throughput technology. Metagenomic sequencing and analysis have potential applications, for example, in the management of environmental carbon sequestration and toxic waste cleanup.

Mission Relevance

This project supports DOE's science and environment missions through microbial genomics. Specifically, through the Microbial Genome Program and Genomics: GTL Program, DOE's Office of Biological and Environmental Research supports research in microbial genomics.

FY 2009 Results and Accomplishments

The component library in the SEED-Viewer of the MG-RAST system was extended to support new viewing metaphors; in essence, multiple different, mutually supporting views on the data that enable data analysis by expert users and enable access by less-experienced users. In particular, metabolic comparisons are now supported for multiple organisms or metagenomes at a time, allowing novel types of analyses with metagenome data sets.

The latest addition to the component library is a novel circular view. This view supports mining of large metagenomic data sets and provides a basis for showing the functional diversity present in environmental data sets. Figures 1 and 2 illustrate two examples of the circular tree view. Figure 1 shows the relative abundance of organisms in a metagenomic sample. Figure 2 compares the relative abundance of organisms between two metagenomic samples. The distribution of each node can be viewed in a tooltip. Clicking on a node allows for re-rooting of the tree for higher resolution of that branch.

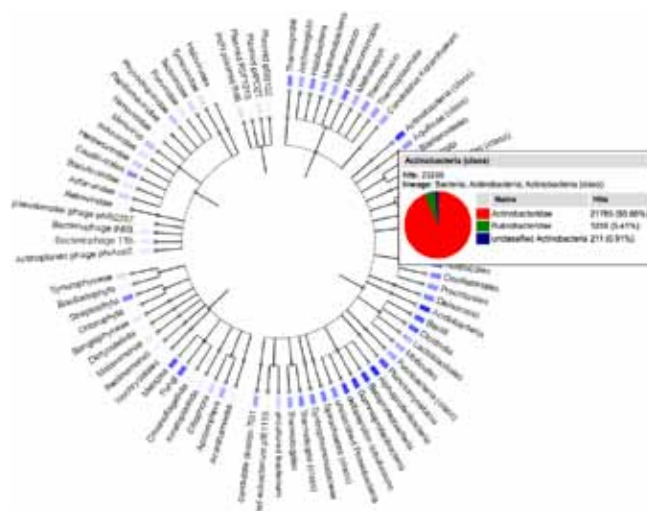


Figure 1. A circular view representing the relative abundance of organisms in a soil sample taken from the National Environmental Research Park (NERP) site at Fermi National Accelerator Laboratory (Fermilab).

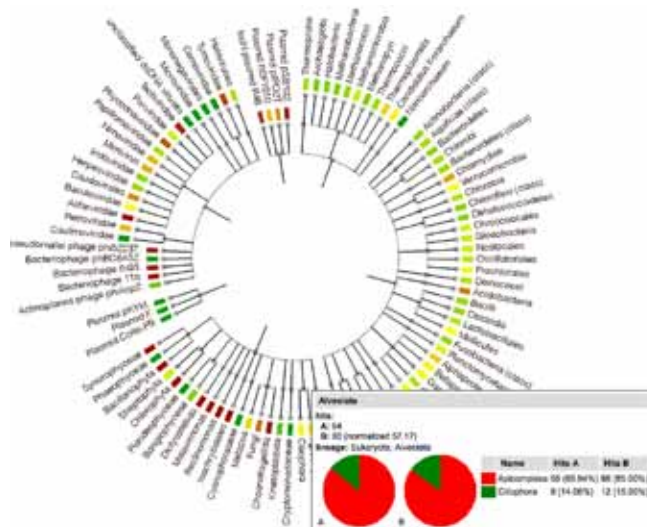


Figure 2. A circular view representing a comparison of the relative abundance of microorganisms in two distinct soil samples from the NERP site.

This plug-in component can be used with any taxonomic data and is highly configurable. The resulting image can be returned in compressed format for web pages or in high resolution for presentations.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Meyer, F., R. Overbeek, and A. Rodriguez, "FIGfams: Yet Another Set of Protein Families," *Nucleic Acids Research* (2009), **37**(20), 6643–6654.

Stabilization of Subsurface Contaminants through Augmentation of Natural Biological and Geochemical Processes

2008-124-R1

Kenneth M. Kemner, Carol S. Giometti, Folker Meyer, and Edward J. O'Loughlin

Project Description

Estimates of the performance of subsurface remediation techniques and long-term stewardship strategies are often based on insufficient knowledge of the mechanisms of natural chemical transformation and the transport behavior of subsurface contaminants. In addition to geochemical effects on transport, the activity of subsurface microbial communities can have a profound effect on the mobility of subsurface contaminants. Integration of Argonne's unique capabilities in high-performance computing, synchrotron-based x-ray measurements, and high-throughput methods for analyzing biomolecules offers a unique opportunity to use high-performance computing in metagenomic studies together with synchrotron-based experimental approaches in studying biogeochemical cycling in lab- and field-based systems, particularly in regard to the physical and chemical transformations of contaminants.

The scope of work includes use of batch experiments to demonstrate the feasibility of integrating metagenomic studies of subsurface microbial communities to identify active microbial processes together with geochemical measurements of subsurface processes to elucidate natural biogeochemical processes that can be augmented to foster stabilization of subsurface contaminants. This includes study of the evolution of a natural microbial community, the speciation of iron and sulfur, and the transformations of uranium within sediment collected from a contaminated DOE site as it is bio-stimulated with the addition of an electron donor and augmented with an electron shuttle.

Mission Relevance

The project is relevant to DOE's environmental mission. The DOE oversees some of the largest environmental cleanup operations in the world. Cold War Era processing of uranium for nuclear power and weapons has left an enduring legacy of contaminated soils, groundwater, and other environmental media requiring innovative solutions to cleanup, manage, and monitor the contaminants at DOE sites. The insights and capabilities resulting from this work will directly address the issues related to remediation of contaminated subsurface environments. These issues and the ability to address them are the foci of several DOE programs, including the Subsurface Bio-

geochemical Cycling Program, the Genomes to Life Program, and a future Exascale Computing Initiative.

FY 2009 Results and Accomplishments

Progress toward our goal included the continued development of a molecular microbiology laboratory having many of the capabilities required to extract, concentrate, and initially characterize DNA from natural subsurface materials before they are provided to the Institute for Genomics and Systems Biology for microbial community analysis. We installed and have begun operating a gas chromatograph for analysis of hydrogen in these systems. We initiated bio-stimulation experiments of iron-rich material in batch reactors in the presence and absence of an electron shuttling compound. The iron-rich sediments used in these experiments were inoculated with sediment from a DOE field site (Old Rifle Uranium Mill Tailings Remedial Action Integrated Field Challenge Site). We continued development of DNA extraction procedures for these materials. We have sampled the batch reactors in these experiments on a daily basis for a period of two months, stored sampled material at -80°C , and have begun extracting DNA from some of these samples. Analysis of Fe(II) production and acetate consumption in these samples indicates the onset of iron reduction is coincident with acetate consumption, which is consistent with optical images of initial batch experiments performed in FY08. Results of these measurements are shown in Figure 1. We have also begun x-ray absorption spectroscopy characterization of speciation of the uranium that was added to each of the batch reactors.

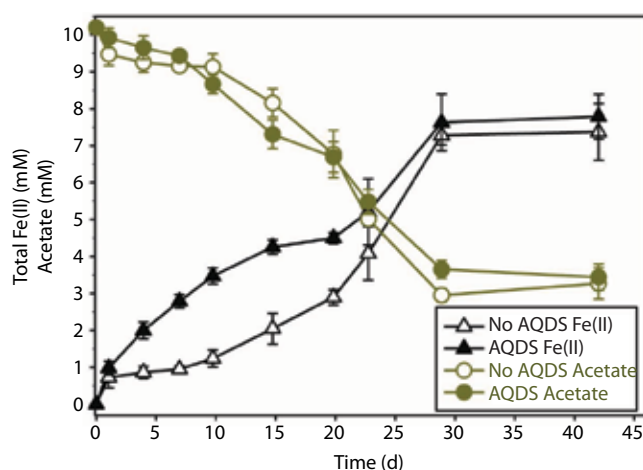


Figure 1. Concentration of ferrous iron and acetate in biogeochemical suspension as a function of time, indicating the microbial consumption of acetate and the onset of iron respiration (AQDS = anthraquinone-2,6-disulfonate).

Proposed Work for FY 2010

Our technical goals for FY10 include:

1. Finish isolation of DNA and characterization of the microbial community within sediments sampled from each batch reactor at multiple times during the experiment.
2. Use bioinformatics tools (Metagenome Rapid Annotation using Subsystem Technology [MG-RAST]) to analyze the metagenomes within sediments sampled from each batch reactor at multiple times during experiments.
3. Draft and submit a manuscript detailing the results of this study.

Non-Refereed Publications and Presentations

Antonopoulos, D.A., A. Ammar, M.I. Boyanov, M.H. Domanus, P. Long, F. Meyer, E.J. O'Loughlin, D. Sholto-Douglas, K. Skinner-Nemec, K.H. Williams, and K.M. Kemner, "Microbial Community Analyses of Iron-Rich Mineral Suspensions Inoculated with Sediments from a Uranium Mill Tailings Site," presented at the American Society of Microbiology Annual Meeting, Philadelphia, PA, May 2009.

Wide-Angle X-Ray Scattering as a Probe of Protein Structure, Dynamics, and Function

2008-128-R1

Lee Makowski

Project Description

Wide-angle x-ray solution scattering (WAXS) is a novel approach with significant potential for characterizing the structure, dynamics, and function of proteins of any size without the need for crystallization. WAXS allows the study of proteins much larger than permitted by nuclear magnetic resonance (NMR) methods. Of special interest to DOE is the ability of WAXS to study membrane proteins, which are exceptionally difficult to investigate by using crystallography or NMR. Finally, solution scattering methods also have exceptional promise for basic and applied studies of protein conformational changes under a variety of physiological conditions. Taken together, these features suggest that WAXS will play an enabling role in 21st century biology.

Mission Relevance

The project relates to DOE's basic science mission. WAXS will be used to establish a basis for high-throughput screening of proteins for functional ligands (as required for systems biology and drug discovery efforts and for deep annotation in functionome studies). As such, development of the technique will benefit DOE and NIH attempts to develop new methods for

functional analyses of proteins and will provide an important adjunct to ongoing structural genomics efforts at NIH as a component of the third phase of the Protein Structure Initiative.

FY 2009 Accomplishments and Results

Using computationally generated WAXS patterns, we demonstrated the classification of protein structures on the basis of WAXS data and the power of this approach for classifying the structure of proteins of unknown structure.

Our programs to evaluate the parameters describing solvation and excluded volume were critical steps in the development of EXCeSS (name of a computer program developed during the project) and will continue to be used for rapid computation of WAXS patterns from very large macromolecular complexes.

WAXS data were collected on five HIV protease mutants and four hemoglobin variants. Analysis using global fluctuation parameters has demonstrated that fluctuations of the flaps of HIV protease are greatly reduced in an inactive mutant. We have similarly demonstrated that fluctuations of hemoglobin are enhanced in the presence of inositol.

Proposed Work for FY 2010

The use of an explicit atomic representation of water for calculation of WAXS patterns was so successful that we intend to use it extensively in the future and to develop a public server to provide community access.

We intend to use EXCeSS as a basis for carrying out calculations combining WAXS with energy minimization in the construction of molecular models. We are working with David Baker (U. Washington) to determine if WAXS can contribute significantly to his protein prediction approach.

We intend to use EXCeSS predictions to estimate the absolute amplitudes of fluctuations of a number of model proteins and then extend EXCeSS to the study of fluctuations during enzymatic cycling of adenylate kinase (working with G. Phillips, U. Wisconsin)

We will use EXCeSS to calculate the expected WAXS pattern of the native (rigid) protein and use the global modeling approach we developed last year to estimate the amplitudes of fluctuations that give rise to changes in the WAXS pattern under solvent conditions known to cause proteins to form molten globules.

Refereed Publications

Bardhan, J.P., S. Park, and L. Makowski, "SoftWAXS: A Computational Tool for Modeling Wide-Angle X-Ray Solution Scattering from Biomolecules," *J. Appl. Cryst.* **42** (2009), 932–943.

Makowski, L., "Characterization of Proteins with Wide-Angle X-Ray Solution Scattering (WAXS)," *J. Structural and Functional Proteomics* (in press).

