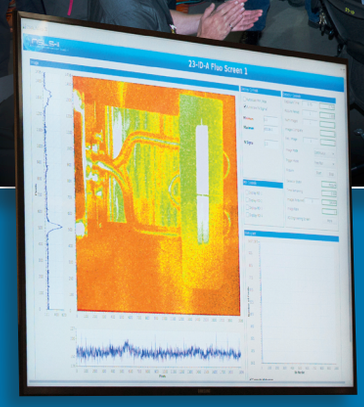
BROOKHAVEN NATIONAL LABORATORY

LDRD 2014 Annual Report

Laboratory Directed Research & Development Program Activities



BNL-52351-2014

BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES
UPTON, NEW YORK 11973-5000
UNDER CONTRACT NO. DE-AC02-98CH10886
UNITED STATES DEPARTMENT OF ENERGY

March 2015

Acknowledgments

The Laboratory Directed Research and Development (LDRD) Program is managed by Diane Hatton, who serves as the Director of the Planning, Performance, and Quality Management Office. Contributions to the FY 2014 report were coordinated by Liz Flynn and edited by Kathi Barkigia. Diane wishes to thank Kathi Barkigia, Patricia Giacalone and Liz Flynn for their assistance in preparing the document. A special thank you is also extended to the Production Services Group for their help in publishing. Of course, a very special acknowledgement is extended to all of the authors of the project annual reports.

Table of Contents

Introduction i

Project Summaries 1

Development of Laser System for Driving the Photocathode of the Polarized Electron Source for the EIC 3

2D Membrane Solution Scattering for Probing the Structures of Membrane Proteins 5

Exploring the Role of Glue in Hadron Structure by an Electron Ion Collider 7

CMOS-Pixel Vertex Detector for an EIC 9

Complex Modeling of Nanostructures 11

Inter-Individual Variation in Radiation Induced Epigenetic Modifications and their Potential Impact on Carcinogenesis 13

Developing an Integrated Atmosphere-Ecosystem Model for Investigating Interactions Between Atmospheric System and Ecosystem Under a Warming Climate 15

Conical Slit for Probing Buried Micron or Sub-Micron Volumes for Dynamic Measurements of Heterogeneous Materials 17

In situ Transmission X-ray Microscopy Studies of Structure and Function in Energy Storage 19

MeV-UED for Ultrafast Science 21

Femto-second X-ray Pulse Generation by Electron Beam Slicing 23

Thermochemical Conversion of Biomass to Fuels and Chemicals 25

Flow-Based Battery Architectures for Large Scale Electrical Energy Storage 27

Laser-driven Proton Accelerator 29

Water-based Liquid Scintillator Detector for Neutrino and Proton Decay Experiments 31

Quantum Electrodynamics for QCD Precision Studies at an EIC 33

Investigating eRHIC Beam-Beam Effects with CeC Linear Accelerator 35

Table of Contents

Permanent Magnet Solution of the eRHIC with the Non-Scaling FFAG……37

Time Resolved Imaging of X-rays and Charged Particles……39

Electrochemical Reduction of Carbon Dioxide on Surface-Modified Metal Electrodes……41

A NSLS-II Workflow Prototype System for Supporting Data Intensive Beamline Experiments..43

Synthetic Control of Lipid Biosynthesis in Plant Vegetative Tissue……45

Tracking Lithium Electrochemical Reaction in Individual Nanoparticles……47

Elucidating the Role of Nanostructured Domains in CIGS PV Device Performance……49

A Probabilistic Approach to Sizing Battery Energy Storage Systems for Improved Grid Inertial Response……51

In situ Studies of Interfaces Under Extreme Environments……53

Modulation Enhanced Diffraction: A New Tool for Powder Diffraction and Total Scattering Studies ……55

Development of At-Wavelength Metrology Tools……..57

Multidimensional Imaging Data Analysis: From Images to Science……59

Atomic Resolution Elemental Mapping Using X-ray Assisted STM……61

Segmented Adaptive-Gap Undulator with Different Period Lengths in Segments for Production of High Flux and Brightness Hard X-Rays at NSLS-II……63

Catalysis Program in Sustainable Fuels……65

Boron Arsenide ($B_{12}As_2$) Thin Films for Next-Generation Thermal Neutron Detectors……67

High Performance Direct Wind Superconducting Magnets……69

In-Situ Investigation of the Strain Distribution in Next Generation 3D Transistors Using X-ray Nanodriffraction……71

Enable Early Sciences in NSLS-II with Experiment-Driven Big Data Stream System……73

Table of Contents

Increasing Efficiency of Nitrogen Use by Plants: A Prerequisite for Bioenergy Crops on Marginal Lands……75

Tissue Specific Metabolic Models in Plants……77

Operando Studies of C1 Catalytic Reactions: Probing Model and Technical Catalysts at High Pressures Using Soft X-rays……79

Correlative Microscopy, Spectroscopy and Diffraction with a Microreactor……81

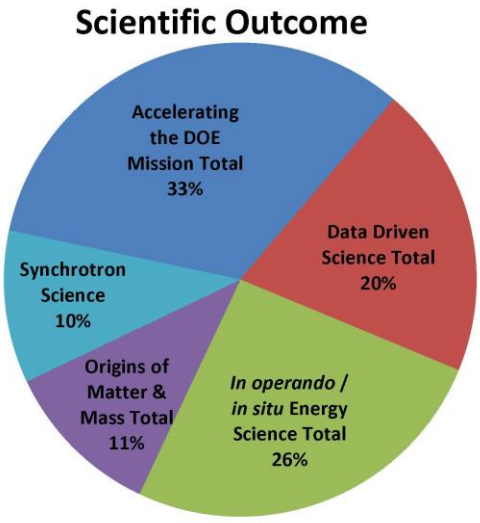
Introduction

Each year, Brookhaven National Laboratory (BNL) is required to provide a program description and overview of its Laboratory Directed Research and Development Program (LDRD) to the Department of Energy (DOE) in accordance with DOE Order 413.2B dated April 19, 2006. This report provides a detailed look at the scientific and technical activities for each of the LDRD projects funded by BNL in FY 2014, as required. In FY 2014, the BNL LDRD Program funded 40 projects, 8 of which were new starts, at a total cost of $9.6M.

The investments that BNL makes in its LDRD program support the Laboratory's strategic goals. BNL has identified four Critical Outcomes that define the Laboratory's scientific future and that will enable it to realize its overall vision. Two operational Critical Outcomes address essential operational support for that future: renewal of the BNL campus; and safe, efficient laboratory operations. The four science Critical Outcomes are:

- Understanding the origins of matter and mass
- Transformational discovery through synchrotron radiation
- *In operando* and *in situ* energy science leadership
- Leadership in data-driven discovery.

In addition, BNL leverages its unique resources to expand its scientific capability beyond the four scientific Critical Outcomes in order to accelerate the DOE mission in high energy physics, biological and environmental research, nonproliferation, and applied energy. LDRDs aligned with the Critical Outcomes and its focused, distinctive programs in the aforementioned areas support the growth and evolution of the Lab's major mission areas and, in turn, the missions of the DOE. Approximately 67% supported the four Critical Outcomes. In total, these LDRD investments supported 55 postdoctoral researchers and graduates students in whole or in part and resulted in 105 publications and 1 award.



This Project Activities Report represents the future of BNL science; it is an impressive body of exploratory work that investigates many scientific and technical directions in support of the DOE and BNL Missions. We hope that you enjoy it.

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

2014 PROJECT SUMMARIES

Development of a Laser System for Driving the Photocathode of the Polarized Electron Source for the EIC

LDRD Project # 10-040
T. Rao, T. Tsang, B. Sheehy

PURPOSE:
The objectives of the project are the development of the laser system that can drive a single cathode and improvement in the performance of the cathode of the "Gatling Gun." The laser should be upgradable to deliver the 50 mA current required for the electron-ion collider (EIC) with appropriate timing and energy stability. In this project, three different laser systems will be investigated; the appropriate system will be chosen and developed. The improvement in the sensitivity of the cathode is achieved by better understanding the formation of the negative electron affinity surface. Different oxygen sources for creating the negative electron affinity surface as well as the changes in the surface morphology as a function of the cleaning temperature will be investigated. A polarized electron source (cathode and laser) capable of delivering up to 50 mA with life time significantly longer than its preparation time is crucial for the eRHIC project at BNL.

APPROACH:
The quantum efficiency of the polarized electron source is in the range of a fraction of a percent at 780 nm. In order to meet the beam requirements of the Gatling gun, the laser should deliver ~ 4 W average power at 780 nm, at a repetition rate of 704 kHz with a pulse duration of ~ 1 ns at each of the gun cathodes Formation of the negative electron affinity surface on the GaAs is crucial for the high quantum efficiency (QE) and the preservation of the polarization. Typically the electron affinity of a very clean GaAs surface is reduced by depositing Cs and an oxidizing agent to result in a fractional monolayer of Cs on the surface. The cleanliness of the GaAs surface, Cs and the oxidizing agent determine the ultimate QE of the cathode and its sensitivity.
The scope of the program is expanded to address both the development of the laser system and understanding the negative electron affinity of the cathode in order to increase the life time of the cathode. In collaboration with Brian Sheehy of the Collider-Accelerator Department, we investigated different laser architectures, decided on the most promising design, interfaced with the industry to complete the preliminary research and development and initiated the procurement process for the laser system.

Experiments to establish the correlation between the QE and the surface properties of GaAs upon heating have been completed. The results indicate that when normalized to the initial QE, the temperature of the substrate during heat cleaning does not affect the final QE as long as the substrate is heated above 560 C .The vacuum system is being modified to accommodate activation using two alkali metals instead of one to decrease the sensitivity of the cathode to contaminants.

TECHNICAL PROGRESS AND RESULTS:
The fiber laser system operating at 1560 nm has been developed by Optilab, a commercial firm. The laser system went through a number of iterations and the laser that meets the design criteria was delivered in November 2013. The performance test results delivered by the vendor are shown in Fig 1-4. The ac power measured indirectly is in the range of 5-10 W, in reasonable

agreement with the specification. The system is currently being configured for direct power measurement. The power distribution as a function of wavelength is shown in Figure 1. 94% of the laser power is contained in the main peak. The out of bandwidth component is due to the input spectrum from the seed diode. The non-linear effect that was observed previously has been addressed by changing the amplifier fiber. The line-width measured with fine resolution scanning, and shown in Figure 2 is 0.04 nm, well within the acceptable range. Figure 3 and 4 show the pulse duration of the amplified beam. As can be seen from Figure 4, the pulse develops a temporal asymmetry with increasing output power. This asymmetry as well as the power fluctuation needs to be addressed in the final configuration for the full Gatling gun. However, these operating parameters are sufficient to test the proof of principle gun.

We have identified a doubling crystal that we would test initially, followed by testing with a higher efficiency device.

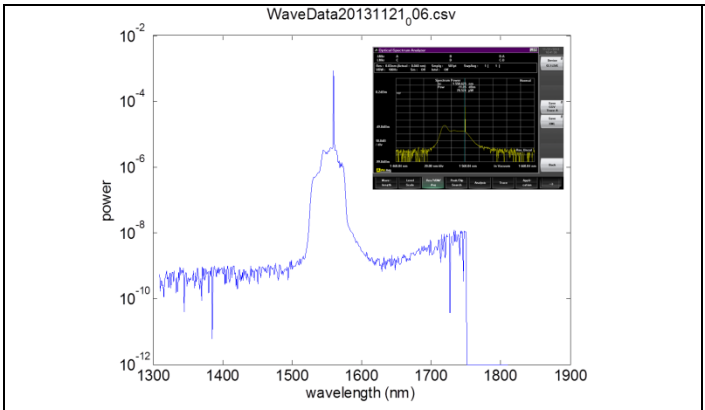


Figure 1 Power spectrum of the amplifier output. Inset: power spectrum of the seed oscillator

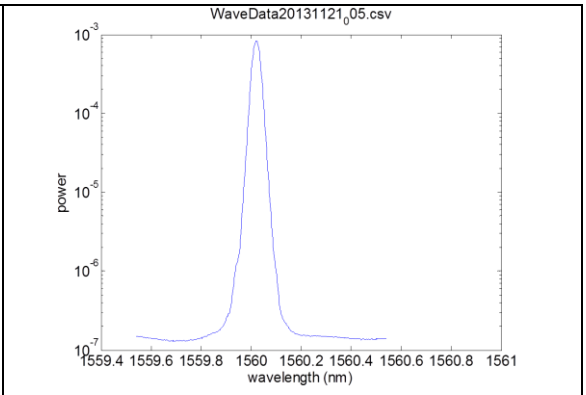


Figure 2 High resolution scan of the power spectrum showing the narrow band width

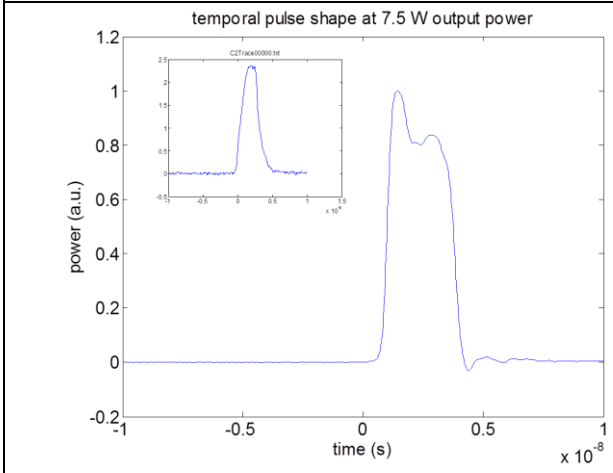


Figure 3 Temporal shape of the amplified beam. Inset: Drive electrical pulse

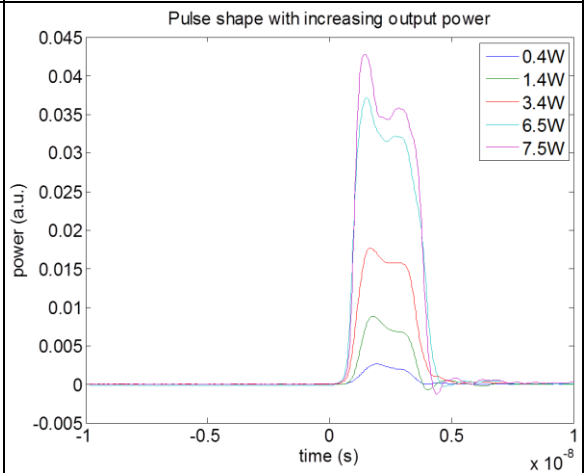


Figure 4 Temporal shape of the amplified laser beam as a function of output power

2D Membrane Solution Scattering for Probing the Structures of Membrane Proteins

LDRD Project # 11-032
L. Yang

PURPOSE:

This project aims to develop the experimental methods needed to utilize x-ray scattering to study the structure of membrane proteins embedded in single-layered lipid membranes that resemble the native environment of these proteins. While this technique has never been demonstrated, we have obtained similar results on plant viruses (much larger than membrane proteins and therefore easier to measure). The difficulty is to collect high quality data free of background scattering and without introducing radiation damage to the proteins, which we will overcome by flash freezing the membrane sample and performing the measurements at liquid nitrogen temperature.

APPROACH:

Structural determination of membrane proteins is a grand challenge in structural biology. A key limitation in these studies is that the membrane proteins must be extracted from membranes using detergents, so that the resulting soluble protein-detergent complex can be studied using methods available for soluble proteins. Unfortunately, the presence of detergents creates some detrimental side effects. Measuring the membrane proteins in substrate-supported, single-layered lipid membranes that mimic the proteins' native environment is a promising alternative. The membrane sample can be created under well-defined chemical conditions that are required for the proteins to function. However, in order to apply this method to membrane proteins, the sample must be exposed to x-rays for long periods of time, implying higher probability of radiation damage to the sample.

Under this project, we will develop methods to flash freeze the membrane samples and measure them at liquid nitrogen temperature. It is known that radiation damage due to the diffusion of free radicals can be dramatically reduced at low temperatures. Once the membrane sample is frozen, it will also be possible to remove the substrate on which the membrane structure is created. Doing so will expose the membrane structure directly to the x-rays, thus virtually eliminating the background scattering from bulk water. This effort is in collaboration with Masa Fukuto of the Condensed Matter Physics and Materials Science Dept. and Dax Fu of the Biology Dept.

TECHNICAL PROGRESS AND RESULTS:

In FY12, we conducted a series of transmission wide-angle x-ray scattering (WAXS) measurements that showed that our first iteration of the slam-freezing instrument produced amorphous ice; however, the content of vitreous ice is mainly determined by the amount of cryoprotectant that is added. Subsequent measurements at the beginning of FY13 revealed that even vitrified samples still produced intense scattering at small angles (SAXS) that would severely contaminate the protein scattering data that we aim to collect. The goals of this project in FY13 therefore are to clarify the origin of the background scattering at small angles, and to explore an alternative implementation of slam freezing that could improve sample vitrification and therefore the quality of the scattering data.

To understand the origin of the SAXS background, we performed tests on samples deposited between a thick silicon substrate that can be easily handled and a glass cover that allowed us to

Figure 1 Representative photographs of frozen samples, with 30% (left) and 48% PEG (right). In general the sample becomes clearer with higher concentration of PEG. The cracks are observed only in clear samples.

visually observe the internal structure of the sample. At low cryoprotectant concentrations that were expected to produce crystalline ice, the samples appeared opaque. As the cryoprotectant concentration was increased, the sample became clear. However, a lot of cracks were observed (Figure 1). Since a high scattering background was not observed in similar studies on frozen droplets, we attribute the high SAXS background that we have observed to the scattering from the interfaces between the clear parts within the cracked sample. The cracks are likely caused by the mechanical stress resulting from the different thermal properties of the sample and the substrate during the rapid decrease of overall temperature.

In order to speed up the cooling rate in the freezing process and to reduce the reliance on cryoprotectants, we explored directly freezing the liquid sample against a cold silicon surface. A new cryostat was acquired, so that the sample could be elevated to be in contact with the cold surface. The frozen sample was then transferred to the original cryostat for x-ray scattering measurements. Having the membrane sample on the frozen liquid surface also has the advantage that the x-ray penetration depth can be controlled by the incident angle to avoid scattering from the internal structure in the sample, which may still be in the form of crystal ice. However, while sample cooling was accelerated, we found the quality of the sample to be inconsistent. Furthermore, when cryoprotectant was used, it was very difficult to prepare membrane samples on the surface of the viscous liquid.

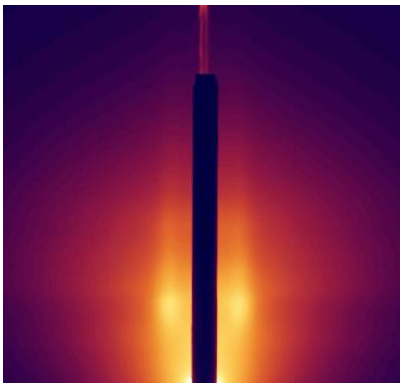


Figure 2 Grazing incident diffraction data from a frozen membrane sample that is exposed in the vacuum.

We therefore went back to the method of preparing the membrane sample on a substrate under water. We worked out a procedure to remove the silicon substrate from the frozen sample immediately after freezing, exposing the membrane sample. The best scattering data we have collected so far is shown in Figure 2, in which the diffraction peaks due to lateral packing of the tobacco mosaic viruses adsorbed to the lipid membrane are clearly visible. The diffuse scattering background is likely due to the high concentration of cryoprotectant (PEG8000), which is expected to decrease with the molecular weight of the cryoprotectant.

This LDRD project has now concluded. In the process of exploring rapid freezing, we have gathered valuable experience. For instance, we learned to reduce the sample mass to speed up cooling, to optimize vacuum in the cryostat to eliminate frosting on the sample, and that different cryoprotectants behave differently in the freezing process. This knowledge will be applied when we continue this research at the life science beamlines at the National Synchrotron Light Source II, to be supported by a NIH P41 grant.

Exploring the Role of Glue in Hadron Structure by an Electron Ion Collider

LDRD Project # 11-033
J. Qiu

PURPOSE:
The Electron Ion Collider (eRHIC) proposed by BNL has the capability of colliding electrons with protons (e+p) and electrons with nuclei (e+A) and could be a powerful femtoscope (or even an attoscope) to explore the quark-gluon structure of protons and nuclei. The goal of this LDRD project is to identify a set of observables/probes in e+p and e+A collisions that could provide direct access to the quark/glue content of a proton or a nucleus and to explore the role of glue in forming stable hadrons. Our investigations focus on two types of hard probes: jets and heavy flavor productions. In addition, we explore the potential role of lattice Quantum Chromodynamics (QCD) calculations in helping to determine the quark/glue structure of a hadron, complementary to the direct measurements at eRHIC. The knowledge gained from this project could help articulate the physics case as well as machine parameters of a future eRHIC.

APPROACH:
The gluon, the carrier of the strong interacting color force, does not carry electromagnetic charge, and therefore is "dark" and cannot be "seen" directly by the electron beam at eRHIC. It is therefore critical to identify observables/probes that are sensitive to the role of gluons inside the colliding hadron while are visible to the colliding electron beam. In addition, the probes have to be sharp enough to see the quark/glue content and structure of the colliding hadron without altering it, or equivalently, the probed content and structure should be universal for any good probes. Technically, this requires the validity of QCD factorization for such probes. It is the QCD factorization that enables us to connect the quarks and gluons, the basic degrees of freedom of QCD, and their distributions inside hadrons to physically measured cross sections with identified hadrons and leptons.

We focus on jet and heavy quark production because both of them have to be produced at a very short-distance due to the jet energy and heavy quark mass. Potentially, jets and heavy quarks (or quarkonia) are good hard probes of partonic structure of hadrons. To assure this, we investigate the validity of QCD factorization for the production of jets/jettiness and heavy quarks/quarkonia, in addition to our effort to calculate the production rate of these observables.

The hard probes at eRHIC are excellent for probing quarks and gluons carrying less than 10% of the momentum of a colliding and fast moving proton or nucleus, or those of momentum fractions, $x < 0.1$. To explore the hadron structure of quarks and gluons carrying much more than 10% of a hadron's momentum (or with $x >> 0.1$), which is very sensitive to the binding of quarks and gluons, but very difficult to be accessed experimentally, we investigated the lattice QCD approach to extract the partonic structure of a hadron.