Makowski, L., D.J. Rodi, S. Mandava, S. Devrapahli, and R.F. Fischetti, "Characterization of Protein Fold Using Wide-Angle X-Ray Solution Scattering," *J. Mol. Biol.* **383** (2008), 731–744.

Park, S., J.P. Bardhan, B. Roux, and L. Makowski, "Simulated X-Ray Scattering of Protein Solutions Using Explicit-Solvent Molecular Dynamics," *J. Chem. Phys.* **130** (2009), 134114.

Yang, S., S. Park, L. Makowski, and B. Roux, "A Rapid Coarse Residue-Based Computational Method for X-Ray Solution Scattering Characterization of Protein Folds and Multiple Conformational States of Large Protein Complexes," *Biop. J.* **96** (2009), 4449–4463.

Non-Refereed Publications and Presentations

Makowski, L., "WAXS Studies of Hemoglobin Function," presented at Carnegie Mellon University, January 6, 2009.

Makowski, L., "WAXS for the Study of Protein Structure, Dynamics, and Ligand Binding," presented at the University of Illinois at Chicago, January 29, 2009.

Makowski, L., "Slow Correlated Movement of Structural Elements in Hemoglobin and Myoglobin," presented at the Biophysical Society, Boston, MA, March 4, 2009.

Makowski, L., "Characterizing the Unsolved Structures of the PSI with WAXS," presented at NIH (National Institutes of Health) Workshop: Enabling Technologies for Structural Biology, March 5, 2009.

Makowski, L., "Linking Protein Ensemble to Function," presented at Boston University, March 17, 2009.

Makowski, L., "Biomedical Applications of Cellular and Molecular Imaging," presented at APS Users Meeting: Workshop on Imaging Structural Hierarchy in Biological Systems, May 6, 2009.

Microbial Basis for Soil-Inorganic Carbon Sequestration

2008-140-R1

Robert A. Edwards, Roser M. Matamala, Folker Meyer, and R. Michael Miller

Project Description

The purpose of this project is to explore the role of soil in carbon sequestration and to create a database linking genomic data with traditional soil biogeochemical and other data.

Mission Relevance

The project is relevant to DOE's environmental mission. The DOE mission of global carbon management requires that we gain a comprehensive understanding of terrestrial and marine microbial communities so we can learn the roles that these communities play in carbon sequestration. This starts at the single-protein level and extends to whole organisms, communities, and ecosystems. Establishing a map of U.S. soil types linked to metagenomic data will provide key information to researchers interested in understanding the role of soil in carbon sequestration.

FY 2009 Results and Accomplishments

1. *Established statistical analysis of protein family abundance data.* We have developed a semi-automated workflow that integrates automated sequence analysis with a statistical analysis-based data-mining step.

2. *Completed additional sequencing of biological replicates for 10 sites.* The requirement for biological replicates became apparent on the basis of interactions with the scientific community. We obtained and sequenced material from all original sites in the study and conducted sequence analysis. The analysis of the data was finished, and the data was integrated with the existing body of knowledge.

3. *Performed mini-time series experiment.* In addition, we performed a mini-time series experiment for samples from the Fermilab National Environmental Research Park site. Sequence analysis and data integration are ongoing.

4. *Integrated physiological factors with sequenced bases analysis.* We have included the integrated analysis of physiological factors (including, but not limited to, pH, carbon content, carbon-to-nitrogen ratios, phosphorus and iron concentrations) with the sequence-based analysis.

5. *Established 16S rRNA-based community analysis by using pyrosequencing.* Using the LR70 DNA sequencing chemistry, we have established a community analysis protocol that supplements the existing metagenome-based analyses (see Figure 1).

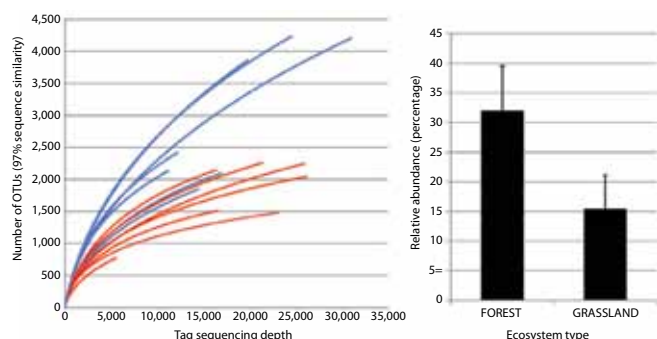


Figure 1. Community structure for 18 samples from National Ecological Observatory Network domains. Rarefaction curves in red indicate forested sites; blue curves indicate grassland sites. (OTU = Operational Taxonomic Unit)

Proposed Work for FY 2010

Further analysis will be conducted and will be submitted for publication in FY10. Potentially, we will extend the mini-time series to a larger experiment, which will provide sufficient material for a publication.

Refereed Publications

Angly, F.E., D. Willner, A. Prieto-Davo, R.A. Edwards, R. Schmeider, R. Vega-Thurber, D.A. Antonopoulos, K. Barott, M.T. Cottrell, C. Desnues, E.A. Dinsdale, M. Furlan, M. Haynes, M.R. Henn, Y. Hu, D.L. Kirchman, T. McDole, J.D. McPherson, F. Meyer, R.M. Miller, E. Mundt, R.K. Naviaux, B. Rodriguez-Brito, R. Stevens, L. Wegley, L. Zhang, B. Zhu, and F. Rohwer, "The GAAS Metagenomic Tool and Its Estimations of Viral and Microbial Average Genome Size in Four Major Biomes," *PLoS Computational Biology* (2009), in press.

Non-Refereed Publications and Presentations

Antonopoulos, D.A., "Soil Microbial Metagenomes Track with Ecosystem Type: Uncovering Soil Metabolic Clusters," presented at the First Annual ANL (Argonne National Laboratory) Soils Workshop, Argonne, IL, October 26, 2009.

Meyer, F., "Metagenomics," presented at the FEMS (Federation of European Microbiological Society) Annual Meeting, Gothenburg, Sweden, June 28–July 2, 2009.

Mapping Protein Binding Domain and Small Molecule Interactions

2008-166-R1

T. Andrew Binkowski, Ian T. Foster, Andrzej Joachimiak, Michael D. Kubal, Benoit Roux, Rick L. Stevens, and Michael J. Wilde

Project Description

Although there is a well-defined paradigm for predicting the ability of small molecules to interact with a protein surface, current computational methods have both theoretical and computational limitations. While advances in algorithms continue to reduce the computational complexity and optimize the scoring of posed molecules, studies have shown that different methods produce accurate results for only a small set of problems (i.e., no docking methodology or scoring functions can be universally applied to all docking problems). To address this challenge, we are developing a computational pipeline that combines an evolutionary analysis of protein binding sites with "cheminformatics" obtained from large-scale computational docking experiments to create a high-quality library of data on protein-ligand interactions. This library will allow a global-scale analysis of interactions between protein domains and small molecules that can be used to derive novel scoring functions and to compute more accurate predictions of small molecule binding.

Mission Relevance

This project is relevant to DOE's mission in science and is expected to be applicable to national security. Advances in exascale computing give researchers opportunities to better understand bimolecular phenomena and complex systems. Algorithmic improvements in modeling protein-ligands have been hindered by their complexity, which makes them computationally prohibitive. Re-implementing these algorithms on a scalable architecture makes this superior technology accessible to a broader class of researchers. Our discovery pipeline serves as a model for showing how scientific applications can benefit from high-throughput computing.

The use of our pipeline to improve modeling and simulations of protein-ligand interactions is also of great value for improving our understanding of biological systems and for use in national security drug discovery efforts. As our advanced scoring functions bridge the gap between theoretical and experimentally obtained small compound binding affinities, our ability to efficiently identify drugs that can combat bioterrorism agents increases.

FY 2009 Results and Accomplishments

We continued to make significant progress in developing and implementing our methodology. We now have a stable and robust framework for our biomolecular simulation methods on the Blue Gene(BG)/P computing infrastructure. The investigators were chosen to receive a 2010 INCITE award to conduct experiments on BG/P. Also in FY09, the computational pipeline was used to perform a functional analysis of more than 2,000 protein structures. The targets included pathogenic proteins from the Center for Structural Genomics of Infectious Diseases and from the National Institutes of Health's Protein Structure Initiative. On a typical workstation, this analysis would have taken about 200 years to accomplish.

We continued work on algorithms and methodologies to make more advanced evaluations of protein-ligand binding accessible to researchers. A significant breakthrough allowed the CHARMM molecular simulation program to perform free energy perturbation/molecular dynamics (FEP/MD) on the BG/P. The step-by-step computational FEP/MD simulation staged protocol breaks down the complete calculation into several MD simulations that are easy to distribute over independent compute nodes. We showed that this technique on the BG/P is highly efficient and has excellent scaling properties. Inefficient scaling has been a major limitation of CHARMM in a supercomputing environment.

Proposed Work for FY 2010

We will continue to improve our existing methodologies and the underlying frameworks that allow them to run efficiently in high-performance computing environments. We will focus on providing experimental validation of our predictive algorithms through coordinated x-ray crystallography and biochemical assay experiments. The results will be used to further parameterize our existing methods. In addition, we will continue working with outside research groups to analyze proteins that are important with regard to human health and disease and national security interests.

Refereed Publications

Binkowski, T.A., and A. Joachimiak, "Protein Functional Surfaces: Global Shape Matching and Local Spatial Alignments of Ligand Binding Sites," *BMC Structural Biology* **8**(45) (October 27, 2008).

Deng, Y., and B. Roux, "Computations of Standard Binding Free Energies with Molecular Dynamics Simulations," *J. Phys. Chem B* **113**(8) (February 26, 2009), 2234–2246.

Jiang, W., M. Hodoscek, and B. Roux, "Computation of Absolute Hydration and Binding Free Energy Using Free Energy Perturbation and Distributed Replica-Exchange Molecular Dynamics (FEP/REMD)," *J. Chem. Theory Comput.* **5**(10) (2009), 2583–2588.

Shivakumar, D., Y. Deng, and B. Roux, "Computations of Absolute Solvation Free Energies of Small Molecules Using Explicit and Implicit Solvent Model," *J. Chem. Theory Comput.* **5**(4) (2009), 919–930.

Non-Refereed Publications and Presentations

Binkowski, T.A. "Protein Surface Analysis for Functional Annotation and Prediction," presented at National Institute of General Medical Sciences (NIGMS) Enabling Technologies Workshop, Bethesda, MD, March 4–6, 2009.

Binkowski, T.A., and A. Joachimiak, "Comparison and Analysis of Protein Functional Surfaces," presented at Keystone Symposium on Structural Genomics and its Applications to Chemistry, Biology and Medicine, Steamboat Springs, CO, January 6–11, 2008.

Binkowski, T.A., D. Shivakumar, M. Kubal, M. Wilde, I. Foster, B. Roux, R. Stevens, and A. Joachimiak, "Mapping Protein Binding Domain and Small Molecule Interactions," presented at American Chemical Society Annual Meeting, Philadelphia, PA, August 17–28, 2008.

Hocky, G., M. Wilde, J. DeBartolo, M. Hategan, I. Foster, T.R. Sosnick, and K.F. Freed, "Towards Petascale ab Initio Protein Folding through Parallel Scripting," presented at Institute of Electrical and Electronic Engineers/Association for Computing Machinery (IEEE/ACM) Supercomputing 2009 (SC09) Conference, Portland, OR, November 14–20, 2009.

Raicu, R., Z. Zhang, M. Wilde, I. Foster, P. Beckman, K. Iskra, and B. Clifford, "Toward Loosely Coupled Programming on Petascale Systems," presented at Institute of Electrical and Electronic Engineers/Association for Computing Machinery (IEEE/ACM) Supercomputing 2008 (SC08) Conference, Austin, TX, November 15–21, 2008.

Roux, B., "Using Simulations to Estimate Free Binding Energies," presented at Keystone Symposium on Computer-Aided Drug Design, Steamboat Springs, CO, March 29–April 3, 2008.

Zhang, Z., A. Espinosa, K. Iskra, I. Raicu, I. Foster, and M. Wilde, "Design and Evaluation of a Collective IO Model for Loosely Coupled Petascale Programming," presented at MTAGS08 Workshop on Many-Task Computing on Grids and Supercomputers (co-located with ACM/IEEE SC08 Conference), Austin, TX, November 17, 2008.

Metagenomics-Enabled Discovery of Protein Function

2009-156-N0

Elizabeth M. Glass, Folker Meyer, Terrence Disz, Christopher S. Henry, and Rick L. Stevens

Project Description

New technology for DNA sequencing (e.g., 454 Pyrosequencer) has enabled discovery of the “DNA world” surrounding us and contributing significantly to the environment we live in. Previously, large teams of researchers sequenced individual genomes, but recently, due to the decreasing cost, small groups have been doing the same. This has allowed more and more researchers to study complex communities of microbes in environments as diverse as marine sediment, soil, and human mucosal tissue. These studies have aimed to dramatically expand our understanding of the microbial biosphere and, more important, to reveal the secrets of the complex symbiotic relationship in various environments. An important prerequisite for such discoveries is availability of computational tools that can rapidly and accurately compare large datasets generated from complex bacterial communities and thereby identify features that distinguish them.

Hundreds of metagenomes have already been sequenced, and we are attempting to play a leading role in the analysis of metagenomic data sets. With small investment, we have been able to create a version of the Rapid Annotation using Subsystem Technology (RAST) server created by a joint Argonne/University of Chicago team for metagenome analysis (called MG-RAST). To meet the growing demand for analysis and the scope and types of comparative analyses, the following are needed:

- Improvements in metabolic reconstruction for metagenomes,
- Development of tools for metagenome analysis,
- Coupling of high-performance computing resources to the existing MG-RAST front-end, and
- Improvements in the user front-end.

Mission Relevance

This project is tied to DOE’s mission in science. Project results will be of interest to the DOE Office of Biological and Environment Research (BER) (carbon sequestration) and the DOE Environmental Remediation Sciences Program (ERSP). The BER Life and Medical Sciences Division Genomics:GTL (formerly Genomes to Life) Program currently supports significant work in the field of metagenomics, and ERSP has accepted metagenomics as a new tool to study subsurface communities. Identifying and defining the characteristics of the micro-

bial communities in the biosphere are vital to understanding their contributions to various ecological systems. Not much is known about microbial communities; therefore, the potential for discovery is great in any habitat chosen for study. Areas relevant to DOE missions include the following:

Climate Change: The development of microbial ecosystem models that describe and predict global environmental processes, change, and sustainability.

Energy: The development of microbial systems and processes for new bioenergy resources that will be more economical, environmentally sustainable, and resilient in the face of disruption by world events.

Bioremediation: The development of tools for monitoring environmental damage at various levels and methods for restoring the health of an ecosystem.

Other federal agencies would also benefit from the proposed work. For example, the Human Microbiome Project of the National Institutes of Health is sponsoring projects that explore and analyze microbial communities of human mucosal tissue for advancing research on human health and disease.

FY 2009 Results and Accomplishments

In FY09, we developed a visualization tool that allows MG-RAST users to compare metagenomes on a tree (Figure 1). This tool allows users to analyze the variations of relative abundance of specific genes or metabolic pathways in various organisms.

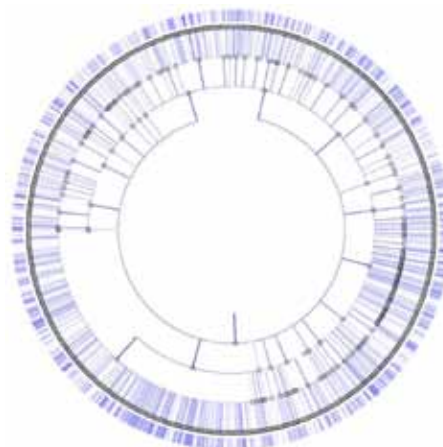


Figure 1. Phylogenetic tree produced by new MG-RAST visualization tool for comparative metagenomics. Tree diagram shows the presence of taxa or subsystems for a given metagenome or set of metagenomes. Specifically, this example tree represents the hierarchy of subsystems (the levels), and the color shows the relative abundance of a given node or leaf. Selecting each node (or circle) provides a summary of the distribution of that subsystem category or system between the two samples. The lines between the nodes are colored to show an overall comparison: the red line suggests that the subsystem category is mostly in metagenome A, green is mostly in metagenome B, and yellow is shared between the two. If looking at one metagenome, the lines and nodes are in blue. The deeper the color, the more fragments were assigned to that category.

The MG-RAST contains metabolic “heat maps” that enable users to compare metagenome analysis results (metabolic and phylogeny) with those of other metagenomes. Users can thus compare the prevalence (relative abundance) of different subsystems or taxonomies in different samples. The functionality of this tool was also expanded to allow users to compare various levels of metabolism and virulence subsystems. This tool provides the user with various views in which to compare metagenomic samples. In addition, the heat maps allow more flexibility in inclusion/exclusion of genes based on similarity scores.

The recruitment plot, which compares the functional roles of the genome to a given microbial genome, has been expanded to include hits and alignments from the Basic Local Alignment Search Tool (BLAST). This enables the user to evaluate overall similarities between the community and an organism as well as on the gene level.

Proposed Work for FY 2010

Most of the work in FY10 will be in software and systems engineering to extend MG-RAST, the user interface, and the application programming interface. The establishment and initial comparison of metabolic reconstructions computed for metagenomes will also be an important part of the work. The three FY10 tasks are as follows:

- Provide detailed comparison of metabolic reconstruction techniques,
- Build sample application using the high-performance computing interface, and
- Extend the user interface.

Refereed Publications

Meyer, F., D. Paarmann, M. D’Souza, R. Olson, E.M. Glass, M. Kubal, T. Paczian, R. Stevens, A. Wilke, J. Wilkening, and R.A. Edwards, “The Metagenomics RAST Server — A Public Resource for the Automatic Phylogenetic and Functional Analysis of Metagenomes,” *BMC Bioinformatics* **19**(9) (2008), 386.

Combinatorial Deletions to Produce a Minimal Strain of *Bacillus subtilis*

2009-171-N0

Rick L. Stevens, Christopher S. Henry, Folker Meyer, and Elizabeth M. Marland

Project Description

Essentiality studies suggest that the number of genes required to synthesize the proteins necessary for an organism to be viable under controlled laboratory conditions is on the order of 300–800, which is far fewer than the number of genes typically encoded within microbial genomes (e.g., 4,105 open reading frames for *B. subtilis*). While some naturally occurring microbial genomes do encode less than 800 genes, these organisms exist in host-dependent environments and are non-culturable outside their hosts (e.g., *Mycoplasma genitalium* with 482 genes). However, the existence of these organisms with reduced gene sets suggests that many proteins used within larger genomes exist purely to confer adaptability and flexibility upon the organism, and these proteins may be deleted without impacting viability in controlled laboratory conditions. In fact, deletion of nonessential proteins may enhance the organism by reducing the metabolic burden and removing regulatory controls on growth rates.

In this project, our objective is to explore gene dispensability by constructing a minimal strain of the microorganism *Bacillus subtilis*. We are constructing a minimal strain of *B. subtilis* by iteratively combining 140 existing gene interval deletions to produce progressively smaller strains. Throughout the deletion combination process, we are also producing a genome-scale model of *B. subtilis*, which is being used to predict the outcome of combinations being performed experimentally. Successful model predictions help explain why certain deletion combinations result in unviable strains; unsuccessful model predictions help elucidate portions of the cellular machinery in *B. subtilis* that are not well understood. This work will produce not only a minimal strain of *B. subtilis* but also an accurate computational model of the organism.

Mission Relevance

This project supports DOE’s mission of improving the quality of life through innovations in science and technology. The simplified strains of *B. subtilis* that we are producing will help to accelerate the validation and curation of whole-cell models. This will provide a means of generating quantitative predictions of cellular behavior, which are invaluable for efforts to engineer an organism to secrete a product or degrade a toxin. Ultimately, we will produce a viable minimal strain of *B. subtilis*, providing an ideal system for testing metabolic engineering theoretical tools and for developing systems biology meth-

odologies. The DOE Office of Biological and Environmental Research (BER) Genomics:GTL (formerly Genomes to Life) Program has a strong systems biology component, and the capabilities and data from this project will support its goals. The results of this project may also address the microbial research interests of the National Institutes of Health (NIH).

FY 2009 Results and Accomplishments

In FY09, our experimental efforts initially focused on screening our complete set of 140 existing mutant strains for suitability in the combination process. The screen was designed to eliminate mutant strains with poor growth rate or viability, as these strains would not be ideal starting points for the genome minimization process. The screen also served to characterize each strain before combination to facilitate our ability to determine if a combined phenotype is a result of the deletion combination or is inherited from a parent strain. We tested the ability of each mutant strain to grow on four media formulations: rich undefined media, rich defined media, glucose minimal media with glutamine as a nitrogen source, and glucose minimal media with ammonia as a nitrogen source. We also experimentally measured the growth rate of each strain in rich defined media. Interestingly, some of the single-interval knockout strains already grow more than 10% faster than the wild-type strain.

Once the screen was complete, 256 combinations were attempted involving 26 distinct mutant strains. Of these combinations, 78 were successful. As a result of these efforts, we have one reduced strain in *B. subtilis* with near-normal growth, and this strain has a net deletion of 989.8 kilobases (KB). This value represents a reduction of 23.4% from the wild-type genome size of 4214 KB.

Also during FY09, we completed work on a new genome-scale metabolic model of *B. subtilis* 168 called “iBsu1103.” This model captured 1,103 genes in the *B. subtilis* genome and predicted growth conditions and knockout viability with 93% accuracy. These characteristics make the iBsu1103 model the most complete and accurate model of *B. subtilis* that is available. This work was subsequently published in *Genome Biology*.

We have used the iBsu1103 model to determine which of the 140 single-interval knockout mutants may be combined without losing cell viability. This analysis will guide future deletion combination attempts, and when combinations proposed by this analysis fail, the model will be updated and the analysis repeated. The analysis currently indicates that the smallest possible genome size attainable using only our current single-interval knockout strains is approximately 1,300 genes.

Proposed Work for FY 2010

In FY10, experimental, computational, and theoretical efforts in the minimal organism project will continue. On the experimental side, we will continue efforts to delete additional gene intervals from our *development strains* to further reduce net genome size. This effort will consist of two parallel strategies: (1) we will continue progressing through the original 140 intervals to combine as many of these deletions as possible, and (2) when a large interval deletion consistently fails to combine with any of our *development strains*, we will split this interval to produce smaller intervals that can be successfully combined. Ultimately, we will drive the genome down to a set of *development strains* where additional deletions are no longer possible through the natural competence method. At this point, electroporation or other methods for inducing competence will be applied.

On the theoretical side, work will continue on the iBsu1103 model to improve the predictive capacity of this model. This work will also proceed on two parallel pathways: (1) optimization of model structure to fit the results of the 140 interval-deletion experiments and (2) integration of transcriptional regulatory and thermodynamic constraints into the iBsu1103 model to enhance predictive accuracy and capture the effects of additional non-metabolic genes on cell viability. When the iBsu1103 model was developed, it was optimized to fit available experimental phenotype data for the wild-type *B. subtilis* 168 strain only. We will be optimizing the model to also fit the new phenotype data generated for our 140 single-interval knockout strains. This will involve the addition/removal of reactions from the model, adjustments to reaction reversibility, changes to simulation parameters, changes to gene-protein-reaction mappings, and changes to the model biomass composition. A manuscript will then be prepared discussing the outcome of all 140 base-interval deletions and the modifications made to the model to fit the data. We will also be generating a “core” genome for the *Bacillus* family of bacteria to identify conserved non-metabolic functions in *Bacillus* that may also be undesirable targets for deletion.

Computationally, we will be developing a generic set of tools for managing phenotype-data and meta-data associated with large numbers of mutant strains. These tools will support the comparison of experimental phenotypes with model predictions, the annotation of experimental data, the analysis of conflicts between observed and predicted phenotypes, and the formation/organization of dialog between all project collaborators. While these tools are essential for the continued success of the minimal organism project, we propose that they will also be useful to any project involving the model-assisted engineering of any organism to meet a given objective.

Refereed Publications

Henry, C., F. Xia, and R. Stevens, "Application of High-Performance Computing to the Reconstruction, Analysis, and Optimization of Genome-Scale Metabolic Models," *Journal of Physics: Conference Series* **180** (2009), 012025.

Henry, C.S., J.F. Zinner, M.P. Cohoon, and R. Stevens, "iBsu1103: A New Genome-Scale Metabolic Model of *B. subtilis* Based on SEED Annotations," *Genome Biology* **10**(6) (2009), R69.