TECHNICAL PROGRESS AND RESULTS:
Due to the late start of the project in FY11, this project had a few months of support available in FY14 for the postdoc, Dr. Yan-Qing Ma, and the Ph.D. student, Mr. Hong Zhang of Stony Brook University (SBU). Like previous years, we obtained a good number of research results and wrote many papers, which are either published or submitted for publication. We were in high demand

to speak about our results at international conferences and workshops, and we delivered many invited talks during this year.

With Dr. Kang of Los Alamos National Lab (LANL) and Drs. Liu and Mantry of Argonne National Lab, we studied nuclear dependence of the newly proposed global event shape 1-jettiness in electron-nucleus collisions [Phys. Rev. D88 (2013) 074020]. The inclusiveness of the 1-jettiness, proposed by some of us [Phys. Rev. D86 (2012) 114011], quantifies the pattern of radiation in the final state, and gives enhanced sensitivity to soft radiation at wide angles from the nuclear beam and final-state jet, which is a great advantage over jet quenching in quantifying the medium induced radiation and energy loss. We performed calculations for a variety of nuclear targets, and included resummation of logarithms at the next-to-next-to-leading log accuracy. Our findings further strengthen the rich physics potential of eRHIC, where a range of nuclear targets was planned.

With Dr. Kang of LANL, Prof. Sterman of SBU, and Dr. Ma and Mr. Zhang, we developed an extended QCD factorization formalism for heavy quarkonium production in high energy collisions in a series of papers [Phys. Rev. D90, 034006 (2014), Phys. Rev. Lett. 113, 142002 (2014), and Phys. Rev. D (in press) arXiv:1411.2456]. Our work laid down a solid foundation for using heavy quarkonium production as a hard probe, and provided much needed physics insights on how a heavy quarkonium is actually produced in high energy collisions. This is very important for understanding heavy quarkonium production at eRHIC, which is a unique observable for directly probing the gluon content of the colliding proton or nuclei.

With Dr. Ma and Mr. Zhang, we not only developed the method, but also completed the first calculations of heavy quark pair fragmentation functions to an observed heavy quarkonium in both S- and P-wave states [Phys. Rev. D89, 094029 (2014); D89, 094030 (2014)]. Because the heavy quark mass $m_Q >> \Lambda_{QCD} \sim 1/\text{fm}$, and the well-separated momentum scales of a physical quarkonium, $m_Q >> m_Q v >> m_Q v^2$, where v is the momentum of the heavy quark in the pair's rest frame, we calculated the fragmentation functions by applying a non-relativistic QCD (NRQCD) factorization approach. Our work effectively reduces all unknown heavy quark pair fragmentation functions, which are necessary for evaluating both the rate and properties of produced heavy quarkonia, into a few universal NRQCD matrix elements for each heavy quarkonium, which could be easily extracted from the experimental data. With our new results, the predictive power of QCD factorization formalism for heavy quarkonium production is enhanced tremendously.

To explore the hadron structure of quarks and gluons carrying much more than 10% of a hadron's momentum (or with $x >> 0.1$), which is very sensitive to the binding of quarks and gluons, but very difficult to be accessed experimentally, with Dr. Ma, we proposed a new QCD factorization based approach to extract parton distribution and correlation functions from lattice QCD calculation of single hadron matrix elements of quark-gluon operators [arXiv:1404.6860, arXiv:1412.2688]. We pointed out that although the lattice QCD calculations are done in Euclidean space, the nonperturbative collinear behavior of the matrix elements are the same as that in Minkowski space, and could be systematically factorized into parton distribution functions with infrared safe matching coefficients. We calculated the first order matching coefficients, and are in the process of developing the first lattice calculation of $d(x)/u(x)$ at large x, for which predictions from various calculations are all over the map.

CMOS-Pixel Vertex Detector for an EIC

LDRD Project #11-036
E. Aschenauer

PURPOSE:
Traditional silicon vertex detectors are unsuitable for applications in an electron-ion collider environment, primarily due to their relatively high material budget. In particular an accurate determination of the scattered deep inelastic scattering electron momentum suffers from bremsstrahlung in the detector elements. The last decade has seen significant improvement in the development of Monolithic Active Pixel Sensors (MAPS) in which the active detector components are combined with the analog signal shaping and the digital conversion in a single silicon chip (see [1], [2] and references therein).. These devices are based on standard complementary metal–oxide–semiconductor (CMOS) technology where an epitaxial layer is the active detector element. They typically provide 2D spatial resolution better than 10 microns and have effective thickness of 0.3-0.4% radiation length per layer. The commercial production is cheap and the chip works at room temperature, thereby removing additional material for cooling. The scope of this LDRD is to study the usability of MAPS technology for vertex and forward/backward trackers of an Electron Ion Collider (EIC) detector.

APPROACH:
The MIMOSA chip developed at the Institut Pluridisciplinaire Hubert Curien in Strasbourg is presently the most advanced MAPS application and was the first to be used in a collider environment at STAR (PXL detector; MIMOSA 28 revision). A later version of this chip (MIMOSA 34) is a candidate for the Inner Tracking System (ITS) upgrade at ALICE. Columbia University and BNL have started to study these chips for an EIC detector. A test stand was set up at BNL in order to carry out checks of prototypes and gather the required know-how that is necessary for the design of a full scale micro-vertex detector in the future. It uses a standard PXI LabView data acquisition system and specific analysis code, TAF, to read out the data.

In the past year, the tests were carried out to quantify the effect of ionizing radiation on the sensitive areas of the chips. This was done at the NASA Space Radiation Lab (NSRL) located at BNL. Another focus was on detailed simulation studies of the momentum resolution of scattered electrons as well as of the magnitude of bremsstrahlung effects due to the interaction with the pixel tracker. The simulation uses the EicRoot software framework, which was developed by the BNL-EIC task force based on the existing FairRoot package.

TECHNICAL PROGRESS AND RESULTS:
The irradiation test: The test was twofold including several different ion beams with varying incident angles on the sensors (MIMOSA 26 in this setup). The ion beams included protons, silicon, and iron. Figure 1 shows exemplary results on pixel cluster multiplicities for proton and iron beams with an incident angle of 45º. These results have to be related to the pixel size of the employed sensors to obtain quantitative estimates on spatial resolution, but there are very obvious differences in the shape and width of the observed distributions.

Unfortunately the sensor was damaged during the early phase of the test, such that the systematic study of different incident angles could not be carried out completely. The broken chip has been

replaced and the data acquisition system has been upgraded with new firmware. The setup was ready prior to the move of the lab equipment from building 490 back to 510 (after renovation).

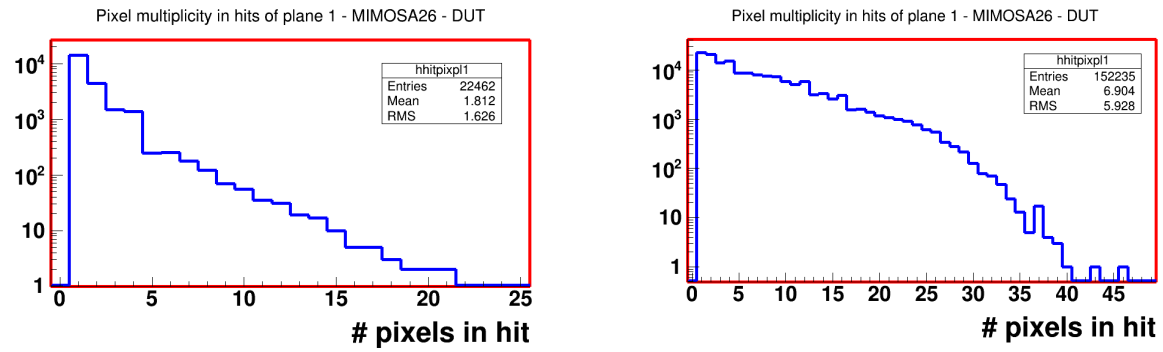


Figure 1 Pixel multiplicities during the test with proton and iron beams at the BNL NSRL. On average heavy ions produce pixel clusters with higher multiplicities than protons.

Full simulation studies: The BNL-EIC task force has developed a modular simulation framework, EicRoot, to study the detector design with a full model of the detector. This framework has also been used for cross checks of possible EIC upgrades of the PHENIX and STAR detectors.

The micro-vertex detectors were included in EicRoot with a geometry based on six layers in the barrel and seven layers in the endcaps using MIMOSA 28 chips with effective thickness of 0.4% radiation length per layer. We studied the effect of the material on electrons at energies between 5 and 20 GeV in a rapidity range from central to forward kinematics, $0 < \eta < 3$. **Error! Reference source not found.** shows exemplary results for the bremsstrahlung-related energy loss of electrons in the material of the vertex detector. We observe in particular a noticeable dependence on pseudorapidity, due to the changing thickness of the layers with respect to the incident angle. Recently a more up-to-date geometry of the pixel tracker was implemented in the simulation, closely following the design of the ALICE ITS tracking upgrade. We plan to continue simulation studies based on this setup.

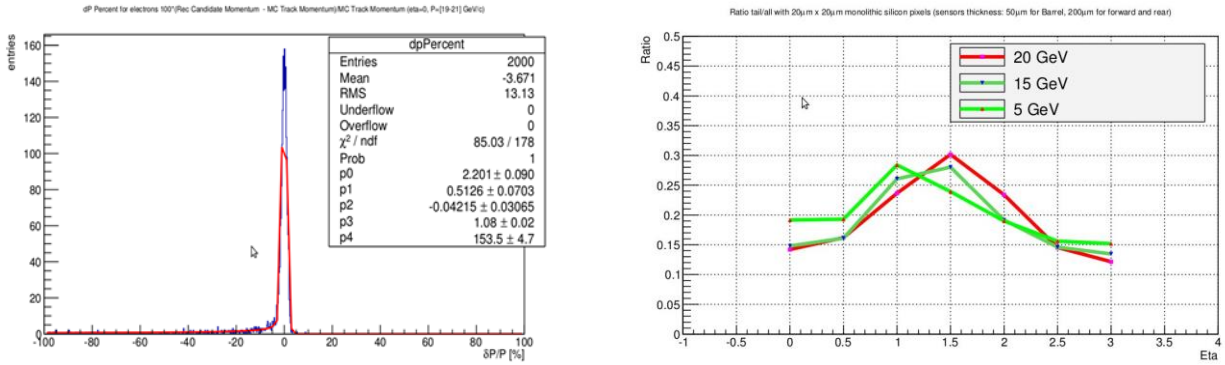


Figure 2 Relative change of the electron momentum due to material in the vertex detector, MIMOSA 28, for all electron energies (left).

[1] R Turchetta et al., Nuclear Instruments and Methods in Physics Research A 458 (2001) 677-689.
[2] Marc Winter for the IPHC-IRFU collaboration, Nuclear Instruments and Methods in Physics Research A 623 (2010) 192-194.

Complex Modeling of Nanostructures

LDRD Project # 12-007
S. Billinge, P. Juhas

PURPOSE:
This project aims to develop data analysis algorithms and software for solving atomic structures of nanoparticles and locally disordered materials. Our objective is to develop software for an easy and highly configurable buildup of specialized structure simulations and exploration of computational routines that would lead to successful structure solution. The codes are developed as open source software to promote sharing, verification and contributions from the community.

APPROACH:
To overcome the increased complexity in the nanoscaled structure, we combine multiple experimental inputs such as pair distribution function (PDF), small angle scattering (SAS), local chemical constraints (coordinations, allowed bond angle ranges) and theoretical energy calculations in a single optimization setup. Besides the Principal Investigators, the project team includes Dr. Kevin Knox, a postdoc at BNL, Xiaohao Yang, a graduate student at Columbia University, and Dr. Michael McKerns, a part-time consultant.

TECHNICAL PROGRESS AND RESULTS:
DiffPy-CMI release and community involvement efforts: We have released the open source software DiffPy-CMI [http://www.diffpy.org], a suite of Python and C++ libraries for structure studies and modeling using multiple experimental and theoretical probes. The DiffPy-CMI release provides 8 Python and 2 C++ libraries with about 90000 lines of in-house written code and makes our software tools readily available on Unix, Linux and Mac platforms. The software is hosted on GitHub, a leading platform for open source software development, which makes it easy for anyone in the community to actively contribute to the project. The DiffPy-CMI was downloaded by over 100 users and has been featured as the first open-source project by the BNL Office of Technology Commercialization and Partnerships. To further engage the user community, we are maintaining a separate GitHub project cmi_exchange for tutorials, tips and user-contributed examples. In addition we also administer the diffpy-users and diffpy-dev mailing lists, where we help the users with their software and research questions.

Au144 nanoparticles: The thiolate-covered Au144 nanoparticles are easy to prepare and very stable, however their structure remains an open question. We found that depending on the organic ligands that protect the nanoparticle surface, the gold core can be either in an icosahedral arrangement as published in the literature or adopt a profoundly different structure based on Marks decahedron. The CMI software tools allowed us to scan a series of Marks decahedral structures and match them to the measured diffraction data to find a plausible structure candidate. We have also attempted several automated search procedures for a symmetry-consistent placement of organic ligands, although these efforts have so far not been successful.

SC-14 demo on CdSe Quantum Dots (QD) shape determination: The CdSe QDs, synthesized by the group of Prof. Owen from Columbia University, show a quantized growth and can be prepared in large quantities in a monodisperse form. Low-quality single-crystal diffraction data as experimental PDF imply tetrahedral nanoparticle shapes that are ⟨111⟩ cutouts from the CdSe zinc-blende phase. To validate these tetrahedral models, we have performed particle shape reconstruction from experimental PDF data. However this yielded a large number of chemically

unfeasible clusters that had a similar or better fit to the PDF data. This showed that PDF measurements alone are not sufficient to unequivocally elucidate the QD shapes, therefore the simulations were enhanced with SAS data and requirement of low surface area that was expressed as a number of open bonds per Cd or Se atom. The CdSe-QD system is an excellent test bed for the complex modeling approach as it combines three different probes (PDF, SAS, area), where each one of those is incomplete and insufficient to identify a unique structure that would match them all. This presents a computationally intensive problem of finding a proper combination of the three probes that would produce a universally matching unique structure. This work was presented as one of the Department of Energy Labs' science demos at the Supercomputing 2014 (SC14) conference on high-performance computations.

Papers published or submitted in 2014 that acknowledge LDRD funding:

1. Vicky V. T. Doan-Nguyen, Simon A. J. Kimber, Diego Pontoni, Danielle Reifsnyder Hickey, Benjamin T. Diroll, Xiaohao Yang, Marcel Miglierini, Christopher B. Murray and Simon J. L. Billinge, Bulk Metallic Glass-like Scattering Signal in Small Metallic Nanoparticles, ACS Nano 8, 6163–6170 (2014).
2. Alexander N. Beecher, Xiaohao Yang, Joshua H. Palmer, Alexandra L. LaGrassa, Pavol Juhas, Simon J. L. Billinge and Jonathan S. Owen, Atomic Structures and Gram Scale Synthesis of Three Tetrahedral Quantum Dots, J. Am. Chem. Soc. 136, 10645-10653 (2014).
3. Michael Ghidiu, Michael Naguib, Chenyang Shi, Olha Mashtalir, Limei Pan, Bo Zhang, Jian Yang, Yury Gogotsi, Simon J.L. Billinge and Michel W. Barsoum, Synthesis and characterization of two-dimensional Nb_4C_3 (MXene), Chem. Commun. 50, 9517-9520 (2014).
4. Chenyang Shi, Majid Beidaghi, Michael Naguib, Olha Mashtalir, Yury Gogotsi and Simon J.L. Billinge, Structure of nanocrystalline Ti_3C_2 MXene using atomic pair distribution function, Phys. Rev. Lett. 112, 125501 (2014).
5. Christopher L. Farrow, Chenyang Shi, Pavol Juhas, Xiaogang Peng and Simon J.L. Billinge, Robust structure and morphology parameters for CdS nanoparticles by combining small angle X-ray scattering and atomic pair distribution function data in a complex modeling framework, J. Appl. Crystallogr. 47, 561-565 (2014).
6. F. Bridges, T. Keiber, P. Juhas, S. J. L. Billinge, L. Sutton, J. Wilde and G. R. Kowach, Local vibrations and negative thermal expansion in ZrW_2O_8, Phys. Rev. Lett. 112, 045505 (2014).
7. D. Prill, P. Juhas, M. U. Schmidt and S. J. L. Billinge, Modeling pair distribution functions (PDF) of organic compounds: describing both intra- and intermolecular correlation functions in calculated PDFs, J. Appl. Crystallogr., (accepted 2015)

Milestones for Next Year:

In the upcoming year we will:

1. Submit a paper describing the Diffpy-CMI concept and software execution
2. Submit a paper describing the discoveries coming from the SC14 data demo on local structure of CdSe nanoparticles
3. Release a PDF peak fitting program and submit a paper describing it
4. Submit a paper describing modeling of intra and inter molecular correlation functions from molecular materials
5. Submit a paper describing the discoveries made on Au nanoparticles
6. Release a paper describing an ad hoc method for extracting differential anomalous PDFs from x-ray scattering data
7. Release the software and submit a paper describing the PDFmorph program for comparison of similar PDFs measured at different temperatures
8. Release a paper describing our first attempts at Bayesian modeling of structural models from PDF data (a reach goal).

Inter-Individual Variation in Radiation-Induced Epigenetic Modifications and their Potential Impact on Carcinogenesis

LDRD Project # 12-012

P. Wilson

PURPOSE AND APPROACH:

The goal of this project was to assess impacts of epigenetic modifications in human normal and tumor cells *in vitro* following photon and charged particle irradiation in terms of DNA repair capacity, cell survival, and translation to higher risks of carcinogenesis and other IR-associated disease endpoints. Our group previously showed that inter-individual genetic variation in DNA damage response (DDR) pathways, *e.g.*, post-translational modifications (PTMs) of DDR chromatin proteins, directly impacts radiosensitivity of primary fibroblast strains particularly after low dose/dose-rate exposures. Here we investigated whether three histone deacetylase (HDAC) inhibitors SAHA (vorinostat), M344 and PTACH impacted DNA damage induction/ processing, cell killing, and transformation (acquisition of anchorage-independent growth in soft agar) following gamma ray and light ion irradiation. Treatment of NFF28 normal fibroblasts (representing normal tissue stroma), U2OS osteosarcoma, A549 lung carcinoma, and U87-MG glioma cells with 5–10 μM HDAC inhibitors 18 h prior to cesium-137 gamma ray irradiation uniformly resulted in significantly delayed/impaired clustered DNA damage and double-strand break (DSB) repair processing and significant radiosensitization by clonogenic survival assays. HDAC inhibitor-treated cells were then irradiated with 200 MeV protons, 290 MeV/n carbon ions or 350 MeV/n oxygen ions at the NASA Space Radiation Laboratory (NSRL) to assess the same cellular endpoints. Unlike uniform gamma ray radiosensitization, effects of the HDAC inhibitors were unexpectedly cell type and ion species-dependent, with the charged particle irradiations showing significantly enhanced fibroblast cell survival and transformation. The results of these *in vitro* studies cast serious doubt on the efficacy of HDAC inhibitors for improving hadron radiotherapy, unlike their proven utility for standard electron-based radiotherapies. In the future, we plan to seek National Institutes of Health (NIH) funding to confirm these findings in an immunodeficient tumor xenograft model, perform clinical Spread-Out Bragg Peak ion irradiations, and test more promising charged particle radiosensitization strategies.

TECHNICAL PROGRESS AND RESULTS:

The following is a brief summary of our results for FY 2014.

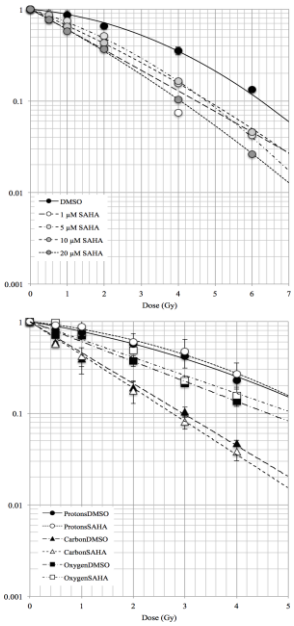


Figure 1 Survival (mean ± SEM) of A549 lung carcinoma cells treated with SAHA/vorinostat or DMSO (drug vehicle control) 18 h prior to irradiation with ^{137}Cs γ-rays (top panel) or 200 MeV protons, 290 MeV/n carbon ions, and 350 MeV/n oxygen ions (bottom panel). Dose-dependent relative biological effectiveness (RBE) values are listed in the table below for doses of 10–400 cGy, and the table on the following page shows radiosensitization ratios for the various HDAC inhibitor/radiation combinations. Significant normal fibroblast ***sparing*** following carbon or oxygen ion irradiation was an entirely unexpected result given the ~1.3-fold radiosensitization at therapeutic doses observed following gamma irradiation, and may limit the utility of HDAC inhibitors for hadron radiotherapy. Radiosensitization was noted for lower proton and oxygen ion doses (*e.g.*, 50 cGy) suggesting ***lower doses per fraction*** could be equally (or possibly more) effective than higher doses for tumor cell killing; HDAC inhibitors were ***ineffective*** for the carbon ion irradiations.

Cell Line	Relative Biological Effectiveness (RBE)[a]		
	200 MeV p	290 MeV/n ^{12}C	350 MeV/n ^{16}O
NFF28 (NHDF)	0.70–1.04	1.29–2.19*	1.42–2.53*
A549 (lung carcinoma)	1.17–2.47*	2.12–8.64*	1.48–5.23*
U2OS (osteosarcoma)	0.78–1.12	1.55–3.37*	1.40–2.00*
U87-MG (glioma)	0.71–0.90	1.60–2.49*	1.54–2.36*

[a] Determined from weighted least-square regression analysis-derived LQ survival curve parameters.
* RBE values highest in low dose region (≤50 cGy); inverse correlation with dose.