A Systems-Wide Assessment of Carbon Economy in Midwest Soils: Agricultural versus Prairie

2009-176-NO

Carol S. Giometti, Folker Meyer, Dionysios A. Antonopoulos, R. Michael Miller, and Kenneth M. Kemner

Project Description

Climate change as a result of air emissions related to industry and transportation is currently a worldwide environmental concern. Although evidence for climate change has been clearly documented at the level of atmospheric and weather changes, little is known about the effects on terrestrial ecosystems. In fact, little is known about the mechanisms controlling the natural process of carbon cycling in terrestrial ecosystems even in the absence of climate change. Argonne's unique capabilities in synchrotron science and computation, together with expertise in environmental science, terrestrial ecology, molecular biology, protein chemistry, and soil chemistry, if integrated, can provide insight into the natural processes involved in carbon dynamics and stabilization and contribute to development of strategies for better carbon management. In this one-year project, an interdisciplinary team of Argonne researchers has sought to apply a range of methods to analyze a known gradient of soil carbon sequestration in order to define the microbial contribution to soil carbon dynamics. The outcome of this effort provided correlations between carbon/nitrogen distribution and microbial community composition that will provide the foundation for more in-depth studies in the near future.

Mission Relevance

The Climate Change Program and Life Sciences Genomic Science Program of the DOE Office of Biological & Environmental Research include mission areas focused on elucidation of the natural biological processes involved in carbon management. This project pursued an integrated multidisciplinary approach to identify such natural biological processes in a well-defined

ecosystem characteristic of the Midwestern states. This project is relevant to the DOE Joint Genome Grand Challenge, initiated in FY09, which is to characterize the microbial communities present in Midwestern grasslands.

FY 2009 Results and Accomplishments

Soil cores (4.8-cm diameter and 5 cm in length, taken from the surface to 5 cm depth) were taken in September 2008 at two transects within each of three plots at the DOE Fermi National Accelerator Laboratory (Fermilab) National Environmental Research Park: (1) a cultivated soybean field annually rotated with corn (BD), (2) a prairie remnant in a railroad right-of-way (RRD), and (3) a 30-year-old restored prairie initially planted in the autumn of 1978 (5D). (Note: Although September 2008 precedes the formal start of the project, we needed to obtain samples at that time because the samples had to be collected at a specific time in their maturation, and the fields were optimal in September 2008.) Ten cores were taken along each transect and pooled together in the field so that a composite view could be obtained from the two transects in each plot; transects were used to compare spatial heterogeneity within and between plots. Soil was sieved in the field through an 8-mm sieve to remove roots and rhizomes. This soil was then divided into aliquots and stored frozen at -80°C until analysis by a variety of techniques, including soil carbon/nitrogen analyses, phospholipid fatty acid analysis, protein profiling, and imaging of soil structure (tomography). Metagenome and metatranscriptome analyses were done as part of complementary efforts.

The carbon and nitrogen levels in the three plots are summarized in Table 1. No statistically significant difference between transects within a plot was observed (results not shown; those in Table 1 represent the average of the two transects for each plot), suggesting minimal spatial heterogeneity in the carbon and nitrogen levels. However, as shown in the table, the carbon and nitrogen levels in the prairie plots (5D and RRD) were higher than those in the agricultural plot (BD), with the native prairie (5D) having higher levels than the restored prairie (RRD).

Table 1. Amount of organic carbon and nitrogen in soil samples relative to total dry mass of the soil

Site Sampled	% Carbon	% Nitrogen
BD	3.35	0.29
5D	5.25	0.45
RRD	9.7	0.8

Differences in the aggregate size distribution were also observed when soil from the three plots was compared. As shown in Table 2, microaggregates were found to predominate in the agricultural soil (BD), while both the native prairie from the railroad remnant (RRD) and the restored prairie con-

tained a higher percentage of macroaggregates compared to microaggregates. The repeated cultivation of the agricultural plots relative to the prairies no doubt contributed to the preponderance of microaggregates, whereas the lack of disturbance and population by perennial grasses would favor the macroaggregates in the prairie plots.

Table 2. Aggregate size distribution of soil in sites sampled

Site Sampled	Average Total Macroaggregates (mass %)	Average Total Microaggregates (mass %)
BD	26.2	50.4
5D	56.8	30.2
RRD	65.7	23.1

Phospholipid fatty acid (PLFA) analysis allows differentiation between the bacterial and fungal contributions to the microbial populations in the soils, with distinct PFLAs serving as markers of either bacteria or fungi. In addition, PLFA profiles are a useful method for identification of which components of the soil community are metabolically active. For this study, the PFLA markers for fungi predominated in the prairie remnant and restoration sites, while the agricultural soil showed more bacterial markers. Therefore, the predominance of fungi correlated with increased carbon and nitrogen and a greater percentage of macroaggregates.

In addition to the above, work was done to extract protein from the soil samples to determine what predominant metabolic processes are present and, if possible, the microbes with which those processes are associated. Extraction methods ranging from pH adjustment to detergent or organic solvent extractions were used, but in all cases, the amount of protein released from the soil samples was below the limits of detection by gel electrophoresis or peptide mass spectrometry. Culturing bacteria from the soil samples by using rich nutrient media did yield sufficient protein for analysis. Enhanced Raman spectroscopy was also explored as a non-destructive approach to characterization of bacteria and fungi in soil samples. Known sugar molecules characteristic of specific microbes were analyzed; Raman spectra were taken of xylose, mannose, and galactosamine hydrochloride. Enhanced Raman spectra from silver oxide and silver nitrate showed dramatically large enhancements in the combination bands with Stokes shifts at $\sim 2,829$ and $\sim 2,936$ cm^{-1} , which reproduced published Stokes features for these molecules. We believe these features may provide a convenient fingerprint for sugar groups that will be indicative of specific classes of microbes.

Proposed Work for FY 2010

This project does not continue into FY10.

Recovery of Full-Length Genes for Expression of Proteins from Metagenomic Sequence Data

2009-177-NO

Deborah K. Hanson, Philip D. Laible, and Folker Meyer

Project Description

Current estimates of the world's genetic diversity are increasing dramatically with the analysis of data arising from genomic sequencing efforts. In particular, sequencing of genomic DNA derived from environmental samples containing microbial communities – so-called “metagenomics” – has revealed a tremendous level of genetic diversity that had not been appreciated previously. Most of the genes that are being identified are derived from unknown or unculturable organisms; thus, the only way that those genes can be approached is via the DNA sequence data that are in hand. To exploit these data to recover enzymes that perform novel reactions, we must develop methods that take us in stepwise fashion from short DNA sequence fragments to complete genes to expressed purified proteins. The scope of work covered in this project includes approaches to recover and clone complete genes for open reading frames (ORFs) of interest that have been identified in available environmental DNA samples, followed by the expression, purification, and functional characterization of proteins from those genes.

Mission Relevance

The project is relevant to DOE's energy and environmental missions. The Genomic Science Program of DOE's Office of Biological and Environmental Research was established to explore and exploit the diverse functions of proteins encoded by microbes. Success in this short-term project would enable us to mine metagenomic sequence data for the expression of novel proteins.

FY 2009 Results and Accomplishments

In FY09, we developed strategies to identify and recover sequences that flank ORFs that were identified from the prairie soil metagenome sequencing project. Ten sequence fragments ranging in size from ~ 200 to 300 base pairs were provided, as was DNA purified from a prairie soil sample. Inverse polymerase chain reaction (PCR) experiments were performed to amplify genomic regions both upstream and downstream of the fragment of the known sequence. Since the relative abundance of the target ORF within the environmental DNA sample was unknown and may be extremely low, we designed a PCR strategy that employs nested sets of primers in which the initial primer sets are biotin-tagged. In sequential steps, the tagged primers were used in the initial round of PCR to amplify or enrich the target sequence, then contaminating

genomic DNA was removed, and subsequent normal cycles of PCR were used to amplify the target sequence to quantities that are useful for DNA sequencing.

The prairie DNA sample was digested with selected restriction enzymes, then self-ligated under conditions that favored the formation of circular molecules from individual fragments. These circular molecules served as templates for the initial round of inverse PCR using the biotin-tagged primers. Amplicons from these reactions were purified from the total DNA by binding to streptavidin-coated magnetic beads. A portion of the bead-purified DNA was used in the second round of inverse PCR from nested primers.

Figure 1 shows results from typical inverse PCR reactions with the nested primer sets. Discrete amplicons were obtained for some targets. The bands were excised from preparative gels and sent for sequencing. Overlapping sequence data were obtained for all three amplicons and identified the beginning and end of ORF 57706068. It encodes a carboxysome structural protein, Ccml. It produces quite a number of hits when queried against the National Center for Biotechnology Information nonredundant database. The best match (6e-20) is with EutN/Ccml from *Solibacter usitatus*. A new set of primers was designed to amplify this gene from the prairie soil DNA sample. The amplified gene was cloned into an expression vector, and protein was produced from induced cultures of *E. coli*. It was purified to homogeneity before crystallization trials were set up. We adapted several of these protocols for use with an automated liquid-handling robot.

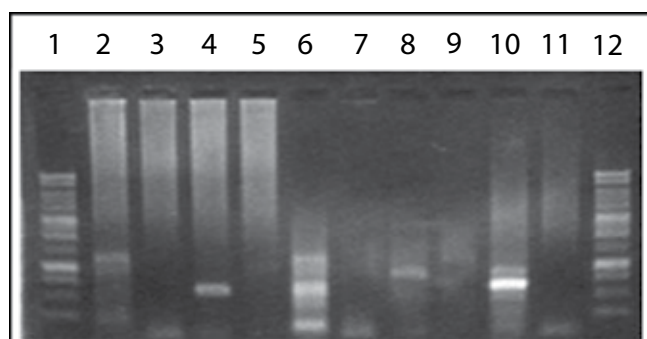


Figure 1. Results from a typical inverse PCR experiment with sets of biotin-tagged, nested primers. Restriction-digested and circularized templates were used in reactions with primer sets specific for target sequences 57706068, 57651003, 57371004, and 57372002. Lanes 2–5: XbaI-digested templates; lanes 6–9: EcoRI-digested templates; lanes 10–11: BglII-digested templates (57706068 and 57651003 only); lanes 1 and 12: molecular weight standards.

Proposed Work for FY 2010

In FY10, we will move to 96 targets in a plate-based format. This increase in scale will benefit from the adaptation of many of the PCR and cloning protocols to the 96-well format and from the use of a liquid-handling robot. Culturing increased numbers of expression strains will also be scaled up by exploiting automated systems, as will protein purification.

Characterization of Microbial Community Dynamics

2009-186-N0

Dionysios A. Antonopoulos, Carol S. Giometti,
Kenneth M. Kemner, and Folker Meyer

Project Description

The focus of this project is on the dynamic microbial populations involved in the biogeochemical cycling of elements in natural subsurface and terrestrial environments. Following microbial population dynamics across spatial and/or temporal scales has traditionally been conducted by inventorying the variation and relative abundance of a single highly conserved gene marker as a proxy for the microbial populations and metabolisms present (for example, the gene encoding the 16S ribosomal RNA [rRNA] molecule, a crucial component of protein translation in all microorganisms). However, a drop in the cost of DNA sequencing technology has led to our ability to directly access the functional gene sequences present in an environmental sample by adopting shotgun metagenomics. The metagenome of a sample represents the totality of all genes present — essentially the metabolic potential of a sampled microbial community. Present efforts are focused on reducing the sequence “search space” for functional genes bestowing unique properties to one microbial community versus another by sequencing its metatranscriptome — the genes actively expressed by the microbial community in total. The project seeks to identify the genetic and metabolic potentials of microbial communities and establish how functions are partitioned in and between microbial populations.

Mission Relevance

This project is relevant to DOE’s missions in the environment and basic science. The present sequencing effort builds on previous work in which an evaluation was made of the kinetics of chloroethene transformation, the enzymes and genes involved, and the composition and activities of the microbial community within these bioaugmented flow column systems. The work described in this project complements these efforts through the study of microbial processes contributing to the degradation of organic contaminants and the transformations of metal and radionuclide contaminants in the context of natural biogeochemical processes. A robust set of chemical and physical metadata for the system will allow the mining of metagenome- and metatranscriptome-derived datasets for the functional genes involved, as well as for novel gene discovery.