Cell Line	HDACi	HDAC$_i$ Sensitization Ratio[a]			
		^{137}Cs γ	200 MeV p	290 MeV/n ^{12}C	350 MeV/n ^{16}O
NFF28	10 μM SAHA	1.24–1.83*	0.87–1.20	0.69–0.76	0.65–0.68
(NHDF)	10 μM M344	1.18–1.71*	1.16–1.41*	0.62–0.84	0.58–0.67
	5 μM PTACH	1.19–2.56*	1.14–1.42*	0.72–0.84	0.51–0.63
A549	10 μM SAHA	1.39–4.16*	0.66–0.96	0.86	0.27–1.13
(lung carcinoma)	10 μM M344	1.36–3.90*	0.93–1.10*	0.95	0.11–1.34
	5 μM PTACH	1.30–4.31*	0.04–0.81	0.83	0.66–1.03
U2OS	10 μM SAHA	1.20–1.75*	0.98–2.30*	0.40–1.07	1.11–1.64*
(osteosarcoma)	10 μM M344	1.11–1.35*	0.96–1.54*	0.38–1.08	1.18–1.57*
	5 μM PTACH	1.02–1.05	0.92–1.32*	0.04–1.23	1.07–1.53*
U87-MG	10 μM SAHA	1.27–1.82*	1.11–1.31*	0.88	0.89–1.19
(glioma)	10 μM M344	1.26–1.46*	1.09–1.65*	1.19	1.13
	5 μM PTACH	1.27–1.76*	1.25–2.27*	1.19	0.95–1.39

[a] Determined from weighted least-square regression analysis-derived LQ survival curve parameters.
* Sensitization highest in low dose region (≤50 cGy); inverse correlation with dose.

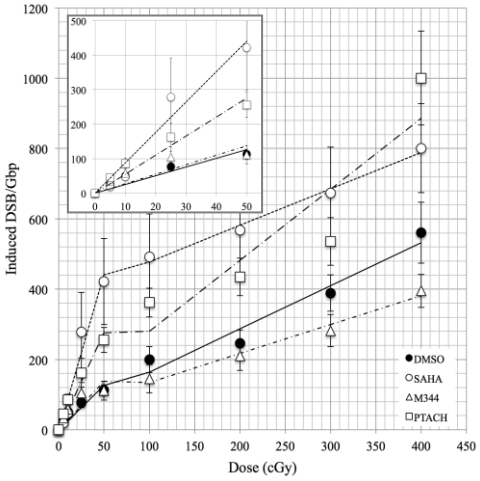


Figure 2 DSB induction in quiescent G0/G1-phase NFF28 normal fibroblasts (mean ± SEM) treated with 10 μM SAHA or M344, 5 μM PTACH or 0.2% DMSO after 200 MeV protons measured by contour-clamped homogeneous electric field gel electrophoresis. DSB induction after 5–50 cGy doses (see inset) was 8.5, 3.3, 2.7, and 2.1-fold higher respectively compared to 100–400 cGy. DSB induction levels for 100–400 cGy (following the low dose increase) were similar for all treatments, with SAHA yielding 2–3.5-fold higher DSB induction than DMSO.

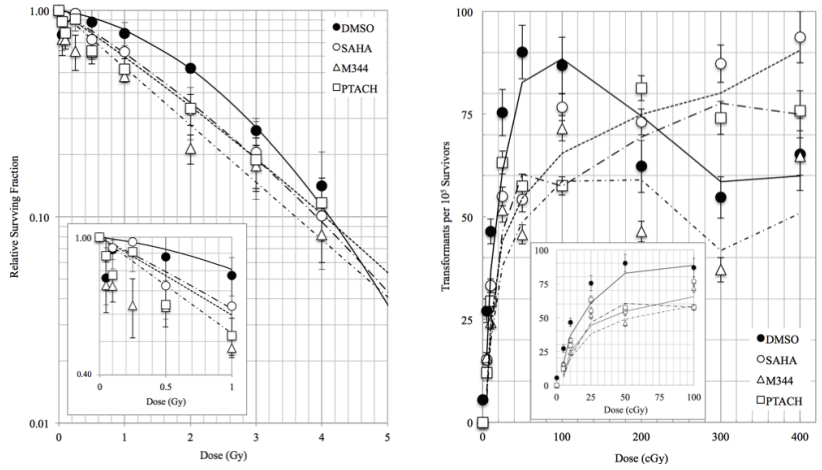


Figure 3 Left panel. Survival of log-phase NFF28 fibroblasts treated with 10 μM SAHA or M344, 5 μM PTACH or 0.2% DMSO (drug vehicle control) 18 h prior to irradiation with 200 MeV protons. HDAC inhibitor treatment resulted in significant radiosensitization similar to G0/G1-phase cultures. Inset shows low dose hyper-radiosensitivity for doses of 5–50 cGy. **Right panel.** Frequencies of anchorage-independent NFF28 fibroblast transformants per 10^5 surviving cells for the three HDAC inhibitors following 200 MeV proton irradiation. Inset shows a rapid increase in transformation for low doses of 5–50 cGy with the HDAC inhibitor treatments resulting in significantly lower transformation compared to DMSO-treated cells. For higher doses >200 cGy, both SAHA and PTACH treatment resulted in significantly increased transformation compared to M344 and DMSO-treated cells. Similar patterns were observed for 290 MeV/n carbon ion irradiation, although measured transformation frequencies were ~50% higher for doses ≥100 cGy (low dose transformation frequencies for the carbon ion irradiations were similar to protons).

For the third and final year of this LDRD, we had continued scientific successes due in large part to the efforts of the team's two lab technicians Alicia Johnson and Paula Bennett, associate scientist Dr. Deborah Keszenman, and student interns from the DOE Science Undergraduate Laboratory Internship/Community College Internship programs: Katherine Sanidad, Lucia Kolodiuk, Benjamin Daniels, Jonathan Millings, and Leonard Chavannes. Several 2015 publications are currently being prepared detailing our results, as well as proposals to NASA and NIH to further explore these findings in an appropriate *in vivo* rodent model system (*e.g.*, U87 tumor xenograft model) and to identify more promising charged particle radiotherapy strategies.

Developing an Integrated Atmosphere-Ecosystem Model for Investigating Interactions Between Atmospheric System and Ecosystem Under a Warming Climate

LDRD Project # 12-015
W. Wu, A. Rogers

PURPOSE:
The goal is to develop an integrated model for investigating the interactions (feedbacks) between the atmosphere and land-surface ecosystems under a warming climate**.** As the Earth's surface temperature and atmospheric CO_2 concentration increase, both the surface and atmospheric energy (i.e., radiation, latent heat and sensible heat) and water vapor fluxes will change, which will in turn influence climate patterns including cloud and radiation properties (e.g., cloud amount and optical depth), seasonal rainfall patterns, and ecosystem responsive behaviors such as photosynthesis and stomatal conductance**.** However, how the coupled atmosphere-land-surface-ecological system responds to the warming climate is still poorly understood. This project seeks to advance our understanding of the response of the coupled atmosphere-ecological system to the warming climate by developing an integrated coupled atmosphere-land-surface-ecological system. The success of this work will advance our capability for climate prediction and enhance our capabilities for climate-land-surface-ecosystem modeling. This will give BNL a significant edge in competing for funding in Department of Energy (DOE) modeling and ecosystem focused programs.

APPROACH: Climate studies have indicated large uncertainties in current climate models, associated mainly with the representation of atmospheric cloud-radiation-precipitation processes. The interactions between the atmosphere and land-surface ecological system (essential for the cloud-radiation-precipitation processes) are likely the culprit of regional climate variations over land. It is thus needed to advance our understanding on atmosphere-land-surface-ecosystem interactions. The scope of the investigation includes: 1) the impacts of soil moisture and vegetation on convection and severe weather under the current climate and a warming climate; 2) the interactions between atmospheric cloud-radiation processes and ecosystem processes under a warming climate; 3) the impact of urban anthropogenic heating to regional climate variations over the Northeastern U.S.; 4) the important processes linking the coupled climate-ecological system such as the photosynthesis process and their optimal parameterizations. The methods employed to carry out the work are: 1) using and adjusting current existing coupled Weather Research and Forecast (WRF) and Community Land Model (CLM) for the investigations; 2) using observations and theories to improve the effectiveness of relevant model parameterizations. The collaborators are: 1) Thomas W. Collow, Mark A. Miller, and Alan Robock (Rutgers University); 2) Luis Ortiz Uriarte and Jorge Gonzalez (the City College of New York (CCNY)).

TECHNICAL PROGRESS AND RESULTS: Research collaborations with Rutgers University and CCNY were established in performing this project. A senior Ph.D. student (Thomas W. Collow at Rutgers University) has been working on the impacts of soil moisture and vegetation on convective severe weather, using the current existing coupled WRF and CLM model. A paper, entitled "Influences of soil moisture and vegetation on convective precipitation forecasts over the United States Great Plains" has recently been published. A major finding is that vegetation changes have a greater impact on precipitation than soil moisture changes and removal of vegetation produced substantial drying (Table 1). Collow graduated in May 2014, and now is a

Research Scientist at the National Oceanic and Atmospheric Administration Center for Weather and Climate Prediction in Maryland. A new facility has been established at BNL, including workstations and a computer server; software includes the WRF and CLM coupled model. Another senior Ph.D. student (Luis Ortiz Uriarte at CCNY) used the facility to model urban effects on regional climate over the U.S. Northeast, during his 2014 BNL summer internship. Two new papers on urban-regional-climate interactions are now in preparation. In addition, we co-organized a workshop with CCNY in April 2014 on *Developing a Strategy to Advance Our Understanding of the Urban Environment and Its Impact on Local and Regional Weather and Climate.* Dr. Rogers organized a *New Phytologist* sponsored workshop on Photosynthesis and Earth System Models in the spring of 2014. Furthermore, we have also conducted studies to examine decadal cloud variations and model parameterizations on photosynthesis linked to carbon absorption. Two papers based on these have recently been published, led by the Principal Investigator (PI) and Dr. Rogers, respectively. Based on research accomplishments and facilities built through this project, the PI has been involved in writing and submitting several white papers and (pre-) proposals, including a DOE Early Career Proposal *A Novel Approach to Understanding and Predicting Land-Atmosphere Feedbacks*, for advancing predictive understanding of key processes in controlling multiscale land-atmosphere feedbacks.

Table 1. Mean total precipitation (mm) for all cases for each vegetation and soil moisture configuration over the area investigated[1]. The number on the left is for the run with no soil moisture change and the right for the run with observationally-based adjusted soil moisture (indicated as +0.10). Time is from 18 Coordinated Universal Time (UTC) the first day through 06 UTC the next day.

Case	Control Vegetation |+ 0.10	Forested Vegetation |+ 0.10	Barren Vegetation |+ 0.10	National Centers for Environmental Prediction Obs.
Apr. 26-27, 2009	13.16 | 13.12	14.29 | 14.34	10.49 | 10.71	13.88
May 10-11, 2010	2.59 | 2.77	3.83 | 4.28	1.05 | 1.10	6.17
May 19-20, 2010	10.78 | 11.20	10.28 | 10.21	8.41 | 7.94	9.98
May 24-25, 2011	6.16 | 7.76	9.44 | 10.107	3.06 | 3.74	11.81
April 14-15, 2012	3.52 | 3.75	3.19 | 4.03	1.97 | 2.37	4.03

[1] Collow, T. W., A. Robock, and ***W. Wu***, 2014: Influences of soil moisture and vegetation on convective precipitation forecasts over the United States Great Plains, *J. Geophys. Res. Atmos.*, 119, 9338–9358, doi: 10.1002/2014JD021454.

Conical Slit for Probing Buried Micron or Sub-Micron Volumes for Dynamic Measurements of Heterogeneous Materials

LDRD Project # 12-018
N. Bouet, E. Dooryhee, S. Ghose, R. Conley

PURPOSE:
Depth resolution in x-ray diffraction experiments is traditionally provided by a cross-beam technique with insertion of slits or pinholes in both the incoming and diffracted x-ray beams. This LDRD intends to design, fabricate and test a complete conical slit system, with openings along the diffracting cones of the sample which will allow unprecedented micron accuracy while using the unique BNL expertise and capabilities with deposition and etching processes. The goal is to surpass the performance of existing slit systems whose smallest slit opening typically is 20-25 microns. The scope of the project is the design, deposition, and etching of the slit followed by a holder design which allows the 5 degrees of freedom necessary to properly align the slit. Experiments on proof of principle and scientific case studies in the area of energy materials are performed.

The ultimate objective of this LDRD is to open this technique into a new area of research at the National Synchrotron Light Source II (NSLS-II), as well as at other synchrotron facilities around the world. The conical slit will enable 3D mapping of the strain tensor, crystallographic orientation, and structural refinement of all grains or sub grains in the defined volume, or the average within the volume, for highly deformed or extremely fine-grained samples (<20 nm). In-situ experiments are important as a function of temperature, strain, or field to follow dynamic processes. Since the properties of many functional materials are strongly influenced by the local nanostructures and heterogeneities, an in-situ study following the buried 3D local dynamics at a micron to sub-micron length scale could dramatically increase the understanding of the processes. In particular, mapping the changes in phase composition, crystallography, and strain state at interfaces and triple phase boundaries could help correlate local nanostructure to properties, leading to new insights in the processing of strategically important classes of materials.

APPROACH:
Depth resolved diffraction experiments can be used to nondestructively investigate local structural features or select diffracted x-rays from regions of interest in heterogeneous or multicomponent material systems. Earlier methods of depth resolution involved pinholes or wires, placed between the sample and detector, which were scanned through diffracted x-rays to probe particular gauge volumes or regions of interest in the Debye-Scherrer diffraction geometry. More recently, a conical slit was developed to rapidly measure specific diffraction cones from a gauge volume of the sample. First developed at RisØ National Laboratory in Denmark, it comprises a set of conical openings positioned in accordance with the Debye-Scherrer rings of the phase to be investigated. Diffracted rays are transmitted through the slit if and only if they originate from a three dimensional gauge volume, defined by the beam size and slit opening size. To operate the slit with high energy x-ray photon beams (up to 70 keV), the challenges are the very low diffraction angles and the manufacturing of a very dense material which is effective enough to block hard x-rays. Wire electro-discharge machining of high Z metals (tungsten) was used to fabricate the slits. Such a process could not create features below 20 microns in size. To reach smaller feature and smaller gauge volume, we developed a spiderweb slit design which

consists of two spatially separated stacks of thin absorbing plates which performs similarly to a conically shaped aperture through a single thick plate, provided either stack of plates can sufficiently absorb diffracted x-rays. This unique design involving stacks of thin plates enables many fabrication techniques that can only be applied to thin plates, such as laser micromachining, electroplating, or photolithography combined with reactive ion etching. These fabrication techniques enable far more intricate designs as well as capability to produce smaller features, reducing the gauge volume probed.

TECHNICAL PROGRESS AND RESULTS:
Milestones achieved during FY14 are as follows:

- Identified and collaborated on x-ray powder diffraction experiments at the National Synchrotron Light Source (NSLS) with research groups who will benefit from the new spiderweb slits: with Simerjeet Gill on "In-Situ corrosion study of zircaloy materials" and with Lynne Ecker on "Investigation of structural changes induced by irradiation in steel alloys". Both are in the Nuclear Science and Technology Department at BNL.
- Refined our ray tracing program to evaluate requirements on slits designs, dimensions and placement with respect to gauge volume of interest and energy of the x-rays.
- Fabricated a prototype using both NSLS-II optics laboratories and the Center for Functional Nanomaterials nanofabrication facility (proposal #32501).
- Integrated the slit system in NSLS X17A beamline set-up.
- Fabricated and tested an optimized version of the slits (based on the results and ease of integration to the beamline of prototype 1) for implementation at the NSLS-II X-ray Powder Diffraction beamline.
- Tested and demonstrated capabilities of the spiderweb slits at NSLS X17A.
- Demonstrated the slits' performance in several science case studies, including in-situ measurements. The experiments were conducted at the Advanced Photon Source.

In-Situ Transmission X-Ray Microscopy Studies of Structure and Function in Energy Storage

LDRD Project # 12-021
J. Wang

PURPOSE:

Lithium-ion batteries are based on insertion/extraction reaction chemistry. All these materials, when subjected to the insertion and removal of lithium ions, undergo structural change that range from minor changes in cell parameters to full-fledged phase transitions or even materials' pulverization. This electrochemically driven structural change directly influences electrode performance in lithium ion batteries. Advancing our understanding of the mechanism necessitates the development of advanced tools with *in operando* capability to track the dynamic phase and structural changes of battery materials. The purpose this project is to develop *in situ*/*in operando* methods to track the electrode materials' behaviors (fundamental electrode reaction kinetics, microstructural evolution, and safety issues) within a working Li-ion battery by using the Transmission X-ray Microscopy (TXM) technique located at beamline X8C (National Synchrotron Light Source – [NSLS]). The innovative research will substantially enhance our understanding of the fundamental mechanisms and stability of battery materials and promote the development of advanced batteries techniques in transportation applications. This project also directly supports the key BNL mission of national energy research. Importantly, this research will develop new *in situ*/*in operando* techniques for energy studies, which will position BNL at a new frontier of energy research.

APPROACH:

This LDRD project will exploit the TXM technique along with *in situ* electrochemistry studies to observe and understand the interior microstructure evolution of these battery materials. TXM imaging with hard X-rays was conducted at beamline X8C of the NSLS at BNL. A field of view of $40 \times 40\ \mu m^2$ with a $2\ k \times 2\ k$ CCD camera was used. To study the chemical state evolution, a full x-ray absorption near-edge spectroscopy (XANES) image series was collected at each charging stage during the delithiation process. The *in situ* and *in operando* TXM imaging was conducted on the assembled coin cell during the charge/discharge process. The *in situ* electrochemical measurements were performed on a versatile multichannel potentiostat. Charge-discharge characteristics were therefore galvanostatically carried out and correlated to structural/morphological/chemical changes. This multidisciplinary approach leads to a key evolution-property-performance correlation for these battery materials in lithium-ion battery systems.

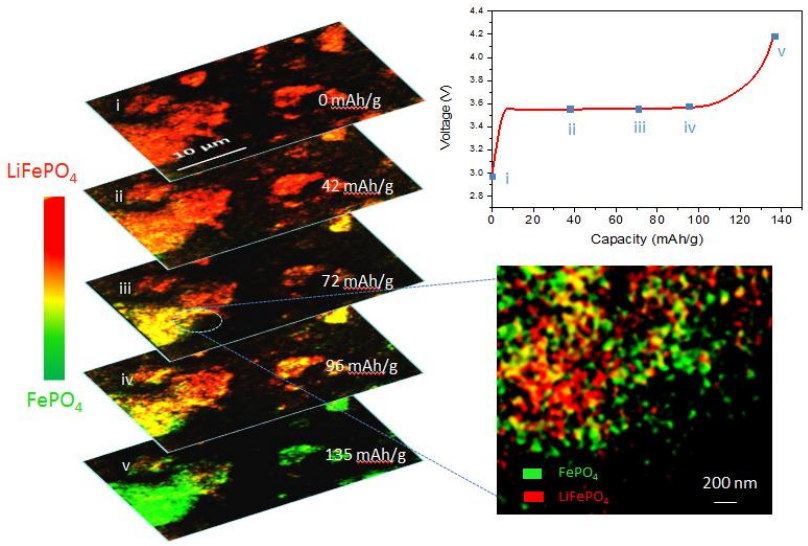
TECHNICAL PROGRESS AND RESULTS:

An electrochemical cell that can fully represent a working battery but that is also compatible with the TXM working distance requirement is the key for *in situ* TXM nanotomography measurements. To develop such a working cell is challenging. We have overcome these challenges, and for the first time, presented a non-destructive *in situ* 3D x-ray nanotomography study for Sn, a typical anode battery material. Severe microstructural changes occur during the first delithiation and the subsequent second lithiation, after which the particles reach a structural equilibrium with no further significant morphological changes. This reveals that initial delithiation and subsequent lithiation play a dominant role in the structural instability that yields mechanical degradation. This *in situ* 3D quantitative analysis and visualization of the

microstructural evolution on the nanometer scale by synchrotron X-ray nanotomography should contribute to our understanding of energy materials and improve their synthetic processing. This work was published in *Angewandte Chemie International Edition* (2014, 53, 4460-4464), a top chemistry journal.

Tracking the phase transformation process at nanoscale resolution during battery operation (*in operando*) provides invaluable information for tailoring the kinetic barrier to optimize the physical and electrochemical properties of battery materials. Using hard X-ray microscopy—which offers nanoscale resolution and deep penetration of the material and takes advantage of the elemental and chemical sensitivity—we successfully developed an *in operando* approach to track the dynamic phase transformation process in olivine-type lithium iron phosphate, a promising cathode material for electric vehicle applications. This *in operando* approach opens up unique opportunities for advancing high-performance energy materials. This work was published in *Nature Communication* (2014, 5, 4570.) Another paper is under review in *Nature Communications* now.

In addition, with the unique capability of TXM, we also confirmed the existence of a new surface phase on the surface of carbon coated $LiFePO_4$. The understanding of this new phase allows further improvement in materials synthesis and manufacturing process for advanced battery materials. This work was also published in *Nature Communication* (2014, 5, 3415.).



In operando 2D chemical mapping of a multi particle lithium iron phosphate cathode during fast charging (top to bottom). The called-out close-up frame shows that as the sample charges, some regions become completely delithiated (green) while others remain completely lithiated (red). *Nature Communication* (2014, 5, 4570.)

MeV-UED for Ultrafast Science

LDRD Project # 12-022

X.J. Wang, J. Hill, Y. Zhu

PURPOSE:

The recent development of ultrafast imaging and diffraction opened a new frontier for studying structural dynamics at nanoscales. It has become one of the key directions for future electron microscopy as concluded by the recent Department of Energy Office of Basic Energy Sciences report [1]. Ultrafast electron microscopy combines the superior spatial resolution of conventional electron microscopy with short electron pulses enabling the detection of electronic and atomic motion on their natural time and lengths scales. The purpose of this LDRD is to develop a relativistic MeV-UED (ultrafast electron diffraction) instrument at BNL to achieve unprecedented temporal resolution and source brightness for the studies of structural dynamics and transit phenomena. During the period of this LDRD, we have successfully tested and optimized the system. The system is currently in full operation. The success of this LDRD has laid a solid foundation for a future ultrafast science program at BNL. A few proposals for future funding have been submitted.

APPROACH:

Among the state-of-the-art electron sources, only photocathode RF guns developed for x-ray free electron lasers such as the Linac Coherent Light Source at Stanford, are capable of generating $>10^7$ electrons per pulse, multi-MeV energy and sub ps-short electron beams. The distinct merit of photocathode RF guns is the very high acceleration gradient (>100MV/m), over two-order of magnitude higher than 200KeV DC-guns. It enables us to considerably minimize the electron-electron repulsion effects, which can be scaled as inversely proportional to the product of the square of the velocity and the cube of the energy of the electrons, thus yielding much higher current density from the cathode and significantly improving beam brightness by at least the same amount. Taking advantage of the time-dependent electric field, bunch compression inside the RF gun could also lead to even shorter electron beam bunches. One of the major challenges in realizing the MeV-UED potential is whether MeV-UED is capable of producing the diffraction quality required to address major challenges in ultrafast science. Another issue facing MeV-UED is the timing-jitter between the electron beam and pump laser. The goal of the BNL MeV-UED is to demonstrate high-quality electron diffraction with a 100 fs time resolution, and to develop a world-class ultrafast science program focusing on transient structural dynamics in strongly correlated electron systems. This LDRD is a collaborative effort between the BNL Photon Sciences and Basic Energy Sciences Directorates. External collaborations with researchers from Shanghai Jiao-Tong University, China and Florida State University were also included.

TECHNICAL PROGRESS AND RESULTS:

After successfully commissioning the MeV-UED setup, we have tested a variety of samples to evaluate the system performance and verified that we have achieved the source brightness of 10^4 electrons per pulse and temporal resolution of 120fs. The timing jitter between the pump laser and probe electron beam was experimentally investigated using a RF deflector. By measuring the electron beam centroid position, we concluded that the timing jitter is less than 100 fs. Here we present two case studies on photoinduced structural dynamics of the charge-density wave (CDW) state in 2H-$TaSe_2$ (left panel of Fig. 1) and the charge-orbital ordered state in bi-layered $LaSr_2Mn_2O_7$ (right panel of Fig. 1) at 77K using MeV-UED. By simultaneously tracking both the

melting of the periodic lattice distortion (PLD) associated with the CDW and the lattice heating, following an impulsive photoexcitation, the separate contributions of electronic excitation and lattice thermalization to the melting process are disentangled in the time domain. Distinct time-constants, reflecting the corresponding individual dynamics of the electronic and lattice systems, are observed. Our results demonstrate, for the first time in 2H-$TaSe_2$, that the PLD is first suppressed promptly by the electronic excitation and scattering, and then subsequently by lattice thermalization through electron-phonon interaction, on a much longer time scale, which leads to the final, full melting of the PLD. For $LaSr_2Mn_2O_7$ our time-resolved electron diffraction study reveals the dynamic path of atoms and ions and indicates that the relative intensity change before and after the photoexcitation of the charge-order (CO) superlattice peaks mostly results from the orbital order (OO). Among various phonon modes, Jahn-Teller distortion dominates the OO process and the CO plays a minimal role during the electronic excitation. Our study shed light on the various and often intertwined degrees of freedom and their responses to external perturbations in strongly correlated electron systems.

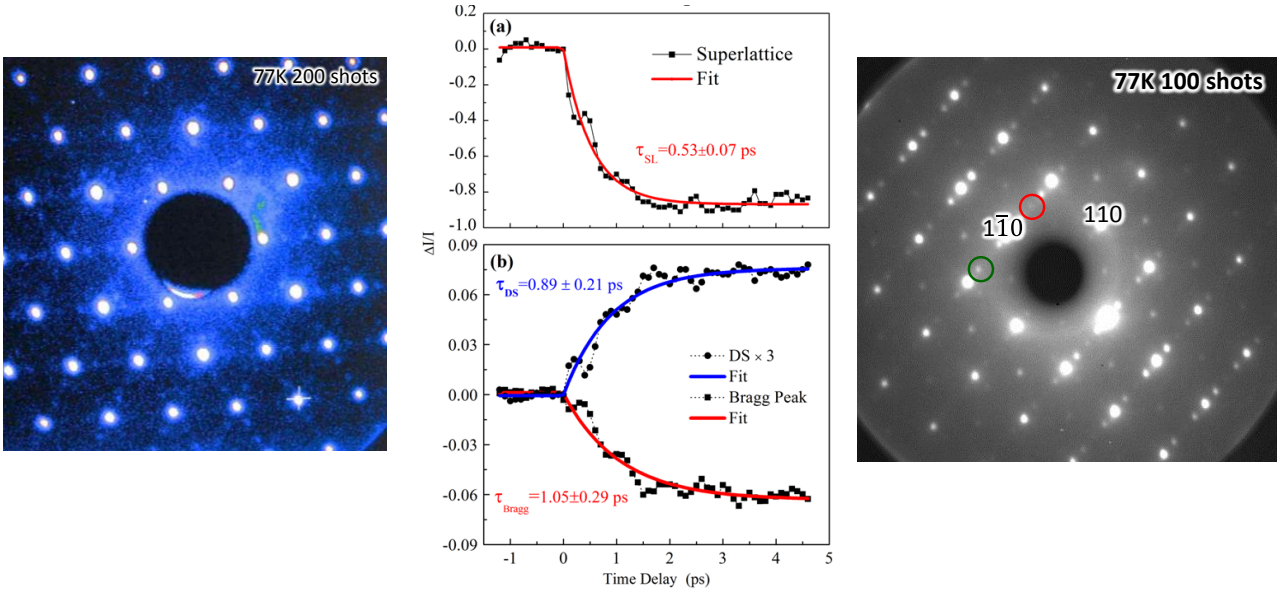


Fig. 1 Photoexcitation induced MeV UED diffraction data from: (left panel) CDW state in 2H-$TaSe_2$; (right panel) Charge ordered state (marked by the red circle) and the orbital ordered state (marked by the green circle) in $LaSr_2Mn_2O_7$. (Center panel): temporal evolution of the CDW peak (a) and the Bragg peak and diffuse scattering intensity (b) in 2H-$TaSe_2$. For clarity, the change of diffuse scattering intensity is multiplied by 3. The pump was a 795 nm optical pulse at a fluence of 1.4mJ/cm^2. The solid lines with given time constants are fits to the experimental data using an exponential function.

[1] http://science.energy.gov/bes/news-and-resources/reports/

MAJOR MILESTONES:

- FY2012: demonstrate high quality electron diffraction
- FY2013: 10 Hz operation; performing time-resolved experiments
- FY2014: improve the time resolution below 100 fs, publish research journal articles, and seek funding for MeV UED operation.

Femto-second X-ray Pulse Generation by Electron Beam Slicing

LDRD Project # 12-023
L. Yu, T. Shaftan, F. Willeke

PURPOSE:

We plan to investigate femto-second x-ray pulse generation in a storage ring by electron beam slicing. When a short electron bunch from a linac (5MeV, 100pC, 100fs) passes above a storage ring bunch (30 ps), it kicks a slice (150fs) vertically. The radiation from the short slice is separated from the core bunch. The new method may be used to create an ultra-short x-ray pulse in storage rings. There is a strong user interest in ultra-short x-ray pulses.

The new method has many advantages when compared to other schemes. It needs a much smaller space in a storage ring for the interaction point, compared with a crab cavity, as used in the Advanced Photon Source upgrade. The pulse length (150fs) is much shorter than the crab cavity method (1-2ps). The flux per pulse may be increased significantly compared with laser slicing (by a factor of 6-10). The repetition rate can be many orders of magnitude higher than laser slicing (about 100 kHz -1 MHz, compared with 1-10 kHz). Compared with the Linear Coherent Light Source, there is a 10^2~10^3 order of magnitude higher repetition rate and the output is much more stable. The success of this study provides a solid basis for developing a program to build an electron beam slicing beamline at the National Synchrotron Light Source II (NSLS-II) for femto-second x-ray pulse generation.

APPROACH:

After our previous study of the possibility of generating femto-second x-ray pulses in the NSLS-II ring, we realized some disadvantages of the method of laser slicing: it takes two straight sections at least, the number of photons per shot is only a few thousands within 1% of the bandwidth, the repetition rate is limited to 1 kHz, etc. Ferdinand Willeke's method of electron beam slicing is attractive from all of these points of view, but it needed an extensive feasibility study in order quantify its advantages over laser slicing.

Clearly we need to study the brightness of this new method first by analytical work then by simulation. Then we need to study how to generate the short electron bunch focused to under 50 micron size and compressed to 100 fs, and simulate the compressor to achieve this. Then we need to study the design of the x-ray beamline for the electron beam slicing to see if there is sufficient separation from the much longer core pulses in the ring. Finally we need to study the realization of the method in the NSLS-II ring to find the appropriate lattice structure for the slicing.

Thus we need to derive an analytical method to analyze the slicing process and study how to design a compressor under the condition dominated by space charge, and how to apply codes such as PARMELA and IMPACTT to study the compressor design. We need to learn how to use the beamline design code developed by O. Chubar. We also need to learn the details of the NSLS-II lattice and its dynamics. For these, we have collaborated with J. Qiang, J. Corlett, O. Chubar, and W. Guo. Our postdoc An He contributed significantly to the success of the work. The other collaborators include L. Yang, T. Shaftan, G. Wang, Y. Li, and Y. Hidaka and many others.

TECHNICAL PROGRESS AND RESULTS:

As a first step in the development of the new method, in this LDRD proposal**,** we have confirmed the feasibility of electron beam slicing using low energy: we designed and simulated a low energy compressor and showed it is possible to focus a 5 MeV electron bunch into a 30 micron beam size and 150fs bunch length, as required by the electron beam slicing method. This provides a solid reference point for the next step, the design of an electron beam slicing beamline at NSLS-II.

As the second step, we then studied the performance of electron slicing on NSLS-II, showing that it is possible to achieve the required separation of the thin slice high energy electrons from the core electrons, and the significant increase of separation and reduction of the bunch length of the slice, when the linac bunch energy is increased from 5 MeV to 12 MeV. We studied the method to reduce the slice bunch length by angled crossing, showing it is possible reduce the bunch lengthening without significant loss of kick angle; this makes it possible to reduce the bunch length to 100fs. This study clarified the importance of the phase advance between the crossing point and the radiator, and the importance of the machine functions at the crossing point. We also calculated the limit on repetition rate if we have only one crossing point to be about 100 kHz to 1 MHz. Hence the repetition rate is lower than the crab cavity method which is on the order of 500 MHz, even though electron beam slicing can generate a much shorter pulse length using a much shorter space in the storage ring.

To be able to increase the repetition rate significantly, we consider using a second crossing point to remove the angular kick after the short x-ray pulse is generated. To realize this, we need to modify the NSLS-II ring lattice to make the two interaction points symmetric to each other. As the next step for electron beam slicing, we propose to study the maximum achievable repetition rate.

During the last half year, we presented and then published the above results in workshops and international conferences such as IPAC13. We then sent the much more detailed analysis to Physical Review for publication. Recently we have received acceptance for the publication of 3 papers in Physical Review:

1. “Ultrashort x-ray pulse generation by electron beam slicing in storage rings”, A. He, F. Willeke, and L. H. Yu, Physical Review Special Topics - Accelerators and Beams 17, 040701 (2014).
2. “Dependence on crossing angle of electron beam slicing in storage rings”, A. He, F. Willeke, and L.H. Yu, accepted for publication in Phys. Rev.
3. “Design of low energy bunch compressors with space charge effects”, A. He, F. Willeke, L.H. Yu, L. Yang, T. Shaftan, G. Wang, Y. Li, and Y. Hidaka, accepted for publication in Phys. Rev.

These papers document our work in great detail, and can be used for future reference and guidance for proposal and development of experimental projects. Thus our work has achieved significant success; it provides a solid ground for next steps for the development of the electron beam slicing project.

Thermochemical Conversion of Biomass to Fuels and Chemicals

LDRD Project #12-024
N. Ofei Mante, S. Babu

PURPOSE:

The purpose of this LDRD project is to identify pathways to evaluate the suitability of commercial and evolving thermochemical conversion (i.e., pyrolysis and gasification) processes to produce efficient and clean forms of renewable fuels and, chemicals and their co-production where appropriate, employing New York State and North East USA biomass materials. The initiative will draw upon the existing know-how in fundamental science to techno-economic and sustainability analysis, in the Biosciences, Chemistry, and Sustainable Energy Technology Departments, and the Center for Functional Nanomaterials. The project should help enhance in-house biomass thermochemical conversion Research and Technology Development capabilities, leading to development of patentable efficient and economical process innovations for commercial applications.

APPROACH:

The primary technical hurdle in biomass pyrolysis includes the production of a wide-range of oxygenates in bio-oil which are unstable and have a low-pH. This LDRD project will extend BNL's catalysts for de-oxygenation, conditioning, and stabilization, while the raw pyrolysis products are still in the gaseous state to produce fungible fuels or high-value-chemicals. In biomass gasification, hot or medium-temperature cleanup of raw product gases is an unresolved technical hurdle for the efficient production of clean synthesis gas. The raw gas contaminants include condensable hydrocarbons (tars), particulates, NH_3, alkali, chlorine and sulfur compounds. The LDRD project will extend BNL's proven expertise with CeO_2 and TiO_2 based nano-structured catalysts to simultaneously reform condensable hydrocarbons, CH_4, and NH_3 in order to produce a clean synthesis gas for subsequent conversion to fuels and chemicals.

SUMMARY OF ACHIEVEMENTS:

A biomass pyrolysis method for the production of hydrocarbon fuel precursors was developed. The process utilizes metal oxide catalyst to make ketonic platform molecules and other monofunctional molecules from biomass which can be used to produce various types of hydrocarbon fuel. Also, a highly selective defunctionalization process was invented to produce bulk chemicals such as phenol, benzene, and toluene from lignin. A provisional patent application was filed in June 2014 for this method. Three research papers were published: one in Green Chemistry Journal (Royal Society of Chemistry) and two in Journal of Analytical and Applied Pyrolysis (Elsevier); these papers focused on understanding the role of biomass composition and the effect of pretreatment on conventional and catalytic pyrolysis of biomass feedstocks. Two abstracts were accepted for oral presentation at the 2014 AIChE annual meeting.

KEY TECHNICAL PROGRESS AND RESULTS:

A new pyrolytic pathway from biomass to hydrocarbon fuel precursors was investigated. The process entailed the conversion of multifunctional oxygenates generated from biomass pyrolysis over a metal oxide catalyst into ketonic-rich monofunctional molecules suitable for making hydrocarbon fuel components for gasoline, diesel, and jet fuel. A number of catalysts were

explored including anatase TiO_2 nanorods, CeO_x-TiO_2 mixed oxides, pure CeO_2, ZrO_2, and MgO. Under pyrolysis conditions, the ceria-based catalysts were effective in the conversion of hydroxy-carbonyls, anhydrosugars, and carboxylic acids into acetone, 2-butanone, pentanones, C6/C7 ketones, cyclopentanone, and 2-cyclopentenones as shown in Figure 1. The highest carbon yield (23.5%) of ketonoic precursors was achieved on the pure CeO_2.

In summary, this investigation demonstrated that it is possible to reform the complex mixture of multifunctional oxygenates generated during biomass pyrolysis over a suitable metal oxide into monofunctional precursors that can undergo further downstream processing such as aldol condensation and hydrogenation for conversion into a wide range of hydrocarbon liquid fuels. The ketonic products are desirable because they have sufficient functional moieties to undergo C-C coupling with each other or other pyrolysis oxygenates into longer chain aliphatic hydrocarbons. Additionally, the simple phenols and the furans are also useful intermediates for forming aromatic hydrocarbons. This demonstrated pyrolytic approach provides a greater degree of flexibility in producing gasoline, diesel, and jet fuels components. The significant finding of the present work is that a variety of pyrolysis oxygenated families (hydroxy-carbonyls and sugars) besides carboxylic acids can be activated to form useful ketonic compounds. Our current results show that not all known active ketonization catalysts reported in the literature are capable of facilitating the formation of ketones even from carboxylic acids under pyrolysis conditions. Among the catalysts tested, we found that ceria-based catalysts are most suitable for the pyrolytic strategy pursued in this work. This suggests that the reducibility of the metal oxide plays an important role in effective conversion of the pyrolysis oxygenates into useful monofunctional precursors. This work opens a new pyrolysis path to renewable fuels or chemicals from biomass.

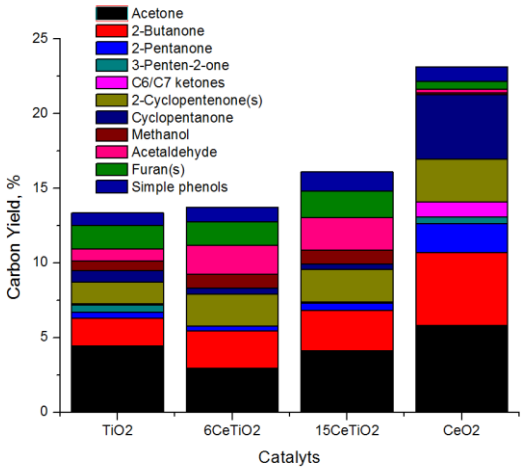


Figure 1 Comparison of the carbon yields of the monofunctional compounds produced from the use of anatase TiO_2 nanopowder, 6%Ce/TiO_2, 15%Ce/TiO_2, and pure CeO_2.

In closing, the findings from these LDRD studies contribute to ongoing research and development in the field of thermochemical conversion of biomass, thus enhancing fundamental understanding of how pyrolysis products from biomass can be altered to produce suitable intermediates for fuels and chemicals.

Flow-Based Battery Architectures for Large Scale Electrical Energy Storage

LDRD Project # 12-025
C. Erdonmez

PURPOSE:

Broadly, the work described here aims to advance knowledge in materials science and electrochemistry of "low-cost" electrochemical couples suitable for grid-scale energy storage. More specific goals of the project are three-fold: (a) demonstrate the adoption of synchrotron methodologies for studying, with greater rigor than before, promising alkaline battery chemistries, (b) establish connections between materials behavior and electrochemical performance, as a function of the chemical and electrochemical environment, (c) use the fundamental understanding derived to start answering scientific questions of engineering relevance and to explore battery designs. Finally, at the most specific level, the battery chemistries chosen for this study are alkaline battery chemistries, i.e. those employing a highly basic aqueous environment, which can be employed in flow-assisted architectures for improvements in reliability and lifetime cost. The project also aims to build up capability at BNL in the areas of flow-assisted and/or aqueous battery systems and in launching collaborations with local institutions in these areas. The synthesis, device fabrication and electrochemical characterization capabilities developed will allow us to develop collaborations with impact, both inside BNL and outside.

APPROACH:

Batteries provide a reliable and energy-dense method of storing energy at small scales, e.g. powering a wide range of portable/personal electronic devices in a sufficiently lightweight and compact form factor. Energy storage at much larger scales using batteries is an attractive proposition and could help adoption of renewable energy sources, as well as lower costs associated with reliable transmission of electricity. The major challenge towards wide adoption of large-scale batteries in such a role is the limited reliability, as well as the relative high cost per energy delivered over their lifetime for batteries. High battery costs, e.g. for the dominant Li-ion technology are driven by multiple factors: scarce active materials, supporting materials required by the selected battery *chemistry* and fabrication of supporting structures required by the *battery* architecture. Flow batteries mitigate some of these concerns through a simplified device architecture, allowing active materials to be stored in tanks and charged and discharged by flow through a reactor. Dominant flow battery technologies, such as vanadium redox or zinc-bromine have other challenges, such as toxicity and continued reliance on scarce active materials. Therefore, this project focuses on materials and electrochemical behavior of systems where solid energy-storing materials can be employed in flow-assisted systems. Particularly, we focus on morphological, structural and chemical evolution of solid-state active materials in flow-assisted electrochemical systems. The bulk of technique development focuses on flow-assisted alkaline batteries where system architecture focuses on converting a non-rechargeable technology into a rechargeable one. A much smaller effort is on studying electrochemical fuels.

The alkaline system is chosen for its potential for deployment, and for allowing studies targeting reliability and performance by multiple advanced materials and electrochemical characterization techniques. Participants in this project provide expertise on synchrotron characterization (Jun Wang, National Synchrotron Light Source) and engineering and electrochemistry in flow-assisted

energy storage technologies (Dan Steingart, Princeton University & Sanjoy Banerjee, City College of New York).

TECHNICAL PROGRESS AND RESULTS:

The project started in June 2012. Therefore, this report refers to progress during months 17 - 29 of the project which fell in FY14. As detailed in previous reports, a number of capabilities had already been developed and a number of initial findings obtained in previous fiscal years. These included the development of flow-capable electrochemical cells and their application to: (a) synchrotron studies of zinc metal electrodeposition both under flow and stagnant electrolyte, (b) *in operando* internal diffraction studies of sealed (non-flowing) alkaline batteries, revealing a number of dynamic aging processes in cycled alkaline batteries, within both the anode and the cathode, (c) *in situ* diffraction study of the most common, low cost alkaline battery cathode (MnO_2), which revealed that specific alkaline electrolyte compositions trigger s structural change which is likely associated with cathode capacity and lifetime improvements.

Progress in the current fiscal year included:

- Quantitative analysis of imaging and diffraction data established more clearly the impact of trace heavy metal dopants in modifying morphology, and this work was published in FY14. Beyond results already established, real time internal diffraction revealed a difference in the sequence of cathode phases formed under discharge than from those published earlier by other researchers; we also used the technique in collaboration with Princeton University to develop and support a new hypothesis, based on formation of percolating rigid ZnO shells on the Zn anode powders, on why alkaline batteries display "bounciness" in drop tests which depend on state-of-charge of the battery. Both of these results have been submitted for publication and one was already recently published in early FY15.
- Further study of the alkaline cathode under differing electrolyte concentrations revealed some complications in data interpretation which delayed the planned publication of an article. In response, we developed and demonstrated the capability to collect *in situ* data and perform Pair Distribution Function analysis on this system. Through a combination of control experiments at the synchrotron and extended electrochemical studies, we eventually established that the most likely mechanism for lifetime extension via the change in electrolyte composition has a very close analogue known from the lithium-ion literature. A new manuscript is under preparation.