FY 2009 Results and Accomplishments

A protocol has been established for whole nucleic acid extraction from environmental samples, removal of DNA, and effective subtraction of rRNA, thereby enriching for the messenger RNA (mRNA) from these microbial communities (Figure 1). Since most of the recovered RNA from any sample is primarily composed of rRNA, this mRNA enrichment step is required to diminish redundancy in the sequencing output. Ongoing work has been focused on refining the workflow involved in metatranscriptome library construction for second-generation DNA sequencing platforms.

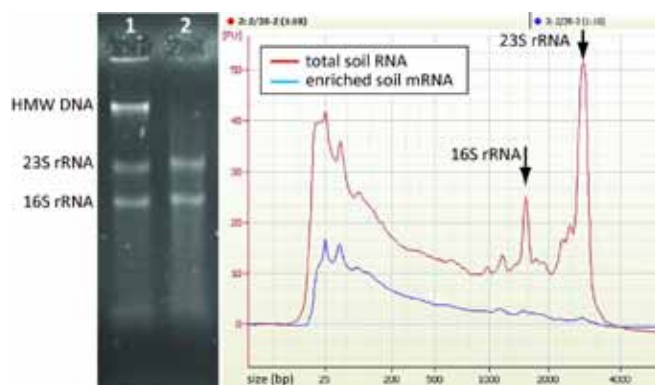


Figure 1. Demonstration of mRNA extraction and isolation from topsoil. In the left-hand panel, extracted nucleic acids from a topsoil sample are size fractionated by using gel electrophoresis to demonstrate (1) the integrity of whole RNA (inferred from the integrity of rRNA) and (2) the removal of high-molecular-weight (HMW) DNA. The right-hand panel shows effective removal (subtraction) of rRNA and enrichment of mRNA from topsoil (blue trace) relative to whole RNA (red trace). The horizontal axis displays the size of the recovered RNA in terms of base pairs (bp), while the vertical axis represents their abundance in terms of fluorescence (FU).

Proposed Work for FY 2010

In FY10, metatranscriptome datasets will be analyzed in the context of previously generated metagenomes from environmental samples, including topsoil and laboratory-scale batch reactors seeded from subsurface environment materials. These results will be used to (1) inform metabolic models of the microbial community and (2) establish bench-scale experiments to verify microbial community requirements for the degradation and transformation of environmental contaminants.



OTHER
NOVEL R&D

Novel Hybrid Nanomaterials via Uniting Top-Down and Bottom-Up Assembly Methods

2006-268-R3

Seth B. Darling

Project Description

Traditional methods for creating nanostructures based on “top-down” techniques are rapidly approaching intrinsic limitations. Even state-of-the-art electron beam lithography cannot reliably assemble structures smaller than 10 nanometers (nm). Furthermore, the majority of advanced lithographic techniques are serial and therefore expensive and slow. To keep pace with advancing basic nanoscience and nanotechnology, innovations that allow parallel synthesis of hierarchical structures in the 1–100-nm size range will be needed. “Bottom-up” self-assembly approaches, predicated on chemical processes, offer a promising route to overcome the shortcomings of lithography. In this project, we focused on a class of self-assembling materials called block copolymers, specifically polystyrene-*block*-poly(ferrocenyldimethylsilane) (PS-*b*-PFS). PS-*b*-PFS was selected because of the large differential etch resistance between the two polymer blocks. The volume ratio of this polymer leads to microphase separation into a cylindrical geometry consisting of PFS cylinders within a PS matrix (Figure 1).

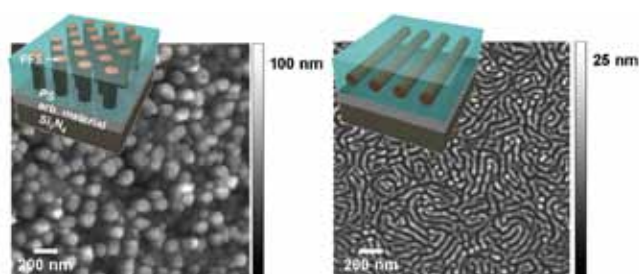


Figure 1. Atomic force micrographs of patterns transferred to Si_3N_4 from thin films of self-assembled standing and in-plane polymer cylinders, creating arrays of nanoscale posts and lines, respectively. The schematics depict the morphology of the polymer films used as etch masks. Scale bars on the right of each micrograph depict the height scales.

Mission Relevance

This project is relevant to DOE's missions in energy and science. Investigations of the guided self-assembly of nanomaterials will yield new basic scientific insights and may be useful in many applications. Controlling the self-organization of materials will provide routes to enhanced efficiency in future devices. This project has potential payoffs in solar energy, biology, photonics, solid-state lighting, and sensor technologies.

FY 2009 Accomplishments and Results

Domain orientation (in-plane or standing) was manipulated simply by varying the film thickness. As control over such geometries is obtained, the block copolymer becomes increasingly useful in patterning applications because in-plane cylinders can be used to fabricate arrays of one-dimensional features such as nanowires, while standing cylinders can be used to fabricate arrays of zero-dimensional posts or dots. To demonstrate their utility for lithographic patterning, we prepared PS-*b*-PFS films on various metal and semiconductor surfaces, all of which are wet well by the polymer. By using the polymer as an etch mask, we transferred patterns to silicon nitride (Si_3N_4) (Figure 1), ultrananocrystalline diamond (UNCD), and palladium films; palladium films are now being investigated for potential application in hydrogen sensor technology.

By studying dewetting phenomena associated with PS-*b*-PFS, we found that mesoscale dendritic structures are induced when the spin-cast thin film of this polymer is subjected to so-called hybrid annealing, which involves both thermal and solvent annealing (Figure 2). Various possible mechanisms for the formation of these structures were explored, and results indicate that the PFS block dominates the structure formation. We also observed a ring- or worm-like nanostructure that develops only when the film is subjected to hybrid annealing at a particular film thickness.

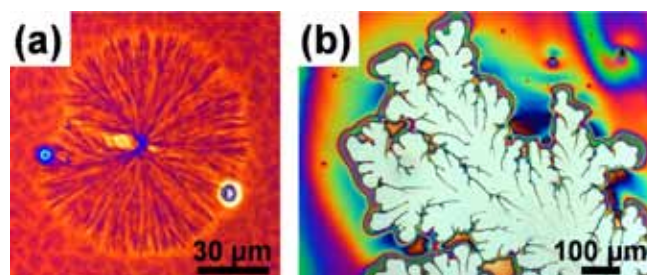


Figure 2. Cross-polarization optical micrographs of patterned silicon nitride substrates. Mesostructures have been developed at initial film thicknesses of 70 nm (a) and 250 nm (b) by means of hybrid annealing. Reactive ion etching was used to transfer the polymeric patterns onto silicon nitride.

Refereed Publications

Darling, S.B., “Mechanism for Hierarchical Self-Assembly of Nanoparticles on Scaffolds Derived from Block Copolymers,” *Surface Science* **601** (2007), 2555–2561.

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Ramanathan, M., and S.B. Darling, "Thickness Dependent Hierarchical Meso/Nano Scale Morphologies of a Metal-Containing Block Copolymer Thin Film Induced by Hybrid Annealing and their Pattern Transfer Abilities," *Soft Matter* (2009) DOI: 10.1039/b902114k.

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Non-Refereed Publications and Presentations

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Metal and Semiconductor Nanoparticle Assemblies: Controlled Quantum Coupling on the Nanometer Scale

2007-150-R2

Matthew A. Pelton

Project Description

The goal of this project was to develop materials with new optical properties by joining metal and semiconductor nanoparticles into designed assemblies.

Mission Relevance

The goals of this project help fulfill the DOE mission of leading-edge research in basic energy sciences. Appropriately designed assemblies of metal and semiconductor nanoparticles will display unique optical properties and lead to devices with novel functionalities. A successful research effort will provide important benefits to scientists in the private and public sectors working on a broad range of research topics, including development of integrated photonic devices, exploration of quantum information technology, improvement of photovoltaic materials, and basic physical understanding of light-matter interactions. Functional nanophotonic devices

and quantum-information technology are areas of ever-increasing interest to agencies associated with the National Nanotechnology Initiative. The results will also be of interest to the Defense Advanced Research Projects Agency (DARPA).

FY 2009 Results and Accomplishments

In FY07 and FY08, we developed experimental capabilities for investigation of the optical properties of individual nanostructures. In FY09, we used these tools to make the first measurements of how emission from single quantum dots (QDs) is modified by the presence of metal. Usually, understanding the coupling between QDs and metal nanostructures is complicated by significant variations in nanoparticle size and shape. Our measurements eliminated these variations by studying single QDs near a smooth gold film, the simplest metal structure that supports surface plasmons. Even in these single-dot measurements, though, large fluctuations in emission rates made it difficult to extract quantitative information. By using the time-resolved single-photon counting techniques developed earlier in the project, we were able to remove the effects of these fluctuations and measure changes in the emission rates of individual QDs as they approach the metal film (see Figure 1).

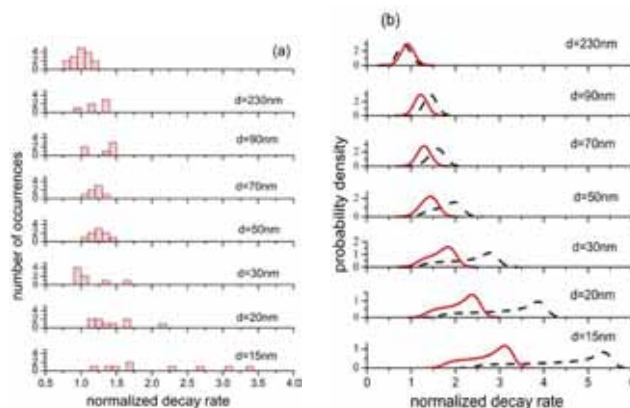


Figure 1: (a) Experimentally measured decay rates. The top panel shows decay rates for quantum dots in the absence of a gold film; the most probable decay rate from this histogram is used to normalize the data. The other panels show decay rates for dots at different distances (d) from a smooth gold film. (b) Calculated distributions of normalized decay rates. Results are shown for quantum yields of 0.5 (solid lines) and 1.0 (dashed lines).

In parallel with this experimental effort, we developed the theoretical tools necessary to guide and interpret the experiments. Following on initial work in FY08, we used rigorous electromagnetic models to simulate the interaction between an emitting QD and a metal nanoparticle. We found that an emitter can strongly couple to "dark" plasmon modes in metal nanostructures – that is, modes that do not couple to incident light and do not radiate. We also varied the nanostructure geometries to optimize the strength of coupling between QDs and metal nanostructures. The calculations indicated that

it should be possible to reach the limit where the electrons in the QDs and the plasmons in the metal nanoparticles are coupled together so strongly that they can no longer be considered separately, but rather form a new, collective system.

Proposed Work for FY 2010

This project does not continue into FY10.

Refereed Publications

Wu, X., Y. Sun, and M. Pelton, "Recombination Rates for Single Colloidal Quantum Dots near a Smooth Metal Film," *Physical Chemistry Chemical Physics* **11** (2009), 5867–5870.

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Non-Refereed Publications and Presentations

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Pelton, M., G. Smith, N.F. Scherer, and R.A. Marcus, "Blinking of Nanocrystal Quantum Dots on Time Scales from Microseconds to Seconds," presented at the Institute for Theoretical Sciences Workshop on Fluorescence Intermittency in Molecules, Quantum Dots, and Quantum Wires, University of Notre Dame, South Bend, IN, April 2007.

Pelton, M., M. Liu, H. Y. Kim, G. Smith, P. Guyot-Sionnest, and N.F. Scherer, "Plasmon-Enhanced Trapping of Individual Metal Nanorods," presented at Optical Trapping and Micromanipulation IV, SPIE Optics & Photonics, San Diego, CA, August 2007; published in *Proceedings of the SPIE* **6644** (2007), 66441C.

Multidisciplinary Theory Investigations

2007-189-R2

Albert F. Wagner, Edmond L. Berger, Julius Jellinek, Lee Makowski, Craig D. Roberts, Robin Santra, Donald K. Sinclair, Carlos E.M. Wagner, and Peter Zapol

Project Description

The need for advanced theoretical understanding has been recognized in many fields, ranging from nuclear physics to national security. This research focuses on developing fundamental theoretical tools and concepts through multidisciplinary theory activities. The research efforts consist of multiple tasks that explore and use theory constructs to provide new opportunities for the close interaction of theory, experimental, and computational scientists. This project spans explorations of theory in the areas of physics, chemistry, nanoscience, and biology.

Mission Relevance

The focus on theory in this project will bring advances to support a number of key DOE missions in the areas of nuclear physics, chemical and materials sciences, energy-related life sciences, and national security. The work is related both to DOE's science and national security missions.

FY 2009 Results and Accomplishments

Areas of focus for FY09 were in high-energy/nuclear physics theory, ultrafast science, the relaxation of complex systems, protein folding, and biochemical self-assembly.

In the area of high-energy/nuclear theory, we have two tasks, the first of which is quantitative predictions of the rates and event characteristics of new physics processes expected to be investigated experimentally at the Large Hadron Collider, along with the 'backgrounds' from standard model (SM) phenomena that can mimic the signals of new physics. Calculations were carried out on Higgs boson and supersymmetry phenomenology and on advanced topics in perturbative quantum chromodynamics (QCD). We computed both new physics signals and their SM look-alikes quantitatively and critically to discriminate against SM mimics of the signatures of new physics. These calculations included detector simulations, both to refine tests of QCD at higher energies and to propose effective search strategies for new phenomena. Three papers were published on these topics.

The second task in high-energy/nuclear theory involves attempts to verify a conjectured relationship between a weakly coupled string theory in five dimensions and the strongly coupled theory of real-world QCD. Our studies included (1) chiral susceptibility that demarcates the domain of coupling strength within a theory upon which chiral symmetry is dynamically broken; (2) derivation of an exact (symmetry-preserving) form for the Bethe-Salpeter equation (i.e., the quantum field theory 2-body, bound-state equation), which is valid when the quark-gluon vertex in the gap equation is fully dressed; and (3) Landau-Khalatnikov-Fradkin transformations to establish that if a critical number of “flavors” for chiral symmetry restoration and deconfinement exists in noncompact QED3 (three-dimensional quantum electrodynamics), then its value is independent of the gauge parameter. Nine papers were published on this work.

In ultrafast science, we pursued the simulation of the production of coherent x-rays via high-harmonic generation (HHG). In the past year, we have developed a code for the time-dependent configuration interaction with single excitations (TDCIS) calculation of HHG spectra. This code can be applied to general atomic systems and allows a non-uniform radial grid so that atomic orbitals can be calculated more accurately. We have calculated the HHG spectrum of hydrogen, helium, and several pseudo-atoms with variable ionization energies that test the numerics of the code.

In the relaxation of complex systems, our work includes the following:

- Development of a new general methodology for dynamical simulation of the very fast heating and cooling of systems (with rates as fast as 10^9 to 10^{13} kbit/s (kilobits per second) — the first that assures uniformity of the heating or cooling process. Application to ionic systems, such as alkali halide clusters, show the differences and similarities in heating and cooling “pathways” as a function of the rate of temperature change.
- Exploration of the effects of the range of interaction (“shielding”) on the structural and dynamical characteristics of ionic systems, in particular the intriguing finding that strong shielding can promote hollow cage structures even for ionic systems.

One paper has been submitted on this work.

In the area of protein folding, our goal to predict the structure of proteins by using experimental wide-angle x-ray scattering (WAXS) data has multiple computational components. To calculate WAXS patterns, the hydration density around a protein surface must be calculated accurately. We have developed an accurate and rapid (<1-cpu min.) algorithm capable of reproducing week-long explicit solvent simulations. We developed

a method for calculating WAXS patterns for proteins by using our model. This method proved as accurate as one that we also developed by using computationally intensive explicit atom representations of water. In parallel, we developed predicting algorithms of protein structure both with or without limited sequence homology. The prediction algorithm will generate models, the WAXS patterns of which are computed and compared to the experimental data to more accurately predict the protein’s structure. Five proposals have been submitted concerning this work; three are still under review (two were unsuccessful).

Concerning biochemical self-assembly, we are carrying out multiscale modeling of amphiphilic diblock copolymers for possible use in stabilizing membranes that are of interest for diverse applications from energy transduction to advanced batteries. The project is designed to describe the segregation of PEO[poly(ethylene oxide)]-PPO[poly(propylene oxide)]-PEO triblock copolymers in artificial membranes. We have carried out coarse-grained simulations and developed analytical models to represent the simulation data over wide ranges of parameter space. This approach enables the interpretation of various different experimental probes in terms of a common model. As part of this work, we have developed a new improved force field for PEO-PPO to provide a comparison to the coarse-grained simulations. Two papers were published (and another is submitted) concerning this work.

Proposed Work for FY2010

This project does not continue into FY10.

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Inducement of Targeted Organ Protective Cooling Using Ice Slurry Coolants

2008-191-R1

Kenneth E. Kasza, Paul F. Fischer, Adrian M. Tentner, and Yue Wu

Project Description

We are working to develop exploratory versions of ice slurry medical cooling equipment and to establish protocols for inducing targeted-organ cell-protective cooling for protection against ischemia, reperfusion, and neurological damage. As surgical procedures push the limits of technical excision and become less invasive through the development and use of laparoscopic procedures assisted by surgeon/machine robotic manipulations, there is an unmet need to protect critical organs and various tissue masses undergoing surgical manipulations. Argonne is developing ice-slurry coolants with

large cooling capacities that result from the melting of transported very-small ice particles. The coolants can be applied topically or injected into selected organs. We are developing ice slurry production and delivery equipment for inducing protective cooling during minimally invasive laparoscopic kidney, cardiac/cardiovascular, and neurological surgeries. We are also developing computational fluid dynamics (CFD) computer simulation tools for predicting how organs are cooled.

Mission Relevance

This project is tied to DOE's mission in science, with potential interest from DOE-OBER. The research represents an important step in utilizing and extending the results of previous breakthrough DOE energy research by developing and applying slurry protective cooling to help improve surgical outcomes and save lives. Patients and the medical community are the direct beneficiaries. The research being conducted is also of relevance to the missions of the National Institutes of Health (NIH) and U.S. Department of Defense (DOD.) This work will be an excellent example of how DOE-developed technological capabilities may also be applied to larger and different needs of the nation.

FY 2009 Results and Accomplishments

During the first year of work, we (1) established the ability to reliably make and deliver 50% ice slurry through various medical delivery ports; (2) demonstrated the ability to pump slurry through catheters one meter long and less than one millimeter wide to the heart and other organs (Figures 1 and 2); (3) automated the slurry equipment under computer control and made it transportable on a cart for use in the operating room; (4) conducted animal experiments in which surgeons established the efficacy of protective cooling during minimally invasive laparoscopic kidney surgery (Figure 3), which led us to seek approval from the Food and Drug Administration (FDA) to conduct human clinical trials; (5) teamed with cardiac surgeons and brain neuro-critical-care doctors to conduct exploratory animal experiments on these two new applications of slurry cooling. This work resulted in the following inventions/patents:

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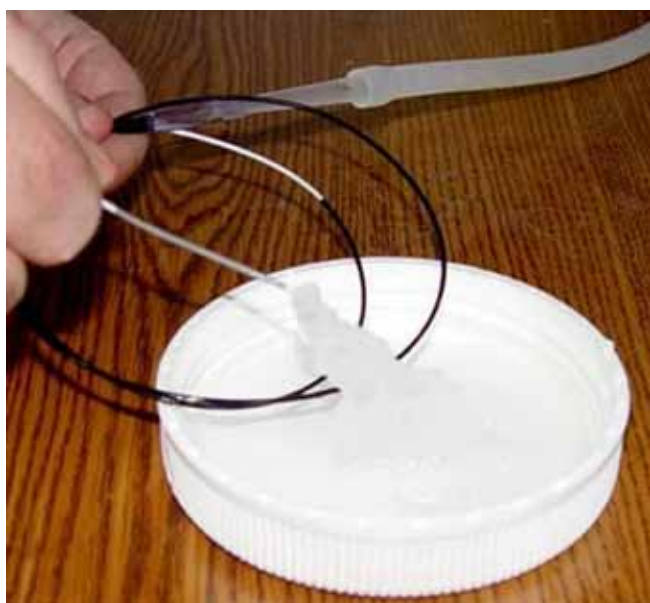


Figure 1. Cardiac catheter delivering ice slurry used to cool the heart and other organs.



Figure 2. Argonne computer-automated, portable medical ice slurry production/delivery system.

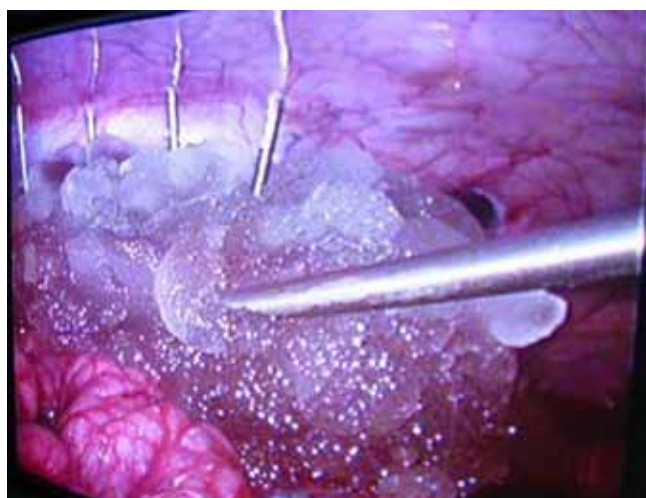


Figure 3. Kidney protectively covered with ice slurry during surgery.

Proposed Work for FY 2010

We propose to (1) conduct exploratory animal cooling experiments for cardiac and brain protective cooling; (2) develop slurry delivery and dosage feedback controls to help control the temperature and implement further safety features on Argonne's ice slurry system; and (3) if the FDA approves, prepare for clinical trials involving human kidney surgery.

Refereed Publications

Kasza, K., Y. Wu, J. Heine, D. Sheradon, and S. Lake "Development of Ice Slurry Phase-Change Coolants for Industrial and Medical Applications," presented at 8th International Institute of Refrigeration (IIR) Conference on Phase Change Materials and Slurries for Refrigeration and Air Conditioning, Karlsruhe, Germany, June 2–5, 2009.

Shikanov, S., M. Wille, M.L. Large, A. Razmaria, A. Chang, Y. Wu, K. Kasza, and A.L. Shalhav, "Microparticulate Ice Slurry for Renal Hypothermia: Laparoscopic Partial Nephrectomy in a Porcine Model," *Urology*, January 2010, accepted.

Smart Polymers as Molecular Therapeutics and Sensing Agents

2008-192-R1

Millicent A. Firestone and Simonida Grubjesic

Project Description

The objective of this work is to design optimal polymeric materials that can facilitate directed interactions with cell membranes, thereby allowing control (as polymeric therapeutic agents) and/or monitoring (as sensing agents) of cell membrane function. More specifically, the goal is to determine how to appropriately functionalize biocompatible tri-block polymers so they retain biological activity while building the robustness of synthesized materials.

Mission Relevance

This project is relevant to DOE's mission in science. The results will lay the groundwork for a much larger effort, in which basic research on the physical principles of polymer architecture and on its relationship to the association and function of cell membranes will be applied to build platforms for developing biomolecular soft materials and devices with energy-related significance in support of DOE's mission. In the long term, this project will address a DOE-identified "grand challenge" in soft materials: design principles for the synthesis of functional self-assembled materials.

FY 2009 Results and Accomplishments

We synthetically modified the block copolymers identified during FY08 to incorporate additional functionality and improve their mechanical properties (i.e., for enhanced site localization). This work will ultimately allow for the development of a biotherapeutic polymer that incorporates multiple functional characteristics. For example, the polymer may initially seal structural defects in a cell membrane damaged by surgical injury and then transform into a barrier-forming tri-block copolymer that may inhibit microbial attack during post-operative healing. Initial synthetic efforts focused on the end functionalization of PEO-PPO-PEO tri-block copolymers with diacrylate groups. Introducing these functional groups transformed the tri-block copolymers into a macromer (polymerizable macromolecule) that was cross-linked to form a durable hydrogel (Figure 1) that could be localized at a particular site. In addition, these cross links were designed to permit programmed biodegradation, thereby permitting controlled release of the tri-block copolymer. Finally, the development of synthetic approaches for preparing phosphate functionalized tri-block copolymers for use as antibacterials was started.



Figure 1. Cross-linked polymer.