Additionally, work on some new directions was also started and has yielded some initial results:

- Study of alkaline cathodes was extended to doped nickel hydroxide cathodes. So far we have demonstrated synthesis of electrochemically active and stable doped nickel hydroxide cathodes.
- Structural (i.e. synchrotron study) of iron oxide anodes in alkaline media as a model for iron electrodes. We have structurally identified the phases that form as a function of particle size (nanoscale vs. micron scale powders) and electrolyte concentration.

FY15 is the final year of the project and in that year, we will:

- Further optimize the MnO_2 and doped nickel hydroxide cathode systems
- Further study the iron oxide anode system as a model system for passivation and efficiency in iron-based anodes
- Undertake evaluation of low-cost battery architectures.

Laser-driven Proton Accelerator

LDRD Project # 12-032

I. Pogorelsky

PURPOSE:

Following the first successful demonstration, realized at BNL's Accelerator Test Facility (ATF), of generating Mega-electron-Volt (MeV) monoenergetic proton beams by focusing a CO_2 laser on a supersonic hydrogen-gas jet, this LDRD project aims at building the foundation of a new approach to develop a future compact, economical ion-source for cancer therapy. The project's objectives include the optimization of the process through gaining a better understanding of the underlying physics and scaling the ion-beam's energy in parallel with implementing new ultra-fast CO_2 lasers techniques at the ATF.

APPROACH:

Hadron (proton or heavy-ion) therapy is an effective way, and the least-invasive one for the radiological treatment of tumors deep within the human body; this is because the hadrons deliver most of their dose precisely at the end of their stopping range, in what is known as the Bragg peak. Applying this advantageous technique presently is hindered by the high cost and complexity of extant hadron-therapy systems based on conventional particle accelerators. Contemporary high-power lasers offer a promising alternative to the conventional approach. The very small size of the laser-driven plasma accelerator, reflecting the enormous accelerating fields that lasers can create (MeV over a micro-meter), means that we can replace the large conventional ion-therapy apparatus by a relatively small arm that moves the laser accelerator around the patient. A typical approach to laser-driven proton acceleration uses a combination of an ultra-intense solid-state laser and a thin-foil solid target. However, this method offers only limited control over selecting the ion beams produced and their spectral purity.

The potential advantages of long-wavelength CO_2 lasers over more conventional solid-state lasers, such as ion-beam drivers, are based on the interplay of several physical parameters, such as the ponderomotive energy conveyed to a charged particle by the laser field ($\sim\lambda^2$), and the critical electron plasma-density ($\sim\lambda^{-2}$). For CO_2 lasers, this critical density, $n_{cr}=10^{19}$ cm^{-3}, easily is achievable in a gas jet that affords good control over the repetition rate and purity of the produced beams. Therefore, combining an ultra-intense CO_2 laser with a gas-jet target offers a unique opportunity for a breakthrough in this research field. This optimism was confirmed by observing the monoenergetic proton beams generated when focusing a CO_2 laser on a supersonic hydrogen-gas jet in the BNL/ATF experiment identified later as the first demonstration of Shock Wave Acceleration (SWA).

The results of this LDRD project support consolidating SWA research under BNL's leadership into a multi-institutional effort aimed at optimizing the laser-driven acceleration process via our gaining an in-depth understanding of the underlying physics, while exploring the relationship between scaling ion-energy and the laser's intensity. This international collaboration includes ATF users from Imperial College (London), and Stony Brook University.

The LDRD funding allowed us to hire and fund (from May 2012 to May 2014) a post-doctoral research associate Dr. Olivier Tresca, a recent Ph.D. graduate from the University of Strathclyde (Glasgow). Dr. Tresca served as a resident-scientist for the experiment, tuning the experimental

set-up for users' runs, maintaining our in-house simulation capability, and actively participating in data collection, processing, and in presenting it. The research under the LDRD concentrated on exploring the importance of special dynamic profiling of the gas density in the jet so as to optimize the generation of shock waves by the high-energy laser pulse.

TECHNICAL PROGRESS AND RESULTS:

Significant progress was achieved in better understanding the SWA physics through simulations and experiments during the earlier year and a half of the project. We elaborated, theoretically and experimentally, the importance of producing a sharp over-critical edge in the gas-jet's transverse density-profile to ensure high efficiency in depositing the laser's energy in a narrow skin layer at the critical plasma-density. This resulted in producing a collision-less electrostatic shock wave that reflects downstream ions at double the velocity of the shock-wave. The desirable distribution of gas density was produced experimentally by our creating a compression blast wave via depositing a calibrated laser pre-pulse that arrived 25 ns prior to the main laser-pulse.

Capitalizing on improvements to the CO_2 laser peak power made at the ATF, the energy of the proton beam was increased to 3 MeV, and furthermore, 2-MeV He+ ion beams also were achieved for the first time.

We studied, in simulations, the temporal evolution of plasma density under irradiation by a low-energy laser's pre-pulse, so to identify the optimum plasma conditions for ion acceleration. The best results were obtained between 2- and 5-ns after irradiating the gas jet with a 100 mJ laser-pulse. This prediction was confirmed in the most recent experiments performed during FY 2014 with the demonstration of better reproducibility in the formation of a blast wave, as illustrated in Fig.1. The results of the research were submitted recently to Physical Review Letters.

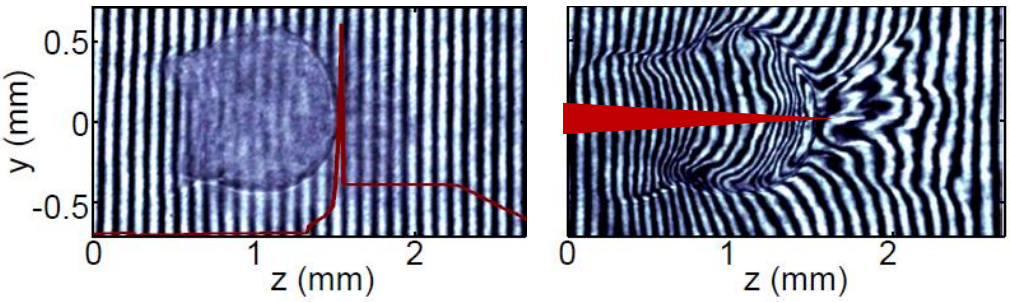


Figure 1 Time evolution of filament formation is observed by optical interferometry. The left image was taken before the arrival of the intense CO_2 pulse, and shows a blast wave imprint, as well as the reconstructed density profile reaching $4n_{cr}$ (shown in a red on a linear scale). The right image was taken 54 ps after the arrival of the intense pulse. It shows strong perturbations at its fringes due to gas ionization, as well as the filamentation of the electron stream originating from the laser's focus (solid red).

In the short time between completion of this project (May 2014) to the writing of this report (January 2015), a spin-off materialized with the expansion of the ATF ion-acceleration collaboration with the Naval Research Laboratory joining our users' group. The blast wave method was improved and new results were obtained and soon are to be published. Furthermore, funds were awarded in June 2014 for an extensive multi-year BNL Project towards constructing a next-generation 100-TW CO_2 laser. Generating therapeutic-quality 100-200 MeV ion beams by the SWA method is the main motivation for this new development.

Water-based Liquid Scintillator Detector for Neutrino and Proton Decay Experiments

LDRD Project # 12-033

D. Jaffe

PURPOSE:

We propose to evaluate water-based liquid scintillator (WbLS) as a detection medium. New techniques developed by the BNL electronic detector and neutrino & nuclear chemistry group for WbLS formulation allow the fraction of scintillating liquid in water to be varied. The primary goal is to measure the WbLS light yield for ionizing particles and the wavelength dependence of absorption and emission of the light. The results will be incorporated into a model for simulation that will allow an assessment of WbLS for potential particle physics experiments such as the search for proton decay ($p \rightarrow K^{+}\nu$) in a large volume detector, improved knowledge of neutrino-nuclear interactions, low energy neutrino detection and dosimetry monitoring.

APPROACH:

Liquid scintillator (LS)-based detectors have demonstrated success in the detection of rare processes such as the discovery of the neutrino, the measurement of the solar and terrestrial neutrino flux, and precision measurements of neutrino oscillations. Compared to LS, WbLS benefits from better material compatibility, lower cost, longer attenuation length and fewer hazards related to the storage of large quantities of chemicals in underground laboratories.

The light yield and optical properties of different formulations were assessed using low energy proton beams at the NASA Space Radiation Laboratory (NSRL) at BNL, Compton-scattered electrons from a ^{137}Cs gamma source, fluorescence and UV-VIS spectrometry, and integrating sphere measurements. WbLS differs from LS in that the scintillation and Cerenkov processes make comparable contributions to the light yield. The relative rate of light production in WbLS is assessed by varying the proton beam energy and the geometrical acceptance of light in prototype detectors. Experimental measurements are used to develop a complete model for accurate simulation. We designed a ~1000 liter prototype detector to assess the capability of a WbLS-based detector to discriminate the distinctive Cerenkov light from isotropic scintillation light.

In addition to the Principal Investigator (PI), collaborators on this work are L. Bignell, a postdoc hired with LDRD funds, M. Diwan, S. Kettell, H. Themann, B. Viren, E. Worcester and C. Zhang of the BNL Physics Department and S. Hans, R. Rosero and M. Yeh of the BNL Chemistry Department. Former postdoc D. Beznosko was a collaborator until July 2013.

TECHNICAL PROGRESS AND RESULTS:

Results obtained in FY2012 show that the light yield scales in an approximately linear fashion with scintillator concentration in WbLS for 0.4 and 1.0% concentrations. Results obtained in FY2013 with a 1% concentration indicate that 58% of the Cerenkov light is absorbed and re-emitted as scintillation light. The analysis and publication of these results were delayed by the departure of D. Beznosko in mid 2013.

L.Bignell performed detailed measurements of the wavelength-dependence of light absorption and emission as well as the quantum yield of the WbLS. These measurements were used to develop a detailed simulation model of Cerenkov and scintillation light production for 1% concentration WbLS that includes the complex, wavelength-dependent effects of absorption and re-emission, and describes the proton beam data acquired in FY2013 and FY2012. The results were presented by L. Bignell at the 2014 IEEE Nuclear Science Symposium and Medical Imaging Conference, 8-15 November 2014 in Seattle, WA. A manuscript for publication is in progress. This detailed simulation model is crucial for reliable predictions of the performance of proposed WbLS applications. We are improving and expanding this model with additional measurements of WbLS properties. The dark box to house the 1000 liter prototype detector was constructed and the detector installed. Commissioning of the detector is in progress.

Encouraged by the results obtained by this LDRD we are pursuing the following new opportunities for WbLS.

1. We (L. Bignell, D. Jaffe, M. Yeh) have entered into a Small Business Innovation Research (SBIR) agreement entitled "An Active Water Phantom for Three-dimensional Proton Therapy Quality Assurance" with PI Steven Vigdor Senior Vice President of Phenix Medical and former BNL Associate Laboratory Director. The SBIR proposal was submitted to the National Institutes of Health in December 2014. If approved, funding is expected to begin in the last quarter of FY2015 and extend through FY2018.
2. We (L. Bignell, D. Jaffe (PI), M. Yeh) were awarded a Technology Maturation grant (TM 14-002) for the proposal “Effect of proton irradiation on water-based liquid scintillator light yield and transparency” in July 2014. Initial results indicate no WbLS degradation at low (~50 Gy) dose. We expect that additional data during NSRL run 15C will allow assessment of WbLS performance with a ~600 Gy dose which corresponds to ~one and a half years of typical dose expected for a WbLS phantom for proton therapy quality assurance.
3. A patent application “Active Water Phantom for Three-dimensional Ion Beam Therapy Quality Assurance” (Inventors: S.E. Vigdor, M. Yeh and D.E. Jaffe) was filed November 2014.
4. A WbLS workshop in May 2014 at Lawrence Berkeley National Laboratory resulted in “Advanced Scintillator Detector Concept (ASDC): A Concept Paper on the Physics Potential of Water-Based Liquid Scintillator”, arXiv:1409.5864 (co-authors: L. Bignell, M. Diwan, S. Hans, D. Jaffe, S. Kettell, R. Rosero, B. Viren, E. Worcester, M. Yeh, C. Zhang). ASDC is envisaged as a ~100 ktonne monolithic detector with a WbLS target surrounded by high-efficiency, ultra-fast photon detectors with high coverage at the Sanford Underground Research Facility in the Homestake mine in South Dakota. The primary physics goals are neutrinoless double-beta decay, solar neutrinos, proton decay and long baseline neutrino physics. A formal research and development proposal is being formulated.
5. We (E. Worcester, D. Jaffe, M. Yeh) are proposing to fill one of Daya Bay’s antineutrino detectors with low radioactivity WbLS to enable a precision measurement of the fundamental quantity $\sin^2\theta_W$ using elastic electron scattering of reactor antineutrinos. This would occur after the termination of the current Daya Bay run at the end of FY2017.

Quantum Electrodynamics for QCD Precision Studies at an EIC

LDRD Project # 12-034
M. Stratmann, E. Aschenauer, H. Spiesberger

PURPOSE:
The main purpose of this LDRD project, which ended in May 2014, was to develop a comprehensive and reliable set of computational tools to control additional photon radiation to a level of precision necessary to meet the objectives of the physics program laid out for a future electron-ion collider (EIC), in particular, the eRHIC project at BNL. Quantum Electrodynamics (QED) radiative corrections affect all measurements with electromagnetic probes and greatly complicate the experimental reconstruction of relevant kinematic variables and, hence, the extraction of vital new information on the structure of nucleons and nuclei. This LDRD project has helped to understand in detail the limitations due to QED radiative effects on key measurements at an EIC. It also helped to initiate several other EIC related projects, which are currently being pursued.

APPROACH:
The key element of devising strategies to systematically unfold QED radiative corrections from the physics observables of interest is the availability of flexible Monte Carlo simulations of additional photon radiation in electromagnetic processes that can be easily merged with programs simulating the detector acceptance and response. The main part of this LDRD project was devoted to develop, verify, and make use of comprehensive software implementations of QED radiative corrections tailored to the needs of a future EIC physics program.

One of the most demanding tasks of the project was the computation of the QED radiative corrections for two-photon processes in measurements of deeply-virtual Compton scattering (DVCS). DVCS is one of the key processes at an EIC to obtain a three-dimensional image of the nucleon structure. To provide missing analytical calculations and turn them into Monte Carlo event generators was one of the milestones for our LDRD project.

The entire project has benefited greatly from having H. Spiesberger from the University of Mainz as one of its investigators. He is one of the few leading experts on simulations of QED radiative corrections. During the course of the LDRD project, H. Spiesberger was able to visit BNL frequently thanks to the availability of sufficient travel funds. The EIC task force at BNL led by E. Aschenauer provided the necessary matching expertise with detector simulations. In particular, the ability to detect the hadronic final-state is critical to reduce QED radiative effects at an EIC but requires a careful detector design.

TECHNICAL PROGRESS AND RESULTS:
The funding for this project concluded at the end of May 2014 after two years of support. A postdoctoral researcher (Martin Hentschinski) was hired in June 2012 for the duration of the project to work mainly on the technically demanding computation of higher-order two-photon processes. He also contributed to several other EIC related studies, which led to publications in peer-reviewed journals.

After developing and exploiting a new event generator for polarized lepton-nucleon scattering in FY 12 and 13 to meet the first of the project's milestones, FY14 was mainly devoted to completing the analytical calculations of two-photon processes in the context of DVCS and to work towards their implementation in a novel event generator package. A first preliminary version of the code at next-to-leading order accuracy was put together in FY14. Before the code can be made publically available and extensive phenomenological studies can be performed, we still need to implement one remaining technical aspect concerning the two experimentally conceivable ways to detect the scattered electron and the unresolved additional photon: (a) they are measured together as a calorimetric "jet" or (b) only the electron is observed in a magnetic field. The latter case is theoretically more complicated as it is not infrared safe. However, there is a known solution available in the literature [S. Dittmaier et al., Nucl. Phys. B800 (2008) 146] to deal with non-infrared safe observables. The implementation of the proposed subtraction algorithm is still a work in progress. We note, however, that first phenomenological studies have revealed several shortcomings in existing codes (available only at leading logarithmic accuracy) such as the MILOU package, which will be fixed in our code.

In mid-March 2014, the Principal Investigator (Marco Stratmann) left BNL to take up a new job at the University of Tübingen, and Raju Venugopalan took the lead for the remainder of the project. The collaboration with the postdoc Martin Hentschinski, who moved from BNL to Universidad Nacional Autónoma de México at the end of FY14, is still very active, and we soon expect to complete and publish a flexible Monte Carlo code for the computation of QED corrections to the Bethe-Heitler process, the major background to DVCS, to meet the final milestone of our LDRD project. We have plans to further expand the developed suite of event generators in 2015 based on the work performed in this LDRD project and in close collaboration with the EIC task force at BNL.

The set of event generators developed during the course of this project was applied in several numerical simulations of deep-inelastic scattering processes at an EIC in FY14. For instance, results were used in the recently completed eRHIC design study and other documents in support of the upcoming Nuclear Science Advisory Committee Long Range Plan.

Investigating eRHIC Beam-Beam Effects with CeC Linear Accelerator

LDRD Project #13-003

V. Litvinenko

PURPOSE:

The proposed future electron-ion collider (EIC) at BNL, eRHIC, is one of the highest priorities for BNL's nuclear-physics program. The high-energy high-luminosity eRHIC is based on a linac-ring scheme, wherein electrons are produced and accelerated in a 20 GeV energy-recovery linac (ERL). The beam-beam effects in such a collider are unknown, and, to date, have been studied only theoretically.

The propose of this proposal to take advantage of the new developing $10M facility – the 22 MeV superconducting linear electron accelerator at the Relativistic Heavy Ion Collider (RHIC) - to study novel ring-linac beam-beam effects, their related instabilities and their suppression, knowledge of which is essential for advancing eRHIC design and performance. This proposal has potential for discovering new phenomena in such a highly-cost-effective novel linac-ring collider.

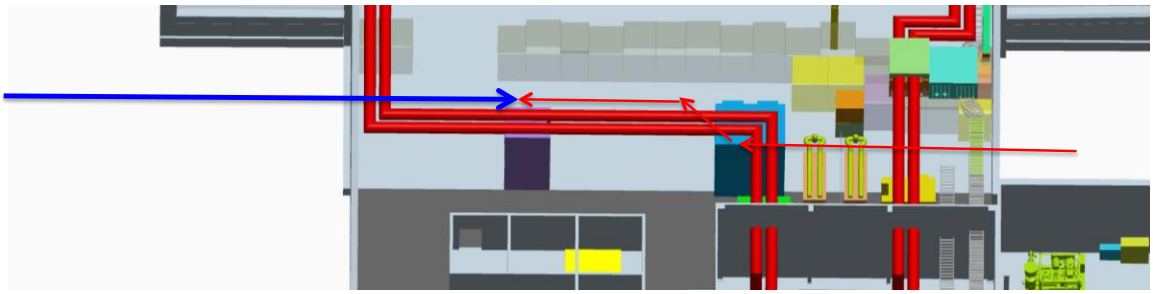


Figure 1 Layout of the experiment: a 22 MeV electron beam from the superconducting linac (red arrow) will collide with the circulating ion beam in the blue RHIC ring (blue arrow).

APPROACH:

We will use the Coherent Electron Cooling (CeC) proof-of-principle (POP) accelerator to supply the electron beam. Our CeC-POP experiment was initiated by an LDRD proposal and it is now funded by the Department of Energy Office of Nuclear Physics competitive accelerator Research and Development program and BNL discretionary funds.

A low energy electron beam (~22 MeV) would propagate along the yellow beam at Intersection Point (IP) 2 of the Relativistic Heavy Ion Collider (RHIC) complex. For our studies of electron-ion collisions, the electron beam will collide with the blue beam at IP2. The beam-beam effects on both beams will be controlled by varying the beams' intensities, their optics at the collision point, and the ion-beam's species and energy. By using these CeC accelerator and RHIC beams, we could study most of the unique features of beam-beam effects in the ERL-based EIC. The effects we would study with this set-up are the following:

- Electron beam disruption due to the nonlinearity of the beam-beam interaction; and E-beam mismatch caused by a significant phase-advance during its collision with the hadron beam. We also could test the full range of disruption parameter (D=5-160) required by eRHIC using the existing set-up;

- The kink instability of the hadron beam caused by the wake field generated by the electron beam during the collisions. We also would explore countermeasures to mitigate this instability;
- The electron pinch effect and its consequences on the ion beam;
- The effect of fluctuations of the electron beam's parameter on the ion beam.

TECHNICAL PROGRESS AND RESULTS:

Operation of the CeC superconducting linac at 22 MeV is planned for RHIC Run 16 (e.g. winter – spring of 2016). The injector of the CeC accelerator (Fig. 2) is undergoing commissioning, which should be completed during RHIC Run 15. The low energy beamline will be also commissioned and part of our diagnostics tested. As soon as the electron beam becomes available, it will be used for conducting beam-beam experiments.

As part of this LDRD project, we had developed and procured the electronics and the diagnostics necessary for detecting and analyzing beam-beam effects in this configuration. These diagnostics will be used for detecting the kink instability and for characterizing the beam disruption and pinch effects. Some portion of this instrumentation is awaiting the installation of the remaining part of the CeC accelerator beamline.

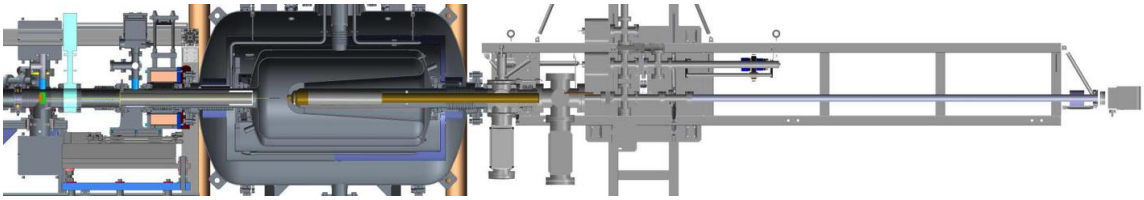


Fig. 2 112 MHz gun with the fundamental power couple and thatching insertion and exchange system.