Proposed Work for FY 2010

This work will build on our efforts to synthetically modify and tailor the block copolymers. Photo-responsive tri-block polymer materials will be designed and synthesized. They will be functionalized to allow for photo-reversible cross-linking of a biomembrane, thereby allowing light control over membrane properties. Our synthetic targets will be derived from our prior work, in which we identified from this family of tri-block copolymers specific polymer architectures that seal defects or form anti-microbial barriers on cell surfaces. This component of our work will address the DOE-sponsored overarching goal of understanding and applying biomimetic principles to develop biomembrane-based materials and devices. The work will also let us incorporate sensing agents with various structures and capabilities to address particular needs.

Refereed Publications

Valuckaite, V., O. Zaborina, J. Long, M. Hauer-Jensen, J. Wang, C. Holbrook, A. Zaborin, K. Drabik, M. Katdare, H. Mauceri, R. Wechselbaum, M.A. Firestone, K.Y. Lee, E.B. Chang, J. Matthews, and J.C. Alverdy, *Am. J. Physiol. Gastrointest. Liver Physiol.* **297**(6) (2009), G1041–G1052.

NEMS-Based Nanosensors for Basic Science Research

2008-195-R1

O. Daniel Lopez and Derrick C. Mancini

Project Description

This project is focused on the design and fabrication of state-of-the-art, nano-electromechanical system (NEMS) -based sensors and actuators to address fundamental issues of scientific importance in the nanometer range. More specifically, we focus on the study and control of small-range forces that might affect nanosystem and nanodevice performance. The devices to be developed in this project will be optimized to detect quantum mechanical forces (Casimir force) and forces acting between nanometer-sized metallic particles. This project focuses on developing new NEMS-based sensors and device architectures, which will pave the way for novel detectors with ultra-high sensitivity levels. Our goal is to understand the fundamental forces acting in the nanoscale world so that these forces may be manipulated and controlled in engineered nanostructures.

Mission Relevance

This project is aligned with DOE's mission in science. The focus of this project is to develop state-of-the-art NEMS-based nano-sensors for a variety of applications of interest to national laboratory, university, and industrial researchers. The main benefit to DOE of the research is the potential for developing new nano-sensors, new materials, materials integration, and device architectures, which could result in the development of novel detectors with ultra-high sensitivity for further exploration of basic physics. The design, development, and characterization of NEMS-based sensors will help DOE apply NEMS technology to a variety of fields in which a precise measurement of small forces is required, or where energy consumption is an issue. Among other fields, the nano-sensors will yield improved results in intramolecular forces measurements, single molecule interactions, and in the efficiency of actuation of nano-devices.

FY 2009 Results and Accomplishments

Most of our activities during the first months of this project were centered on obtaining the hardware and software needed to simulate, design, and test microelectromechanical systems (MEMS) and NEMS devices. One of these tools is the Optical Profilometer Wyco NT-1100, which is installed in the Center for Nanoscale Materials (CNM) laboratories and employs coherence scanning interferometry, also known as white-light interferometry, to produce high-quality, three-dimensional surface maps of the object under test without

making any mechanical contact. Another tool, CoventorWare software, is required for performing finite-element simulations of NEMS and MEMS devices.

Casimir Interaction in NEMS Devices

We studied the validity of the electrostatic calibration used in our Casimir force experiments. To do this test, we fabricated torsional MEMS oscillators with specific geometries, and the calibration procedure was intensively studied. Several new designs were considered in order to extend our measurements to distances below 100 nm.

Plasmonic Interaction between Nanodots

We have designed, simulated and fabricated the first models of devices that will be used to control the gap between nanoparticles. These are novel MEMS actuators capable of the in-plane motion of a silicon (Si) probe with better than 0.1-nm control of its position. The mechanical behavior of these devices was simulated by using CoventorWare, the finite-element analysis software. Several MEMS devices were simulated, designed, and fabricated. To minimize the effect of thermally induced mechanical vibration on the probe, we fabricated these devices by using silicon-on-insulator (SOI) wafers consisting of a 10- μm (micrometer) layer of Si. A typical result of one of these finite-elements analyses is shown in Figure 1a. Following the mechanical simulation task, a detailed layout of the devices was performed, and, subsequently, the layout was submitted to MEMSCAP (the leading provider of innovative products and solutions based on MEMS technology; see memscap.com) for processing and fabrication of the MEMS probes. A scanning electron microscopy (SEM) picture of a typical probe is shown in Figure 1b. The microprobe (tip) is mechanically connected to a comb-drive actuator that, when energized, produces a linear displacement of the tip. The gap between tips in Figure 1b is 2 μm . The mechanical properties of these microprobes are currently under evaluation.

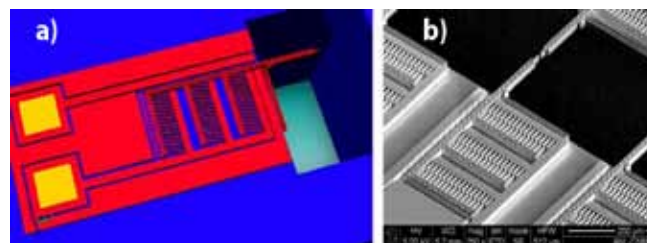


Figure 1. Finite-elements analysis schematic (a) and SEM (b) of a potential MEMS probe under evaluation.

Because this project is focused on controlling the interactions between nanoparticles, instead of measuring the interactions, we have designed micro-mechanical actuators with a very *stiff* elastic constant.

This design ensures that once the metallic nanoparticles are integrated onto the probes, any interference effect created by the interaction between nanoparticles with the microprobes is negligible. In this way, we can precisely control the interactions between the plasmons at the surface of nanoparticles.

In parallel to the design of the MEMS probes, we studied new fabrication processes to deposit onto the probes metallic nano-structures with sizes in the 50–200-nm range. We have already used a maskless focused ion beam (FIB) fabrication approach to make individual metallic nanoparticles on top of the Si probes. This process is very flexible as it allows direct “writing” of nanometer features at the end of the probes. Figure 2 shows an SEM picture of the nanodots deposited at the end of opposing tips. By actuating the MEMS devices, the relative distance between probes is reduced in a controllable and reproducible manner. The optical properties of these nanoparticles are under measurement. An alternative method of nano-fabrication using e-beam evaporation and FIB etching is under development at CNM.

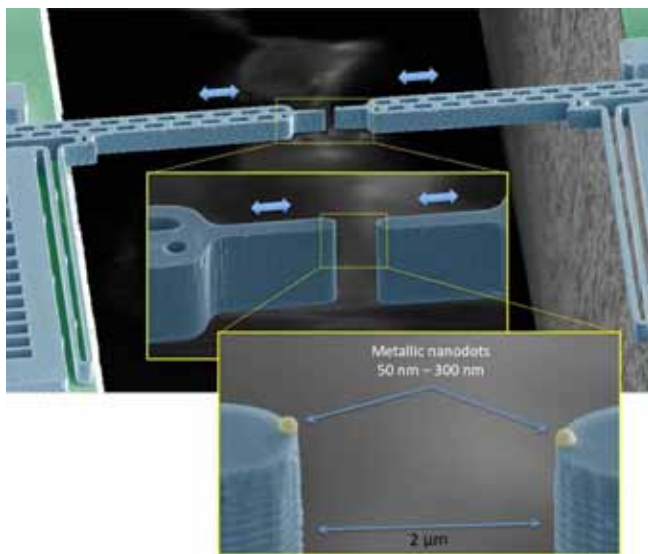


Figure 2. SEM photograph of the tips of two MEMS-probes with 100-nm Pt nanodots. The metallic structures were deposited using FIB techniques.

The process to integrate these nanodots onto the MEMS probes will be optimized during FY10. An optimum integration process should allow us to deposit nanoparticles of any shape, size, and metal at any position on top of the probes.

Patent application, “Microelectromechanical (MEMS) Manipulators for Control of Nanoparticle Coupling Interactions,” (ANL-IN-09-050).

Proposed Work for FY 2010

During FY10, we will optimize the nanoparticle-MEMS integration process, and we will optically characterize the plasmonic resonance frequency of these two metallic nanoparticles as a function of their separation. A demonstration of dynamic control of nanoparticle interaction is expected.

Refereed Publications

Decca, R.S., E. Fischbach, G.L. Klimchitskaya, D.E. Krause, D. López, and V.M. Mostepanenko, “Application of the Proximity Force Approximation to Gravitational and Yukawa-type Forces,” *Phys. Rev. D* **79**, 124021 (2009).

Decca, R.S., E. Fischbach, B. Geyer, G.L. Klimchitskaya, D.E. Krause, D. López, U. Mohideen, and V.M. Mostepanenko, “Contribution of Drifting Carriers to the Casimir-Lifshitz and Casimir-Polder Interactions with Semiconductor Materials,” *Phys. Rev. Lett.* **102**, 189303 (2009).

Decca, R.S., E. Fischbach, G.L. Klimchitskaya, D.E. Krause, D. López, and V.M. Mostepanenko, “Anomalies in Electrostatic Calibrations for the Measurement of the Casimir Force in a Sphere-plane Geometry,” *Phys. Rev. A* **79**, 026101 (2009).

Decca, R.S., E. Fischbach, G.L. Klimchitskaya, D.E. Krause, D. López, U. Mohideen, and V.M. Mostepanenko, “Capacitance Measurements and Electrostatic Calibration in Experiments Measuring the Casimir Force,” submitted to *Phys. Rev. A*, under review.

Decca, R.S., and D. López, “On the Electrostatic Calibration for Casimir Force Measurements,” *Int. J. Mod. Phys. A* **24**, 1748 (2009).

Mostepanenko, V., R.S. Decca, E. Fischbach, B. Geyer, G.L. Klimchitskaya, D.E. Krause, D. López, and U. Mohideen, “Why Screening Effects Do Not Influence the Casimir Force,” *Int. J. Mod. Phys. A* **24**, 1721 (2009).

Mostepanenko, V.M., R.S. Decca, E. Fischbach, G.L. Klimchitskaya, D.E. Krause, and D. López, “Stronger Constraints on Non-Newtonian Gravity from the Casimir Effect,” *J. Phys. A: Math. Theor.* **41**, 164054 (2008).

Materials Theory

2009-214-N0

Alexei Abrikosov, Konstantin Matveev, and
Michael R. Norman

Project Description

This project consists of research on (1) the transport properties of quantum wires, (2) local order in transition metal oxides and layered dichalcogenides, and (3) fluctuation effects in high-temperature superconductors.

Mission Relevance

This project supports the DOE science mission and, in particular, Office of Basic Energy Sciences (BES) goals in materials research, as outlined in the BES Grand Challenges report (Directing Matter and Energy: Five Challenges for Sciences and the Imagination, Dec. 2007). In particular, the work on quantum wires has direct implications for future device technologies. The work on local order supports experimental programs that develop diffuse scattering capabilities at Argonne's Advanced Photon Source (APS) and the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. The work on superconductors also has impact for the next-generation energy grid.

FY 2009 Results and Accomplishments

We explored the effect of equilibration of electrons in quantum wires on their transport properties. The equilibration was accomplished via rare three-electron collisions. We developed a quantitative theory of the equilibration rate in the case of weakly interacting electrons and applied it to calculate the transport properties of finite-length quantum wires. As the wire becomes longer, its conductance acquires a small correction. A more dramatic behavior is observed with regard to thermopower and thermal conductance. In a short wire, the thermopower vanishes. As the wire becomes longer, the equilibration processes give rise to a non-vanishing thermopower and, at the same time, suppress thermal conductance. As a result, the so-called thermoelectric figure of merit of the quantum wire becomes large, making such wires a promising component for future thermoelectric refrigerators.

We also studied the nonlinear current voltage characteristics of a quantum wire in the regime of strong electron-electron interactions. In this case, the electrons in the wire form a so-called Wigner crystal. The most significant difference between a Wigner crystal and the conventional liquid state is the fact that electron spins in the crystal are very weakly coupled to each other. As a result, the differential conductance of the wire shows a nontrivial peak structure at a voltage equal to the exchange energy of the spin coupling in the crystal. Our con-

clusions are in qualitative agreement with recent experimental results on nonlinear transport in quantum point contacts [S.M. Cronenwett *et al.*, Phys. Rev. Lett. **88**, 226805 (2002) and R. Danneau *et al.*, Phys. Rev. Lett. **100**, 016403 (2008)].