(a) (b)

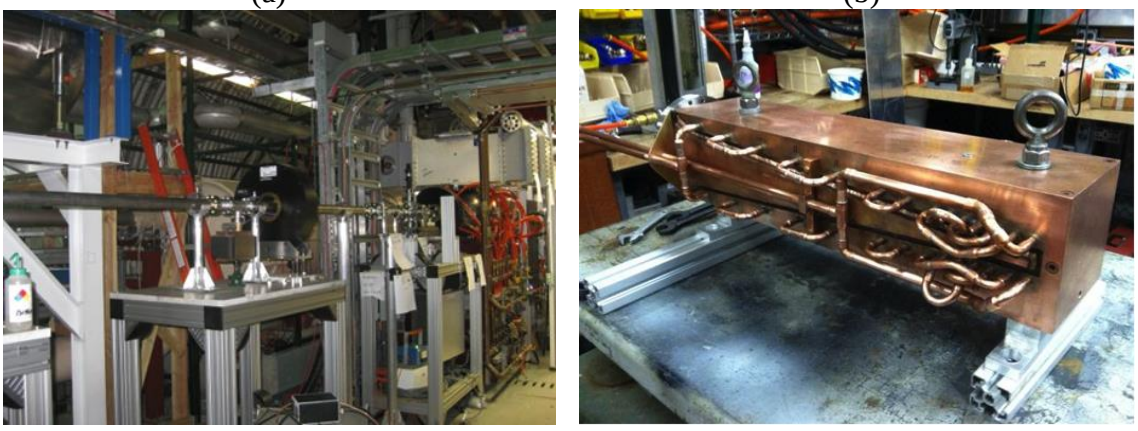


Fig. 3 (a) Assembled low energy beam line. (b) Full power 22 MeV beam dump during assembly.

We had developed a RHIC ramp suitable for the beam-beam effects studies. We also continued theoretical studies of the beam-beam effects and published two refereed and five conference papers related to the linac-ring beam-beam effects. The LDRD program is nearly completed and we are waiting for other systems to be ready for our beam-beam experiments.

Permanent Magnet Solution of the eRHIC with the Non-Scaling FFAG

LDRD Project # 13-005
D. Trbojevic

PURPOSE:

The Laboratory has previously defined a new electron-ion collider (EIC) called "eRHIC" as its highest priority project. To get the project approved, it is necessary to show clear scientific benefits as well as not to exceed $500 million for the overall cost. The LDRD program has chosen to support the new approach to the solution of eRHIC using non-scaling Fixed Field Alternating Gradient (NS-FFAG) arcs. The RHIC International Advisory Committee (MAC) accepted the novel NS-FFAG approach during the Project Review in November 25-27 2013: "The MAC congratulates the eRHIC design team for its ingenious novel use of the FFAG concept." A major advantage of the new concept is a significant cost reduction for eRHIC. The innovative concept allows passage of electrons with a range of energies through the same fixed field permanent magnets during their acceleration towards the final energy where they will collide with polarized protons/He^3 or heavy ions. The two NS-FFAG rings will replace six separate rings, thus reducing the number of magnets, correction elements, instrumentation, vacuum pipes etc. This LDRD project is one of the most beneficial to the future of BNL.

APPROACH:

The Principal Investigator developed the principle of the NS-FFAG independently and presented it on September 30, 1999 during a muon collider workshop. The main property of the concept is very large momentum acceptance of three, four, or five times the energy of the beam. This allows a reduction of the previous six rings with fixed energy with two NS-FFAG rings accepting multiple energies. By allowing more passes through the linac, the energy can be reduced. To achieve electron energy of 20 GeV with six rings of fixed energies, the total energy of the two linacs needs to be ~3.3 GeV. With multiple passes through the linac, the energy can be reduced to half.

TECHNICAL PROGRESS AND RESULTS:

The project design uses the Non-Scaling FFAG lattice requiring two or more rings for the same energy range as previously proposed. As time progressed the previous proposal of the NS-FFAG energy range up to the electron energy of 10 GeV got more ambitious and solutions were developed to achieve the highest electron energy of 20 GeV, using two NS-FFAG beam lines and a single linac with an energy of 1.332 GeV. This LDRD funding enabled us to hire a very talented young physicist Stephen Brooks (position S1) and progress in the design is evident. The cost estimate for the eRHIC project to be presented to the Nuclear Science Advisory Committee (NSAC) Subpanel during the January 26-28, 2015 meeting in Chicago uses the NS-FFAG design. Figure 1 shows the present design of the NS-FFAG magnet for the higher energy ring.

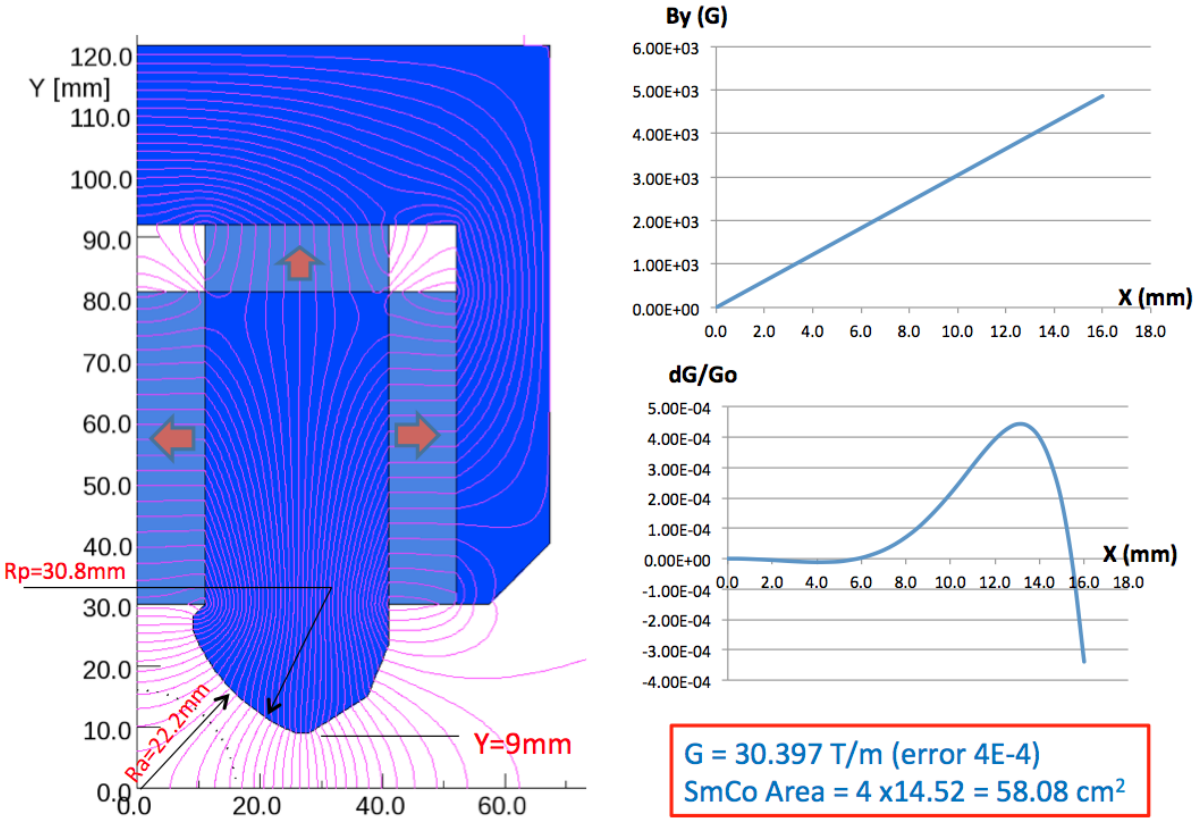


Fig 1 The magnet design for eRHIC is made using iron combined with the permanent magnet material, (as shown in lighter color with arrows showing the direction of the magnetic field.

The eRHIC concept is in direct competition with the design promoted by JLab. BNL has an advantage in already having a high-energy proton/ion synchrotron. With help of the LDRD, we were able to obtain the NS-FFAG design of eRHIC with the highest electron energy of 20 GeV, but at the cost of the previous 10 GeV multiline regular magnet design. 2014 achievements are:

1. The main focus in the last few months was to provide a cost estimate for the eRHIC permanent and correction magnets as accurately as possible. This was accomplished and on January 12, 2015 the cost estimate for eRHIC was sent to the NSAC committee members.
2. The second main subject was writing the White Paper: "The Cornell University FFAG-ERL Test Accelerator", presented as a final version at a collaboration meeting in New York City.
3. Regular weekly meetings continued and a few new studies were performed: one on the effect of radiation and temperature on the magnetic properties of the permanent magnet material, and the other on optimization of the eRHIC magnet design with respect to the cost, reduction of the synchrotron radiation, and a reduction of the chromaticity.
4. The established collaboration between Cornell University, JLab and BNL was confirmed by a meeting in New York City. Presentations were given by: Thomas Roser, Chair of BNL's Collider Accelerator Department about eRHIC and goals for the ERL collaboration at Cornell; Ritchie Paterson, Chair of the Physics Department at Cornell; JLab on their experience with ERLs (2 talks); and the final version of the White Paper.
5. The company Shin-Etsu Magnetics will be delivering the LDRD magnets during February 2015.

Time Resolved Imaging of X-rays and Charged Particles

LDRD Project # 13-006

A. Nomerotski

PURPOSE:

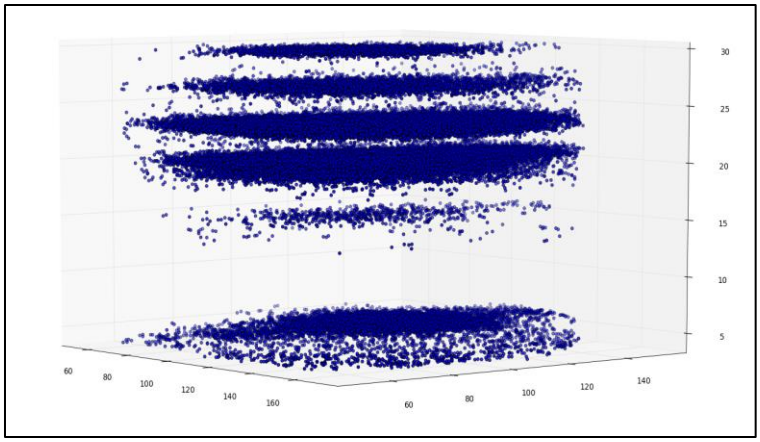
Resolving the time evolution of fast processes, measuring the time-of-flight of particles, and looking at time correlations in spatially resolved events are the main drivers for the development of sensors with the best possible time resolution. In this project we design, characterize and apply fast cameras with 10 ns resolution to time resolved x-ray imaging at the National Synchrotron Light Source II (NSLS-II) and to imaging mass spectrometry (MS) in the BNL Chemistry Department. Time resolved x-ray registration is required in photon correlation spectroscopy (XPCS), which is an important tool in studies of nanoscale dynamics of materials, while the time-of-flight MS is an important analytical tool used widely in chemistry, biology, and medicine.

APPROACH:

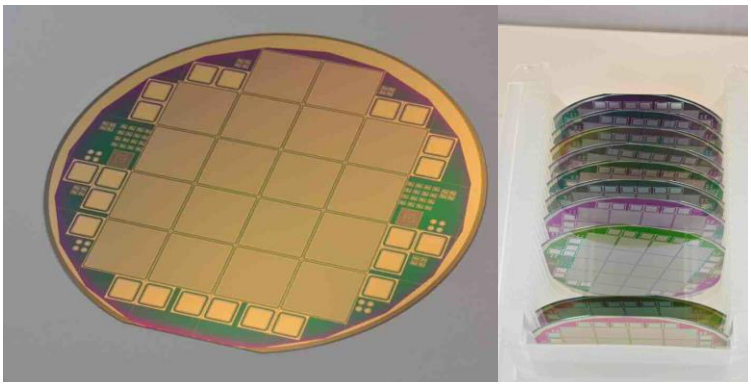
We combine features of several established technologies in order to produce a novel device with as-yet unachieved capabilities. We have designed a new silicon pixel sensor, which in combination with the Timepix chip, will provide 10 ns time resolution and high quantum efficiency (QE) for photons with wavelength between 350 and 1050 nm. This would result in an imager with characteristics far superior to cameras currently available commercially, and which also compares favorably to the Pixel Imaging Mass Spectrometry (PImMS) CMOS camera, developed in the United Kingdom, which has a QE of about 7%. We will employ a commercially available readout system and software to characterize the new device, which will already be of great value for many imaging MS groups. A concept of improved camera prototype will be developed and its commercialization venues explored. We also plan to fully characterize the new PImMS sensor and compare the two camera technologies for the above BNL applications.

TECHNICAL PROGRESS AND RESULTS:

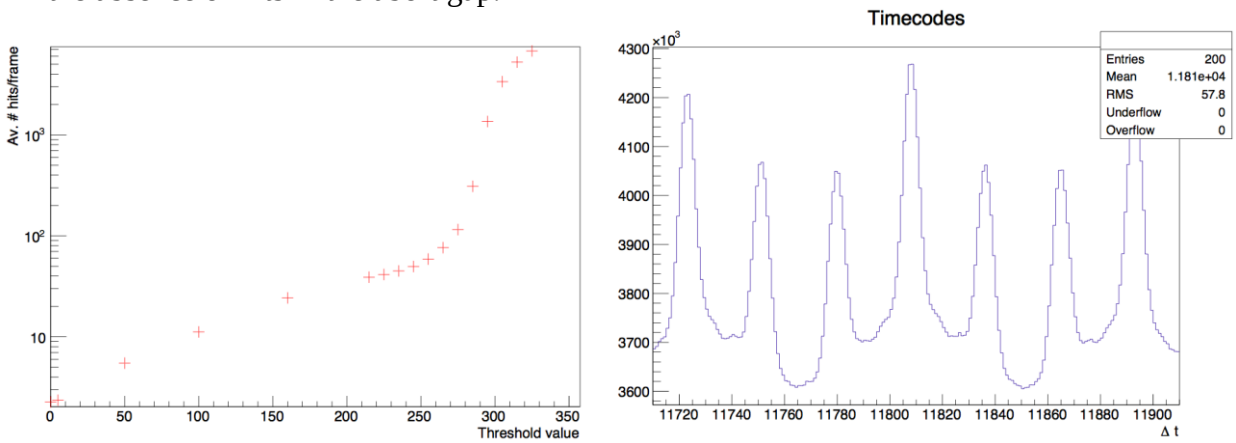
- M. Fisher-Levine, the project postdoctoral research associate, started in January 2014. We procured necessary equipment including the Timepix camera and modified the camera's silicon sensor to make it sensitive to 450 nm photons. We characterized the camera for x-ray and visible light measurements.
- Successfully performed a proof of principle MS experiment in M. White's group in the BNL Chemistry Department. The graph below shows a 3D representation (x,y,t) of butanone data where different "pancakes" correspond to (x,y) distributions of ions for different mass peaks. BNL experiments on imaging MS using the PImMS camera were featured in the Oct 2013 issue of Physics Today. Work is in progress to prepare and perform improved imaging experiments with the new camera.



- By May 2014 we designed and submitted for production a new silicon sensor with a thin passivation layer, which allows high QE for the shorter wavelength (400 nm) photons. Six wafers were completed by October 2014 (see photo below). Post-processing, dicing and packaging of the sensors are planned in early 2015.



- We used the above camera at NSLS in August 2014 to acquire 8 keV x-rays and to perform a proof of principle demonstration of time correlations due to the abort gap in the NSLS beam. The left plot below shows the average number of hit pixels in the Timepix sensor as a function of threshold. The right plot shows the distribution of time differences between all hits in the same frame. The distribution is structured with the beam revolution period due to the absence of hits in the abort gap.



- Adapted the Large Synoptic Survey Telescope DMStack software to analyze the above Chemistry and NSLS data. We started developing specialized code for MS and x-ray applications based on DMStack.

The main milestones for FY2015 are to:

- Characterize the newly produced sensors and choose a configuration, which optimizes the camera sensitivity
- Use the optimized fast camera for MS experiments at BNL and other institutions
- Conduct the first XPCS experiments at NSLS-II using the Timepix detector.

In summary, we proceed on budget and on schedule, all first year milestones have been met.

Electrochemical Reduction of Carbon Dioxide on Surface-Modified Metal Electrodes

LDRD Project # 13-013
D. Polyanskiy

PURPOSE:

The objective of this project is to explore new strategies for more efficient electrochemical catalytic conversion of carbon dioxide to reduced carbon products, such as carbon monoxide, formic acid, alcohols, and methane. Our approach is based on the tailoring of a catalyst's surface properties to improve the efficiency of CO_2 electro-reduction. Mechanistic understanding of chemical transformations on a catalyst's surface and insight into the structure/reactivity relationship are the key driving factors in designing new catalysts. The employment of advanced characterization methods including those available at the National Synchrotron Light Source, Center for Functional Nanomaterials (CFN) and through collaboration with other BNL groups will play a critical role in establishment of such mechanistic insights. New funding opportunities are explored by building upon gained knowledge and strong collaborative ties.

APPROACH:

A wide variety of materials was studied for electrochemical reduction of carbon dioxide in the condensed phase, including molecular and solid state catalysts; however no system was found to be efficient for practical applications, mainly due to the lack of catalytic efficiency, selectivity or stability. Metal cathodes have been shown to act as robust electro-catalysts for CO_2 reduction; however significant electrode potentials were usually required to achieve desired catalytic efficiency of CO_2 conversion. Furthermore, the competing hydrogen evolution reaction posed an additional challenge for the use of metal cathodes for CO_2 electro-reduction. It has been recently demonstrated that surface morphology of metal electro-catalysts has a strong effect on their catalytic performance. Our approach is based on manipulation of both surface structure and surface chemical composition of metal electro-catalysts to improve their efficiency and selectivity toward reduction of CO_2.

TECHNICAL PROGRESS AND RESULTS:

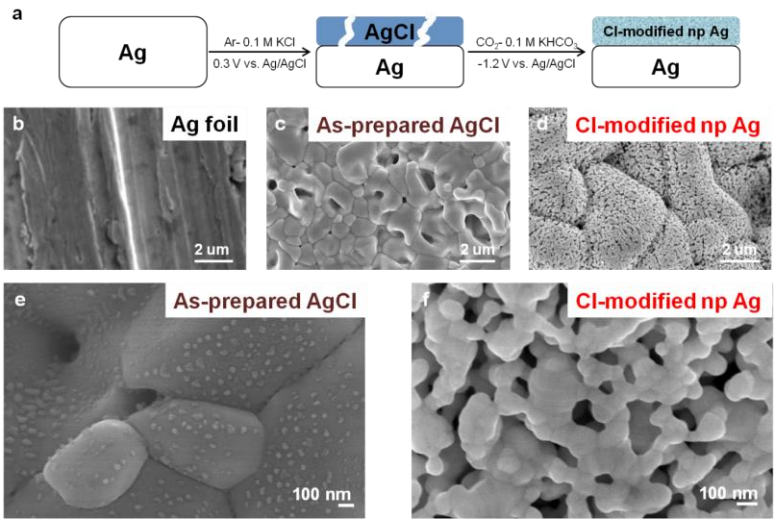
In FY 13, a new research associate was hired. The product analysis protocols, including specialized equipment in the Principal Investigator's lab, were developed and streamlined. Access to the CFN Scanning Electron Microscope and Transmission Electron Microscope was obtained. Several catalytic systems including Pt/Cu and Pt/Ag and chloride-modified silver were tested and the later was chosen as the most promising catalyst for the more detailed study.

FY 14 milestones:

a. The manuscript detailing our findings described below has been submitted to *ACS Catalysis* and is currently under revision.

b. The results were presented by the post-doctoral research associate Yu-Chi Hsieh at the 2014 Materials Research Society Fall Meeting (November 30 - December 5, 2014, Boston, MA) at the symposium: "Materials as Tools for Sustainability". Title of the talk: "The Role of Chloride Anions in CO_2 Electro-Reduction on Silver Electrodes". Authors: Yu-Chi Hsieh, Sanjaya Senanayake, Yu Zhang, Dmitry Polyanskiy.

c. The chloride-modified silver electro-catalyst was studied in more detail. It was shown that this catalyst can be prepared by simple electro-oxidation of silver foil in the presence of chloride anions in aqueous solutions. The resulting electro-catalyst demonstrated a highly developed nano-structured surface.



d. The major product of CO_2 reduction on the Cl-modified Ag is carbon monoxide with a current efficiency of 95% at overpotential as low as 0.37 V and current density of 2 mA cm^{-2}. A current density of 10mA cm^{-2} can be achieved at overpotential of only 0.53 V with the current efficiency still remaining at 95%. A lower limit of the turn over frequency of 0.5 s^{-1} and turn over number > 1×10^5 (over 72 h) was estimated for the Cl-modified Ag catalyst at -0.6 V (vs. RHE – reversible hydrogen electrode) based on the assumption that all silver atoms on the surface are catalytically active.

e. The 65-fold increase in surface-area-normalized specific activity at -0.6 V (vs. RHE) of the Cl-modified Ag sample was observed as compared to the unmodified Ag electrode, which is a greater enhancement, compared to the 20-times increase using the nanoporous Ag electrodes prepared by de-alloying methods as reported in the literature.

f. We demonstrate that in addition to the effect of nanostructured surface morphology, adsorbed chloride anions are contributing to the increased activity of the Cl-modified Ag electro-catalyst. Detailed X-ray Photoemission Spectroscopy studies together with a series of control experiments suggest that the chloride remains adsorbed on the metal surface under electro-catalytic conditions and it can effectively inhibit the hydrogen evolution reaction, therefore enhancing the activity for CO_2 reduction.

g. The performance of chloride-modified silver catalysts was evaluated during 72 hour continuous CO_2 reduction at -0.6 V (vs. RHE). The performance decreased by only ca. 30%, which was attributed to the deposition of K^+ formed on the catalyst surface from the $KHCO_3$ electrolyte. An oxidative treatment in the presence of chloride anions recovered the original catalytic performance, but resulted in the lower rate, due to smaller surface area.

The following are the milestones for the remainder of the project:

a. Study the effect of other halides (e.g. bromide and iodide) on the catalytic performance of silver electro-catalysts.

b. Investigate the effect of inert metal-oxide supports on the stability and activity of highly dispersed metallic electro-catalysts.

A NSLS-II Workflow Prototype System for Supporting Data Intensive Beamline Experiments

LDRD Project # 13-017
C. Yong, D. Yu

PURPOSE:
The big volume of data generated from the National Synchrotron Light Source II (NSLS-II) will require a real-time (*in-situ*) streaming analysis pipeline at the beamline to reduce the raw data and to perform data transformation and visualization right at the beamline, in order to assure data quality control and to provide feedback for experiment reconfiguration. Our proposal has three objectives: first, the proposed workflow system will simplify assembling the entire pipeline for reducing, visualizing, and analyzing on-line data; second, it will automate continuous data-streaming throughout this pipeline and facilitate decision-making and experiment steering; third, it will extend the on-line workflow system to support post-experiment data reduction, visualization, and analysis so as to extract scientifically relevant parameters and content from the large amount of experimental data.

APPROACH:
We leveraged the existing software from NSLS and co-designed image processing software with beamline scientists. We shared domain expertise, software development, and project management tools with the personnel on the data management LDRD to ensure quick adoption by NSLS-II.

TECHNICAL PROGRESS AND RESULTS:

DOE Science Data Pilot Pipeline and Supercomputing 2014 Demo
We collaborated with the National Energy Research Scientific Computing Center (NERSC) at Lawrence Berkeley National Laboratory to deploy the X-ray Absorption Near Edge Structure (XANES) tomography pipeline at NERSC for 3D chemical mapping. We chose the case of correlating 3D morphology and chemical state distribution at the nano-scale to better understand the mechanism of the microstructural evolution and chemical/bio-chemical reactions of biomaterials, biological and bio-chemical systems. In particular, resolving the chemical valence state (oxidation state) as a function of position within a sample is of great interest. Novel XANES techniques at the X8C beam line at the NSLS and the sub-resolution X-ray spectroscopy (SRX) beamline at NSLS-II enable such a capability. We demonstrated this distributed data processing pipeline during Supercomputing 2014. This activity is aligned with the Department of Energy (DOE) data pilot initiative among ten DOE National Laboratories which showcases their big data processing and management capabilities and illustrates the potential value of a virtual facility that would build on the experimental facilities at the DOE's national laboratories and the DOE Office of Advanced Scientific Computational Research infrastructure.

Differential Phase Contrast Image Processing Pipeline
The PyLight Team and its collaborators (Cheng Chang, Ken Lauer, Wei Xu, Hanfei Yan) developed a fast Python-based Differential Phase Contrast (DPC) imaging tool to address the urgent need of real-time data processing for DPC imaging during the experiment.

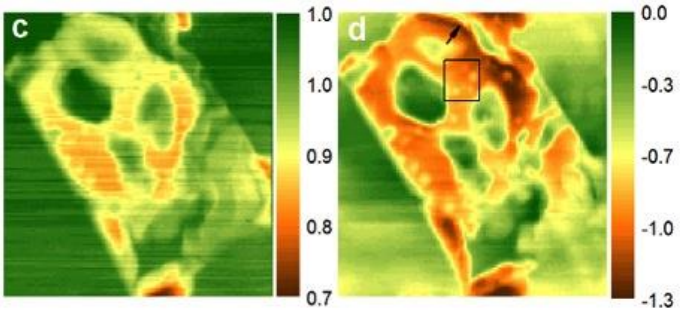


Figure 1: Absorption Phase

The new software is two orders of magnitude faster than the original MATLAB-based implementation. It took ten minutes for the original software to process a small image sample. The new version of the software takes only six seconds, and is a hundred times faster than the original MATLAB code. It has a Graphical User Interface for general parameter inputs, an integrated functionality that enables reading data acquired during the experiment automatically and supports parallel computation. The tool was used for a recent experiment at the Diamond Light Source. With the new imaging tool, the immediate availability of phase images, which would otherwise not be possible without this tool, helps us to perform *in-situ* analysis, identifying and locating interesting patterns from a variety of samples ranging from transparent biological chromosomes to fuel cells. We published the Python based source code in GitHub.

Fluorescence Analysis Package

We developed a new fluorescence analysis package for two project beamlines (the Hard X-ray Nanoprobe and SRX) at NSLS-II. This software package includes automatic element searching based on least-squares error fitting, an advanced fitting engine for each pixel, a comprehensive command-line interface, and rigorous physics calculations to ensure the fitting accuracy. Our contribution is that we implemented the intelligent element identification package for users to easily search fluorescence-related information of different elements in the sample images. We eliminated the tedious manual step of selecting elements. Furthermore, we produced an iterative parameter fitting algorithm for various input samples.

FY15 Milestones

- Complete the Phase Contrast Image Processing Pipeline and the associated user interfaces
- Complete the design of the Fluorescence Analysis Package and associated user interface
- Continue to develop two different types of tomography reconstruction algorithms: Filter-back projection and Iterative tomography
- Generate science papers for the image analysis conference and journal publications
- Write DOE/National Science Foundation proposals on NSLS-II image data analysis, machine learning and data processing pipelines.

Synthetic Control of Lipid Biosynthesis in Plant Vegetative Tissue

LDRD Project # 13-020
J. Shanklin

PURPOSE:

This proposal addresses the issue of increasing plant oil yield by engineering plants to accumulate oil in non-seed tissue. The eventual target for such engineering will be biofuels crops, such as sugar cane, energy cane or sweet sorghum. However, work to establish proof of concept will be performed in Arabidopsis because its genome is fully determined and annotated, its transformation is facile, it grows rapidly and it is small enough to grow large numbers in our standard growth chambers. Currently plant oils are extracted from seeds, which are a relatively small and fixed proportion of the mass of the whole plant. Thus, the volume of the seeds represents an absolute upper limit for the accumulation of oil. To circumvent this limit, we are actively exploring the possibility of engineering plants to accumulate oils, or triacylglycerols (TAG) in vegetative tissues. These efforts are based on our detailed knowledge of the biochemical apparatus for the synthesis and assembly of plant TAGs. Most approaches are based on the use of naturally occurring "tissue- and temporal-specific" plant promoters that are coupled to structural genes or transcription factors that regulate oil biosynthesis. Our goal is to rewire the genetic regulatory network that results in the synchronous expression of genes encoding enzymes that facilitate TAG assembly. This approach is commonly referred to as synthetic biology. This project is designed to produce proof-of principle that synthetic biology (or Biosystems design) can be applied to lipid accumulation in plants. If successful, we will be in a strong position to compete for funding from the Department of Energy Office of Biological and Environmental Research when they announce an expected Request for Proposals in Biosystems design.

APPROACH:

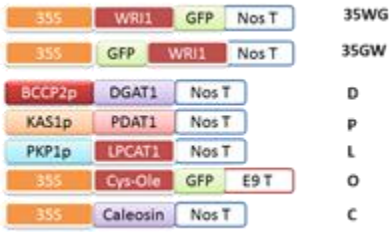
The project essentially involves two parts, 1) expanding the wrinkled 1 (WRI1) regulon, and 2) controlling the expression of the WRI1 transcription factor.

WRI1 can be thought of as a master switch that turns on a set of genes. It is a transcription factor that controls the coordinate expression of approximately 18 genes that encode enzymes from central metabolism through to fatty acid synthesis by binding to a DNA region upstream of the coding region of the genes that it regulates. This causes them to become transcribed into RNA, and hence turned on. WRI1 thus controls the synthesis of fatty acids by regulating the expression of enzymes that direct carbon compounds of central metabolism to fatty acid synthesis. The conversion of fatty acids to TAG requires the action of an additional set of TAG assembly proteins, comprising enzymes and other factors, which are not expressed in vegetative tissues. Thus, to accumulate TAG in vegetative tissues we would need to express both WRI1 and an additional set of TAG assembly enzymes. This proposal is designed to provide a synthetic solution to this problem, i.e., to expand the constellation of 18 genes that are controlled by WRI1. To achieve this we have identified regions of DNA that have previously been shown to become activated upon the binding of WRI1, and we chose the three promoters from the 18 candidate promoters that showed highest levels of expression when coupled to marker proteins using a short (~300) base pair fragment of the promoter. These promoters will be fused with our TAG assembly genes and the genes will be transformed into Arabidopsis using Agrobacterium-mediated gene transfer. Together this part of the workplan will generate an extended WRI1 regulon in which 24 genes will be under the control of the WRI1 transcription factor rather than the naturally occurring 18-gene regulon.

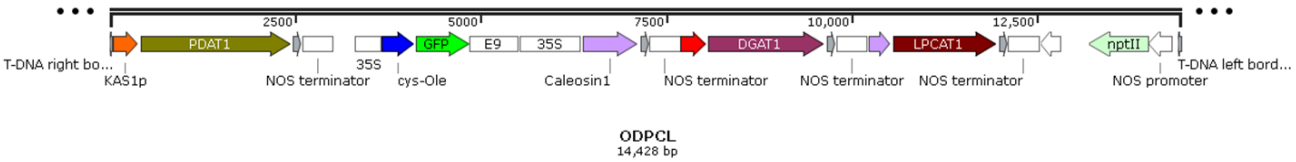
Examination of The Arabidopsis Information Resource expression database shows that WRI1 is not expressed to any significant level in vegetative tissues, and expression in leaves is specifically low. Thus, in order to turn on the expanded WRI1 regulon we need to specifically express the WRI1 in leaf tissue. We will test the use of a constitutive promoter to drive WRI1 expression. Based on the work of others, we anticipate that this will likely cause negative pleiotropic effects especially with respect to growth rate and normal development. Our collaborator June Medford (Colorado State University) has agreed to make a custom transcription activator-like effector responsive to galactose induction that employs feed-forward and feedback regulation. For preliminary experiments, we will create several other WRI1 expression lines of Arabidopsis within which we can test our expanded regulon constructs. An initial experimental test of the system will be made in *Nicotiana benthamiana* (*N. benth.*) using Agrobacterium-mediated transient gene expression.

TECHNICAL PROGRESS AND RESULTS:

In FY 2013 we identified a strategy for assembling the multiple gene constructs. Custom oligonucleotides were designed and synthesized for each key gene, including lysophosphatidyl choline acyltransferase (LPCAT), diacylglycerol acyltransferase 1, (DGAT1 –AT2G19450), phospholipid:diacylglycerol acyltransferase (PDAT1 AT- AT5G13640), oleosin 1 (OLE1–AT4G25140), caleosin (CLE1–AT4G26740), and promoter segment (PI-PKβ1, BCCP2 and Kas1). Individual promoters and genes have been amplified. See schematic below.



In FY 2014, we assembled the following binary vector consisting of LPCAT diacylglycerol acyltransferase 1, (DGAT1 –AT2G19450), phospholipid:diacylglycerol acyltransferase (PDAT1 AT-AT5G13640), oleosin 1 (OLE1 –AT4G25140), caleosin (CLE1 –AT4G26740) under the control of specific WRI1-responsive promoter elements.



We are in the process of expressing the multi-gene expanded WRI1-controlled regulon in both *N. benth.* and Arabidopsis and are performing quantitative analysis of samples using silica thin layer chromatography and gas chromatography coupled mass spectrometry. We have transformed the WRI1 transcription factor under the control of the 35S promoter into Arabidopsis and confirmed its expression by quantitative polymerase chain reaction. We then transformed the multi-expression binary vector shown above into this line and selected transformants. We are now growing these plants for lipid analysis.

FY 2015 Milestones

Analyze Arabidopsis lines expressing WRI1 created in FY 2014, and transform June Medford's WRI1 expression lines. Perform quantitative analysis of samples using silica thin layer chromatography and gas chromatography coupled mass spectrometry. Design and test second generation constructs based on results of first generation analysis.

Tracking Lithium Electrochemical Reaction in Individual Nanoparticles

LDRD Project # 13-022

F. Wang

PURPOSE:

The goal of this project is to develop new capabilities that allow for correlative *in-situ*, *operando* transmission electron microscopy (TEM) and synchrotron X-ray studies of lithium transport and reactions in batteries with unprecedented spatial resolution. Tools and techniques will be made available for '*first light*' experiments at the National Synchrotron Light Source II (NSLS-II), for *real-time* probing of electrochemical (de)lithiation of individual nanoparticles in a working battery electrode.

APPROACH:

Most of the available *in-situ* techniques, such as those based on hard X-ray scattering, are powerful for *real time* probing electrochemical reactions in batteries, but very often limited in spatial resolution. The recent development of *in-situ* TEM techniques pushes the resolution down to the nanoscale, by using a solid electrolyte in an open cell configuration. A critical component of the approach is to develop a liquid electrochemical cell as a new sample environment for correlative TEM and synchrotron X-ray studies of electrochemical reaction in the same electrode during battery operation (Figure 1a). A unique feature of the liquid electrochemical cell is the use of a thin SiN membrane to seal liquids, making it compatible with the high-vacuum and ambient atmosphere of different equipment, and so allowing for multiple measurements using *in-situ*/*operando* TEM/X-ray techniques. In a parallel effort, a solid-electrolyte based *in-situ* cell (Fig. 1b) will be further developed, to take advantage of the open cell configuration that allows for atomic imaging and spectroscopy, to complement the *in-situ* studies using the liquid cell. Those developed *in-situ* techniques and capabilities will be applied for *real-time* probing of electrochemical (de)lithiation of individual particles, and in combination with computational modeling, to determine the kinetic transformation pathway during battery operation under *non-equilibrium* conditions.

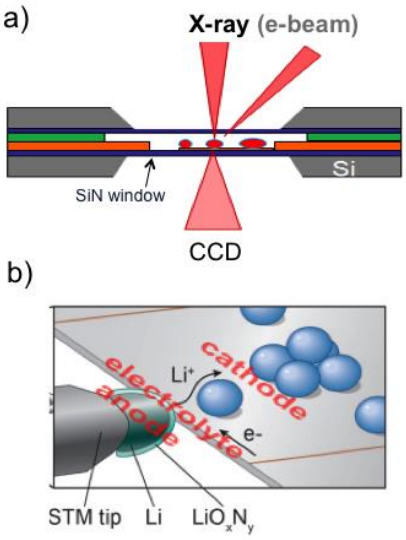


Figure 1 Schematic illustration of *in-situ* electrochemical cells, using (a) liquid and (b) solid electrolytes, to study single-particle electrochemistry by TEM and synchrotron X-ray methods.

This project involves multidisciplinary collaboration with scientists at BNL including Eric Stach and Yimei Zhu on electron microscopy, Yong Chu on nano-beam X-ray diffraction/spectroscopy, and Gerbrand Ceder (at Massachusetts Institute of Technology) on modeling. Collaboration with Hummingbird Scientific involves the development of a unique liquid electrochemical cell.

TECHNICAL PROGRESS AND RESULTS:

A whole suite of *in-situ* liquid-flow cells, along with a biasing option and peripheral equipment, were set up in FY13, and during the period sample loading, cell assembly and TEM measurements were also performed. In FY14, significant progress was made in the cell development through collaboration with Hummingbird Scientific as summarized below:

- We have developed procedures for assembling active electrodes into the liquid cell with real electrolyte (such as $LiPF_6$ salt in ethyl carbonate and dimethyl carbonate that are commonly used in batteries).
- We have developed capabilities and techniques for *in-situ* TEM studies of electrochemical reactions of electrodes in the liquid cell. By using a single nanorod as the active electrode, we made the first *real time* observation of the surface passivation, revealing a gradual growth of surface layer on the rod. Representative images are given in Figure 2. This result, along with other observations such as dendrite growth, demonstrated the electrochemical functionality of the liquid cell. This is an important development for the project.

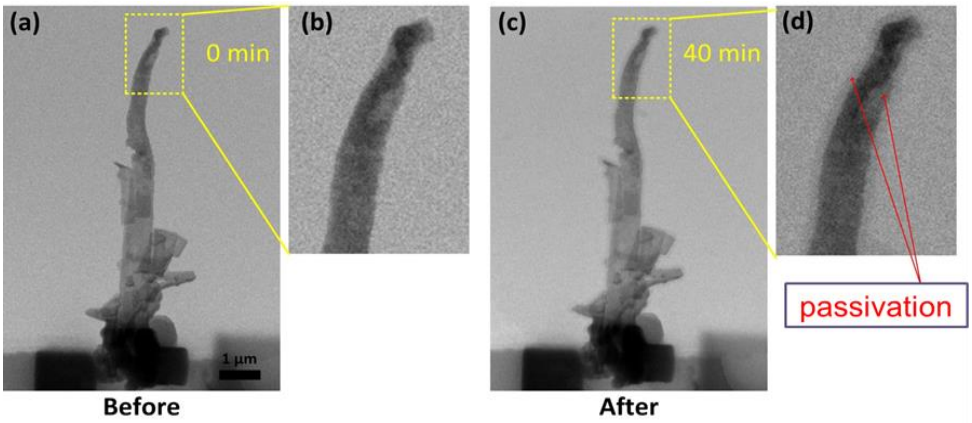


Figure 2. *Real time* observation of the surface passivation on nano-rod electrodes using a liquid cell, demonstrated by bright-field TEM images obtained at *0* minute (a, b) and after *40* minutes (c, d).

In addition, *in-situ* TEM and synchrotron X-ray techniques specialized for tracking local electrochemical reactions in a solid or liquid cell have been developed (as listed below).

- Based on a previously developed design of electrochemical cells for tracking conversion reactions in individual particles, we have developed a new design of electrodes and *in-situ* techniques that allow for tracking lithiation-driven subtle lattice evolution in intercalation-type electrodes that were utilized for *in-situ* TEM studies of single-particle phase transformations in some model electrodes. Two drafts are being developed from the results.
- We have developed new synchrotron techniques with high sensitivity to the electrochemical reaction at liquid-solid interfaces. Some *ex-situ* tests were made at NSLS for the proof of concept, and the techniques will be applied for *in-situ* measurements at NSLS-II.

Some of the developed techniques and experimental results have been used for writing proposals for external funding. By far, most of the capabilities and techniques have been made available for *in-situ* TEM and synchrotron experiments. In FY15, our efforts mainly focus on *in-situ* measurements of single-particle electrochemistry at the Center for Functional Nanomaterials (CFN), NSLS-II and other facilities.

Milestones: In the 1st year, a liquid cell was made available and extensive cell assembly and electrochemical tests as well as some *in-situ* TEM measurements were made in our lab and at the TEM facilities in the CFN. In the 2nd year, the whole suite of instruments and *in-situ* techniques was developed and made available for the *in-situ* TEM and 1st light experiments at NSLS-II. In the 3rd year, *in-situ* studies of single-particle electrochemistry of advanced battery systems will be completed.

Elucidating the Role of Nanostructured Domains in CIGS PV Device Performance

LDRD Project # 13-024
M. Eisaman

PURPOSE:
Although CIGS ($Cu(In_{1-x},Ga_x)Se_2$) holds the record for thin-film photovoltaic (PV) power-conversion efficiency (20%), it is not cost-competitive with conventional silicon in part due to high manufacturing costs. It is not understood why, contrary to expectations, the performance of CIGS degrades with increasing Ga concentrations for $x > 0.3$. A model has been postulated wherein individual grains of polycrystalline CIGS films are two-phase mixtures consisting of an α−like ($Cu(In_{1-x},Ga_x)Se_2$) n-type domain and a β-like copper deficient p-type domain. This model suggests that these domains segregate at the nanoscale to form interpenetrating networks which permit percolation transport of electrons and holes in physically distinct paths, and that recombination within this network will be dependent on their real-space separation and local chemical composition (i.e., the structure at the nanoscale). Our goal is to connect regional device performance (microns) with nanoscale chemical and structural properties of the films to test the validity of this model, and to ultimately gain control over these nanoscale structural properties (and thereby over the performance) by connecting the process conditions to the resulting structure. Achieving these goals would strengthen BNL's energy strategy by supporting the U.S. CIGS manufacturing industry via improved fundamental understanding that is then leveraged to reduce the cost of thin-film photovoltaic manufacturing.

APPROACH:
We have developed a three-pronged approach that addresses the project goals:
1. Fundamental structural properties of the CIGS absorber layer. It is hypothesized that an ordered vacancy compound (OVC) layer within the CIGS layer at the CIGS/CdS interface is essential to high performance by greatly reducing the interface recombination. Measurements have combined Raman spectroscopy and Transmission Electron Microscopy (TEM) at the Center for Functional Nanomaterials, capacitance-voltage measurements in our lab, and Grazing-Incidence Wide-Angle X-ray Scattering measurements at the National Synchrotron Light Source (X9) to confirm the presence of this OVC layer in certain grains throughout the CIGS absorber. These samples are being studied via atom probe tomography (APT) by our collaborators at Colorado School of Mines (CSM), who have seen similar OVC phases in other samples via APT.
2. Correlation of single grain material properties with single grain electronic transport properties. We have pioneered a new nanocontact method of single-grain measurement by depositing contact onto single grains using lithography.
3. Novel devices architectures for improved performance. In addition to the above work to understand structure function relationships in the CIGS absorber, we are investigating novel CIGS device architectures that replace the CdS and ZnO layers (that are toxic and have parasitic optical absorption) with a graphene front contact.

TECHNICAL PROGRESS AND RESULTS:
1. Fundamental structural properties of the CIGS absorber layer. During 2014, we confirmed existence of the OVC phase in the bulk of the CIGS absorber in additional samples using TEM and established a collaboration with the APT group at CSM for direct confirmation using APT. The samples are currently with CSM.

2. Correlation of single grain material properties with single grain electronic transport properties. During 2014, for the first time we measured low-temperature current-voltage (I-V) curves of single CIGS grains via the novel nanocontact method (Fig. 1).