When one applies a thermal gradient, a transverse voltage develops. This is known as the Nernst effect. It is typically small in most materials. On the other hand, superconducting vortices that are not pinned exhibit a large Nernst signal. As the Nernst signal persists above the superconducting transition temperature in cuprates, this raises the question of whether vortices persist as well. We have fit the Nernst data and found that for overdoped cuprate superconductors like $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x > 0.16$, the Nernst signal follows the behavior expected for Gaussian fluctuations, implying that vortices are not relevant. On the other hand, for underdoped cuprate superconductors like $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x < 0.16$, the Nernst signal follows a power law behavior in temperature, which is consistent with the presence of vortex-like objects that persist above the superconducting transition temperature [Y. Wang *et al.*, Phys. Rev B **64**, 224519 (2001)].

Proposed Work for FY 2010

Our goal is to understand the effects of the equilibration of electrons on the transport properties of quantum wires. This knowledge will build on our recent results on equilibration in the limit of weakly interacting electrons. We want to expand the results to the much more challenging regime of arbitrary interaction strength. We will explore the effect of electron equilibration on the conductance, thermopower, and thermal conductance of quantum wires. We will also calculate the transmission coefficient of the wire for non-zero voltage biases by using a semiclassical approximation. This calculation will enable us to determine the linear conductance of the wire in the presence of a magnetic field. We will then consider the problem in which a section of the wire characterized by a weaker hopping of the electrons is moving at a constant velocity. This will enable us to calculate the current-voltage characteristic of the quantum wire for strong interactions.

We will also consider a Ginzburg-Landau theory in the context of superconducting dichalcogenides (such as NbSe_2), comparing it to the extensive amount of angle-resolved photoemission spectroscopy (ARPES) data and scanning tunneling microscopy (STM) data on these materials at Argonne. Our goal is to understand the origin of the momentum dependencies seen in these measurements, as revealed by autocorrelations of the ARPES spectra and by Fourier transform of the local density of states from STM. We will then relate these to the nature of the charge order and its influence on superconductivity.

Finally, we will try to understand the qualitative change of the Nernst effect when the material is heated above the superconducting transition temperature. In particular, we want to determine if the giant enhancement of the Nernst signal in this phase is due to fluctuating vortices or to the strong temperature dependence of the number of low-energy electronic states caused by the formation of a pseudogap. The answer will be determined by generalizing the Gaussian theory for the Nernst signal to account for both (1) the reduced density of states due to the pseudogap and (2) the short wavelength fluctuations due to vortex-like objects.

Exploratory Examination of the Feasibility of Computing Financial ROI for Completed LDRD Projects from Existing Data and Information Sources

2009-228-NO

Michael E. Samsa, Gregory W. Handke, and Ignacio J. Martinez-Moyano

Project Description

In the context of optimizing management of an R&D portfolio, one would like to have an accurate and reliable quantitative measure of the benefits that result from completed R&D projects. At Argonne, this holds true for laboratory-directed research and development (LDRD) projects. The question arises as to whether there exists a method for quantifying benefits derived from such projects that is based on sound economic and decision analysis principles. The primary objective of this project was to examine a sample of completed LDRD projects to determine if adequate data exist to calculate a financial return on the LDRD investments. This information would enable management to evaluate the value of the LDRD program to the Laboratory and its stakeholders.

When the work was first proposed, researchers did not anticipate that a significant effort would be needed to develop the theory and logic for choosing an appropriate financial measure of merit for the LDRD program. As the research team began to explore more fully the objectives of the LDRD program, the various possible stakeholder perspectives, and the characteristics of alternative measures of merit, it became apparent that an additional objective was necessary: to recommend an appropriate quantitative measure of merit.

Mission Relevance

The U.S. Congress has given the Secretary of Energy the authority, subject to certain limitations, to permit national laboratories to apply a portion of their budgets to discretionary research and development (R&D) projects, as selected by the director of the laboratory. However a consistent, quantitative, and generally accepted way to measure the efficacy of that discretionary resource and therefore its benefit to the programmatic missions of the Department and to the laboratories does not exist. In this project, we are exploring a method that could be applied to the Department's laboratories and possibly to the broader R&D community. The results of this project would therefore be relevant to all R&D-supported missions of DOE.

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FY 2009 Results and Accomplishments

The study team recommended that a benefit-cost ratio (BCR) rather than return on investment (ROI) be adopted as a measure of merit for the LDRD program. The team determined that programmatic and intellectual property (IP) -derived revenue that can be attributed to LDRD is an appropriate financial surrogate that encompasses the expressed values sought by DOE and the Laboratory for the LDRD program. As such, this measure should generally convey a consistent meaning among major stakeholders.

The research team suggested one option for a possible attribution methodology and scale that is believed to be applicable to follow-on funding, IP-derived revenue, and program revenue procured by certain LDRD-supported hires. Of the three LDRD benefit factors investigated, attributable follow-on funding appears to be the most significant benefit factor. It is thought that IP-derived revenue may be a very minor factor in the aggregate but an important one with respect to individual projects. Except in limited situations, the attribution of LDRD benefits to staff hires originally supported by LDRD projects runs the risk of double-counting benefits with those attributed to the LDRD results.

Although the results are based on a very limited sample of completed LDRD projects, they suggest that it may be possible to eventually implement an appropriate methodology across a full range of LDRD projects, provided that there is adequate flexibility to adapt the attribution methodology to currently undetermined unique characteristics of LDRD projects and strategic initiatives. Successful implementation would also require the revision of existing databases, collection of additional data, and development of new processes and procedures. The details of these requirements were not addressed in this work, pending review and further interest by the Laboratory or other stakeholders.

Proposed Work for FY 2010

This project does not continue into FY10.

APPENDIX





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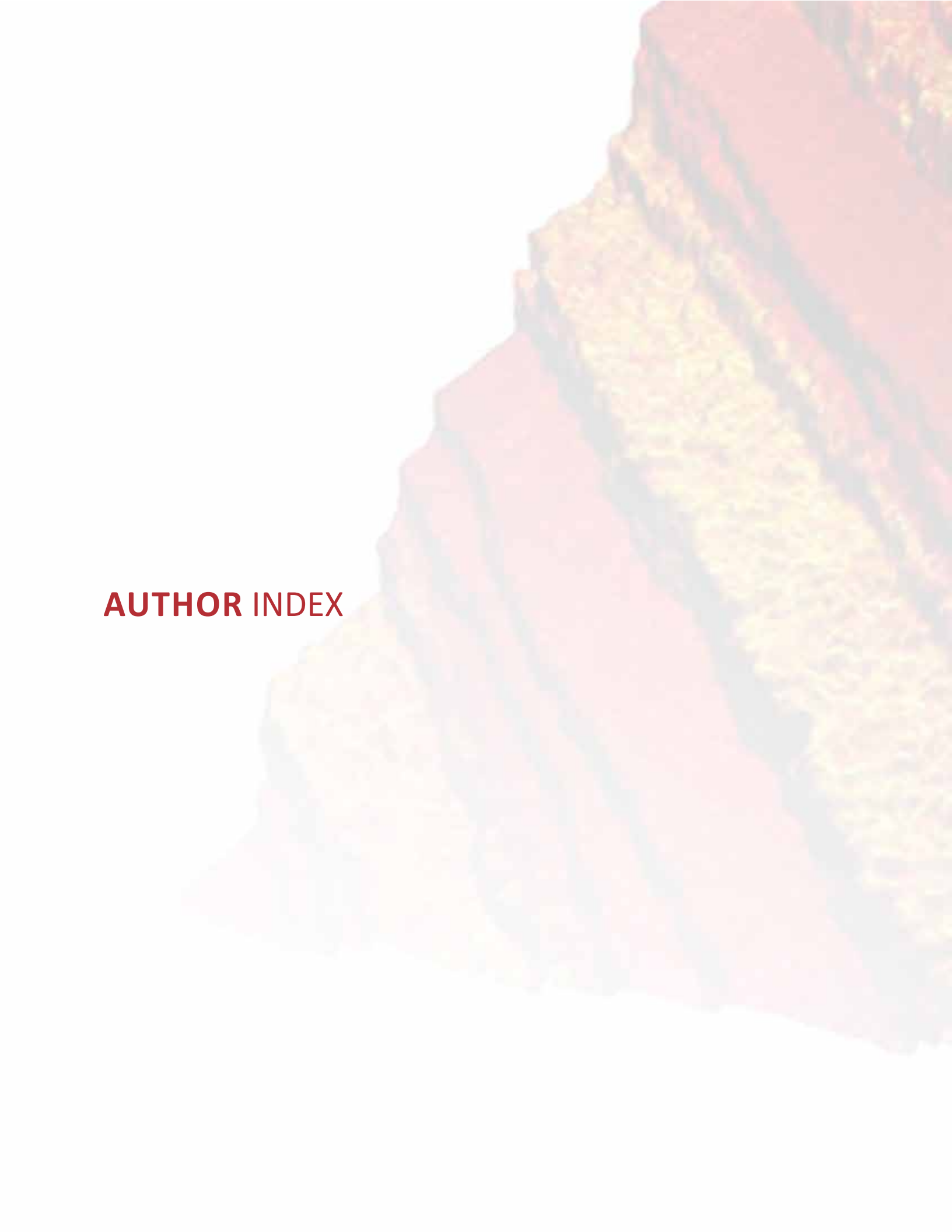
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2010-010-N0	Laser Manipulation of Nuclear Spin Embedded in Nobel-Gas Ice	Zheng-Tian Lu
2010-029-N0	Single Quantum Flux Magnetometer	Wai K. Kwok
2010-042-N0	Emerging Technologies for Scientific Databases	David Malon
2010-043-N0	Low Mass Optical Read-out for High Data Bandwidth Systems	David Underwood
2010-044-N0	Novel Power System Operations Methods for Wind-powered Plug-in Hybrid Electric Vehicles	Jianhui Wang
2010-047-N0	Optimization of Luminescent Solar Concentrators	Seth Darling
2010-049-N0	Compact Solid-state Sources of Coherent THz-radiation	Ulrich Welp
2010-050-N0	Highly Efficient SERS-active Substrate with Designer Hot-spots and Multiple-stage Light Amplification	Vitalii Vlasov-Vlasov
2010-063-N0	Tactile MEMS-based Sensor	Young Soo Park
2010-073-N0	Polymerized Ionic Liquid Nanostructures for Biocatalytic Production	Millicent Firestone
2010-074-N0	Combined Approaches Towards a Hierarchical Understanding of Battery Materials	Mahalingam Balasubramanian
2010-093-N0	Molecular Characterization of Spore Coat Proteins	Daniel Schabacker
2010-108-N0	Multi-user Virtual Reality Environments for Emergency Response Planning and Training	David LePoire
2010-110-N0	Dual-polarization Bolometric Focal Plane Detector for Inflation Era High Energy Physics	Valentyn Novosad
2010-114-N0	Can We Raise the Q of Superconducting RF Accelerating Structures?	Mike Pellan
2010-117-N0	Development of Picosecond X-ray Pulses at the APS using MEMS-based X-ray Optics	Jin Wang
2010-119-N0	Development of a High Throughput Approach to Soil Physical and Chemical Characterization in Tandem with Soil Metagenome Analysis	R. Michael Miller
2010-129-N0	Layered Oxides for Thermoelectric Energy Conversion	Kenneth Gray

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2010-137-N0	Novel Bifunctional Low-Temperature Catalysts at the Sub-nanometer Scale	Larry Curtiss
2010-138-N0	Trapped Field Magnets: A Paradigm Shift for Applications of High-field Magnets at a Synchrotron	Zahirul Islam
2010-139-N0	High-throughput Reconstruction of Metabolic Models for Organisms with Applications in Energy, Bioremediation, and Carbon Sequestration	Rick Stevens
2010-150-N0	Next Gen Sequencing Core: Expanding the Number of Environments Reachable with Metagenome-directed DNA Sequencing	Kevin White
2010-151-N0	Next Gen Sequencing Core: Increased Resolution Metagenomics	Kevin White
2010-156-N0	Study of Superconducting Films by Atomic Layer Deposition	Thomas Proslie
2010-158-N0	Converting CO ₂ to Fuel through Functionalized MOFs	Di-Jia Liu
2010-161-N0	The Biochemistry of Plant-fungal Symbiotic Relationships	Deborah Hanson
2010-167-N0	Probing Catalytic Transient Intermediate in Ultrafast Time Domain	Di-Jia Liu
2010-175-N0	Detection of Low Copy Number of Pathogenic Microbes by Litmus Strip	Qiaoling Jin
2010-181-N0	Development of High Power Targets for Isotope Production with Low Energy Beams	Jerry Nolen
2010-183-N0	X-ray Nanoimaging for Life Sciences	Barry Lai
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