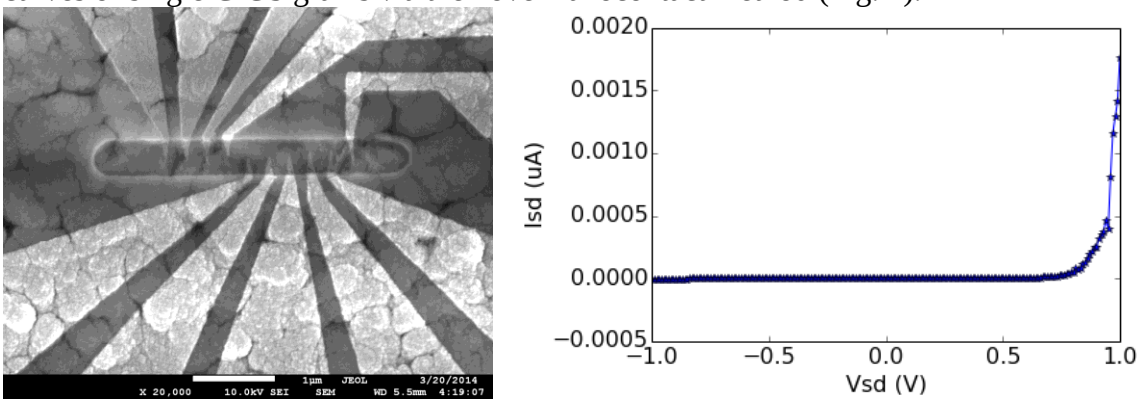


Figure 1 (Left) Scanning Electron Microscope micrograph of nanocontacts probing the CIGS layer through a window etched out of the top oxide layer. (Right) I-V curve from a nanocontact.

3. Novel devices architectures for improved performance. During 2014, we perfected the transfer of graphenes made by chemical vapor deposition and from highly ordered pyrolytic graphite onto bare CIGS, followed by the formation of complete devices (Fig. 2). We discovered an unexpected and fortuitous n-doping of the graphene (good for device formation with the p-type CIGS). We narrowed down the doping source to either nitrogen or sodium, and current work is aimed at determining which of these two elements is responsible. We successfully formed photovoltaic devices with these structures that exhibit good diode behavior.

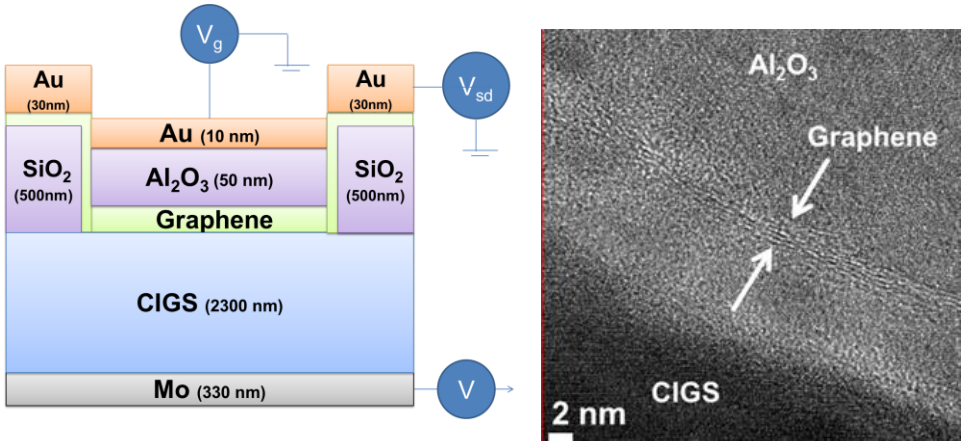


Figure 2 (left) Schematic of CIGS/graphene device. (right) TEM showing interface

Milestones achieved: 1. I-V curve of single CIGS grains measured via novel nanocontact method. 2. Novel n-doping of graphene on CIGS discovered and used to make novel CIGS/graphene photovoltaic device exhibiting good diode behavior.

FY15 milestones: 1. Corroboration of OVC grains in the CIGS bulk via APT and correlation of single-grain electronic transport properties with absence/presence of OVC. Publish peer reviewed paper on this topic (in preparation). 2. Publish peer reviewed paper on novel graphene-CIGS devices (in preparation).

A Probabilistic Approach to Sizing Battery Energy Storage Systems for Improved Grid Inertial Response

LDRD Project # 13-025
X. Wang

PURPOSE:

Grid inertia plays a vital role in suppressing grid disturbances that originate both inside and outside of the grid. However, as the reliance on renewable energy generating sources increases to accommodate the growing demand for "clean energy," traditional generating sources will be displaced. This will result in a corresponding reduction in grid inertia since renewables, such as wind and solar, provide little or no inertia to the grid. This reduction in grid inertia is of particularly concern under light load conditions with a high penetration level of renewable sources since, in addition to the inertia reduction, large power mismatches may be caused by the large power fluctuations inherent to renewable generation. Therefore, a loss of grid inertia could create a barrier to deploying high penetration levels of renewable generation and is a great concern to grid operators. A possible means to achieve a satisfactory grid inertial response with high penetration levels of renewable generation is to use energy storage systems (ESSs). ESSs possess response speeds that are superior to conventional generators and thus can improve the grid inertial response, or equivalently enhance the grid inertia. While the effectiveness of the ESS response is well-known, it is difficult for utilities to determine the desired capacity that will optimize inertial response while minimizing the capital cost of the storage system. The technical objectives of this project are to develop a probabilistic-based methodology for sizing battery (BESSs) that can be used as a tool to optimize ESS design and provide an acceptable grid inertial response while minimizing capital cost.

APPROACH:

To achieve the project goals, the following approach has been taken: 1) identification and statistical characterization of grid disturbances: mainly focused on the common power system disturbances, such as loss of large generator(s) or large changes of the load and the disturbances associated with solar generation. These disturbances can potentially have a much larger impact on grid performance due to the potential for sudden changes in generation compared to, for example, a loss of a conventional generator. These disturbances will be characterized based on historical data to generate profiles that can be used as input to the grid model. Another major grid disturbance associated with renewable generation comes from the availability and the reliability of the renewable energy systems, and this will also be analyzed using failure-modes-and-effects analysis (FMEA) and probabilistic safety assessment approaches; 2) selection and modeling of a sample system: a dynamic model of an existing grid, e.g. a 16-machine system extracted from the New York Independent System Operator, will be built using a commercial planning tool commonly used in the power industry, PSS/E, which includes the traditional generators, renewable generation, including solar and wind, BESSs, and their associated control systems. A virtual inertial controller for the BESS for enhancing the system inertial response will be developed to investigate the functionalities of the BESS in inertial response improvement for different penetration levels of renewables; 3) Monte Carlo simulation for comparing the performance of proposed BESS designs with acceptance criteria to determine required BESS capacity. Using the grid model, a Monte Carlo analysis will be performed to evaluate grid inertial response for different BESS designs in response to all of the credible disturbances. The analysis results will be compared to acceptance criteria, which will be established based on

utility/customer satisfaction and regulatory requirements. The capacity of BESS can be optimally specified considering both its cost and the payback from performance improvements.

TECHNICAL PROGRESS AND RESULTS:

Work completed under this project from Jan. to Dec. 2014 produced the following technical progress: 1) after taking training courses on performing dynamic simulations in the PSS/E platform, dynamic models for photovoltaic (PV) generation and BESS within PSS/E have been developed for provision of a schematic study on impact of different PV penetration levels on the grid inertial responses and the mitigation strategies by using BESS; 2) developed a virtual machine-based control system to provide inertial response; integrated this control system to a two-machine power system to investigate its effectiveness for provision of inertial response. The simulation results have been summarized and published in an IEEE conference paper; 3) collected and statistically analyzed solar transient data from the Long Island Solar Farm (LISF) and failures of grid components; developed and implemented in MATLAB an algorithm for generating statistical samples representing variability of solar generation and random failures of grid components; 4) implemented the automated process of performing the simulations assessing grid frequency responses in MATLAB. The simulation results have been summarized and are accepted for publication in an IEEE journal paper; 5) analyzed the weather conditions for the BNL location to establish patterns and define probabilities and distributions to use in the development of the probabilistic risk assessment analysis for evaluation of production-oriented risk; conducted FMEA analysis to identify failure modes, effects and causes for PV systems; results obtained from this analysis were incorporated into the studies in 3. Some highlights of the results are briefly presented below.

The virtual machine based control system for the BESS inverter was developed based on the digital integration of the differential equations that describe the electromechanical characteristics of the synchronous machines. The voltage and current outputs from the virtual machine were used for generating the pulse width modulation signals to control the grid connected inverter. In this case the virtual machine speed, herein the grid frequency deviations can be mitigated by provision of the BESS during the grid disturbance occurrence.

The solar transient frequency was obtained in this study using the high-resolution (1-sec) solar resource data from the LISF collected in a one-year period (2011). A fast transient is defined as a transient that starts with the solar irradiance above 500 W/m^2 and the percentage of deviation from the initial value is above 50% within 15 seconds. By applying this criterion, a total number of 2,283 transients were identified from the actual measurement data. From these results, the distributions of the three random variables to characterize the solar transient were determined, including the initial irradiance values, the maximum irradiance changes during the transients, and the transient times. Together with the existing generator failure rate, disturbance samples originating from the generator trip and solar transient were automatically generated from MATLAB and fed to the simulated 16 machine system. A Monte Carlo simulation approach was adopted to specify the optimal BESS capacity to meet the pre-specified reliability criteria in terms of the grid inertial response.

The control systems and methodologies developed in FY14 will be migrated to the commercial software PSS/E in FY15. Python language has been adopted to automate the probabilistic simulation progress by using PSS/E software as a lower level ‘calculator.’

In situ Studies of Interfaces Under Extreme Environments

LDRD Project # 13-027
S. Gill, M. Elbakhshwan, L. Ecker

PURPOSE:

Currently there is lack of fundamental understanding of kinetics and reaction mechanisms that occur at nuclear cladding-steam interfaces under extreme environments in nuclear reactors. Such understanding is vital to design and develop advanced cladding materials for more economical and safer nuclear power. This project aims to address that lack of understanding. The proposed approach is to develop a reaction cell for *in situ* investigation of interfacial interactions under high-temperature conditions to investigate the corrosion and hydriding mechanisms in both conventional (Zircaloy-2 and -4) and advanced cladding materials using X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) techniques at the National Synchrotron Light Source II (NSLS-II). Such studies will help in elucidating the phase and structural changes associated with corrosion of nuclear claddings, which will aid in design and development of corrosion-resistant next generation cladding materials.

Successful demonstration of the proposed *in situ* capability will make high impact science opportunities available at NSLS-II and pave the way for BNL towards the development of advanced synchrotron-based X-Ray methods for *in situ* studies of materials under extreme environments. In addition, development of such a capability will help enable BNL's vision of transformational discovery through synchrotron science and help achieve *in situ* energy science leadership.

APPROACH:

Corrosion of zirconium (Zr) alloy in fuel cladding in water or steam and the associated hydrogen pickup is a limiting factor for increasing fuel burn-up in current and future reactors. In addition, the acceleration of corrosion, known as breakaway oxidation, that occurs during severe accidents, such as Loss of Coolant Accidents, leads to the production of hydrogen and fuel rod failure due to embrittlement from hydrides formed within the cladding. The explosions in two reactor buildings at Fukushima during the accident there were caused by hydrogen produced by the zirconium-water reaction.

The proposed new approach to address understanding of corrosion of Zr alloys and new potential candidate alloys for next generation cladding materials will investigate *in situ* corrosion. For *in situ* studies we have successfully developed and commissioned the proposed *in situ* reaction cell at both NSLS and the Advanced Photon Source (APS). *In situ* studies of single crystal Zr alloy samples with a few large grains and polycrystalline bulk Zr alloys treated with saturated steam at 400°C and 1500 psi for 3-4 days are planned as a first light experiment during 2015 at the XPD beamline at NSLS-II. Such *in situ* investigation of large grain Zr alloy samples will help understand the changes in grain structure and oxide structure that occur during stress produced by corrosion conditions, which will further help optimize the design of corrosion resistant next generation cladding materials. This work has been done in collaboration with Eric Dooryhee and the XPD team, Juergen Thieme and the Submicron Resolution X-ray Spectroscopy (SRX) team and Arthur Motta at Penn State University.

TECHNICAL PROGRESS AND RESULTS:

In FY14 and FY15, four main scientific efforts under LDRD project are:

1. **Commissioning of the cell at NSLS to perform *in situ* corrosion studies using transmission geometry:** The *in situ* cell (shown in Fig.1) was commissioned at the X17A beamline at NSLS in July 2014. Corrosion data for Zr metal under steam at 250°C was collected for 31 hours using the transmission mode sample holder. However, it was difficult to isolate the oxide signal from the bulk alloy signal due to the string contribution from the bulk alloy in the transmission mode XRD measurements.
2. **Design of reflection mode holder:** A new sample holder was designed (inset of Fig.1) where glancing incidence measurements can be used to monitor changes in surface structure and evolution of the oxide at the metal-oxide interface. Using this holder the signal from the oxide can be collected with high sensitivity and without much contribution from the bulk alloy.
3. **Commissioning of the cell at the APS to perform *in situ* corrosion studies using reflection geometry:** The *in situ* sample environment was commissioned at the 6-ID-D beamline at the APS in November 2014 for grazing incidence XRD corrosion studies using the sample holder shown in the inset of Fig. 1. A metallic Zr sample (200μm thickness) was used due to its faster oxidation kinetics as compared to Zircaloy. The sample was exposed to steam at 350°C and 50 psi for a total time of 64 hours. Results showed the presence of α-Zr as the dominant phase (shown in Fig. 2). After 32 hours of exposure to steam, three oxide peaks in the low diffraction angle side started to develop with time. The oxide peaks were found at diffraction angles of 1.54°, 1.75°, and 2.3° degrees which can be attributed to the growth of the Zr_3O, Zr_3O_{1-x}, and Zr_3O_{1-x} oxide phases respectively.
4. **Testing the cell design for XRF data collection:** The cell was tested for XRF data collection at the Cornell High-Energy Synchrotron Source using the MAIA detector. It was found that the backscattering configuration using the MAIA detector was compatible with the cell geometry for XRF measurements.

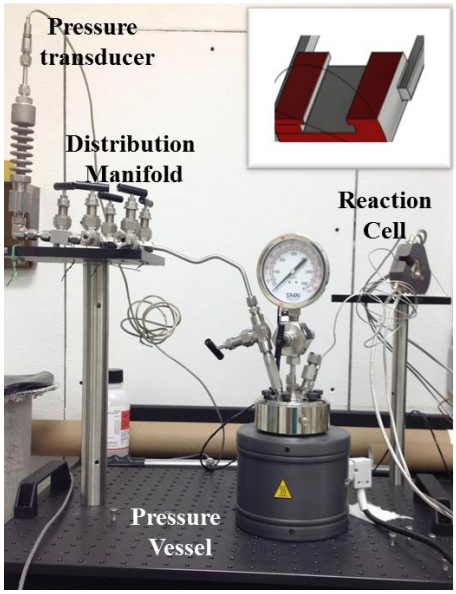


Figure 1 Reaction cell and fluid delivery system developed. Inset shows the reflection mode holder.

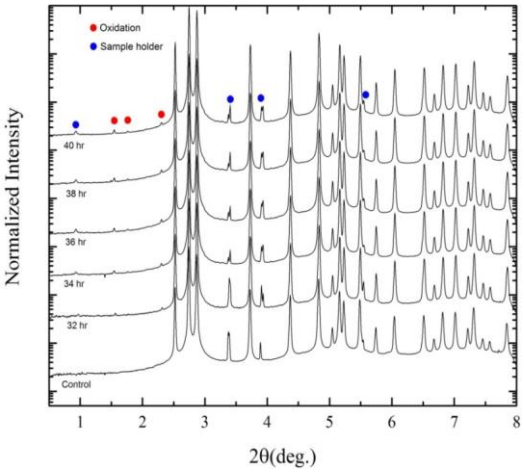


Figure 2 Diffraction patterns of a Zr metal sample collected at 6-ID-D.

SUMMARY: The milestones for FY 14 and 15 include: commissioning of the *in situ* reaction cell for corrosion studies under a steam environment for both transmission and reflection mode XRD measurements was successfully achieved. The target milestone for FY 15 is to commission the cell on the XPD and SRX beamlines at NSLS-II and collect the *in situ* XRD and XRF data for large grain Zr alloy samples. In addition, corrosion studies of advanced steels such as APMT and Alloy-33, which are candidates for nuclear claddings, will be performed.

Modulation Enhanced Diffraction: A New Tool for Powder Diffraction and Total Scattering Studies

LDRD Project # 13-031
E. Dooryhee

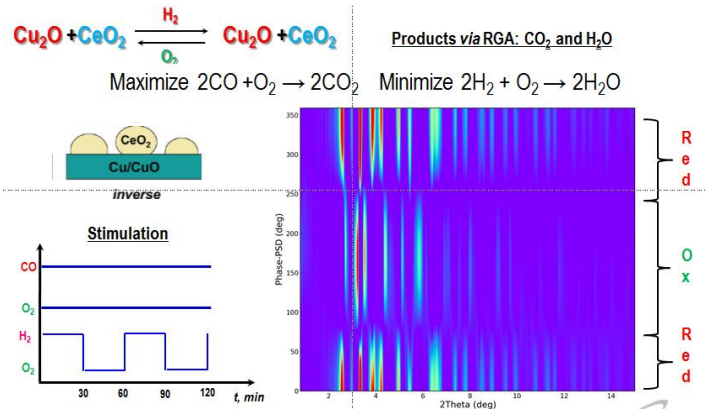
PURPOSE:
The MED (Modulation Enhanced Diffraction) project aims at expanding the *in situ* and *in operando* time-dependent diffraction capabilities at the X-ray Powder Diffraction (XPD) beamline and at other diffraction and scattering beamlines at the National Synchrotron Light Source II (NSLS-II). Research on battery materials, catalysis, applied materials and other technological materials can be directly impacted by this method. The proposed method is well established in spectroscopy, but was very new in powder diffraction. Over the past year, we have shown that MED introduces structural selectivity into time-dependent diffraction experiments in a range of catalytic, physical and chemical processes.

APPROACH:
The team has been active in developing the MED technique through an aggressive experimental program at several facilities and beamlines: NSLS X17A, X7B and X14A, the Advanced Photon Source 11-ID-C and 17-BM. A large variety of compounds were examined, under the effect of a periodically alternated parameter like temperature and gas environment: Cu/CeO_2 catalysts, Gd doped ceria, $CuFe_2O_4$, FeCrAl, Ni-Pd, Metal Organic Frameworks. We have also reached out to new user groups within and outside BNL: Lynne Ecker, BNL; A. Frenkel, Yeshiva University, Israel; R. Caliandro, Consiglio Nazionale delle Ricerche, Bari, Italy. This has contributed to extending the applicability of MED to other classes of materials including Pt/Pd vapochromic materials, poly propyl compounds and WO_{3-x} nanotubes. A collaboration with Stony Brook includes the study of the production of clean hydrogen and the removal of CO_2 from the atmosphere. The measurements have been successful and the results were presented as oral talks.

Our demonstration measurements have also revealed some shortcomings of the MED technique when for example several structural changes occur simultaneously or when the structural response is time-lagged. Our current efforts consist in mitigating these limitations in order to make MED applicable to a broader range of cases.

TECHNICAL PROGRESS AND RESULTS:
The goal was to develop an algorithm for data analysis and the hardware to conduct MED measurements at NSLS-II, which was achieved. Past and current efforts are to showcase the capabilities of MED in different experiments.

MED eliminates the diffraction signal due to passive phase and background and adds selectivity to the phase which responds to the external periodic stimulation. We have now established MED as an alternative approach to anomalous or resonant diffraction methods that are normally used to enhance sensitivity and selectivity. With MED a higher signal-to-noise ratio is gained and small signals from the active structural part that are normally buried in a large signal can be recovered, while achieving high time-resolution for kinetic studies.. MED can be executed over the time scale of interest for most functional materials, which ranges from seconds to minutes or even hours.



Oxidation-reduction of $Cu_{60}Ce_{40}$ in a H_2/O_2 flow at 250°C in a CO/O_2 stream.

The software is now well developed and comprises two packages: 2DFLT (to edit the *in situ* data set) and 2DMED (demodulation of data). See http://sourceforge.net/projects/twodmed/ and http://sourceforge.net/p/twodmed/wiki/Home/. We have purchased all the necessary equipment for the experiments at the NSLS, which has now migrated to NSLS-II/XPD.

Tasks	Status (accomplished)	Next Actions/Milestones
Sample screening and Tests	High-impact science cases selected through approved peer-reviewed proposals. Reach-out at conferences.	Extend MED to other important systems for day-1 experiments at NSLS-II. Extend MED to pair distribution function.
Setting-up Experiment controls	Instrumentation and set-up at NSLS finished. Implementation at NSLS-II XPD in progress. Purchased a fast switching valve and a Residual Gas Analysis system.	More testing. Continue to develop the MED hard/software for early science at NSLS-II. Develop/test the reaction cell. Complete gas system with new flow controller and a pumping unit for special gases.
Experiment	MED benchmarked in real-case studies and test applicability.	1st experiment at XPD: • *In Operando* XRD+DRIFTS of Cu-CeOx-TiO2 for synthesis of alcohol from CO2 hydrogenation. • *In situ* XPD Studies of High Pressure Gas Loading to Metal-Organic Frameworks
Data analysis	Kinematical theory and algorithms to model the structural parameters. Compute frequency filtering (demodulation and correlation) algorithms and phasing of the demodulated diffraction signal. The program 2DMED is developed in Python, successfully benchmarked and tested. Data can now readily be analyzed using this software. The software package is released to the community.	Publish our results (2 papers in preparation). Organize a MED workshop at the Center for Functional Nanomaterials FN/NSLS-II users meeting.

MED opens new research opportunities in at least four Laboratory mission areas: solid state physics and chemistry, energy and materials research, catalysis and transformation of materials, and operation of NSLS-II.

Development of At-Wavelength Metrology Tools

LDRD Project # 13-032

M. Idir, K. Kaznatcheev

PURPOSE:

The most precise tools for metrology and those most relevant to measure the ultimate beamline performances will use the incoming X-ray beam as a probe. Most beamlines today have minimal tools for assessing the performance of the optical system and for complex optical system alignment. We need a standard set of tools that allow minimally invasive measurements of beamline performance and that can be used routinely as part of user operation. The simplest tools are based on techniques such as Hartmann masks and grating shearing interferometers. Our at-wavelength metrology "tool case" will enable these measurements to ensure optimal performance of the National Synchrotron Light Source II (NSLS-II) beamlines during the commissioning phase.

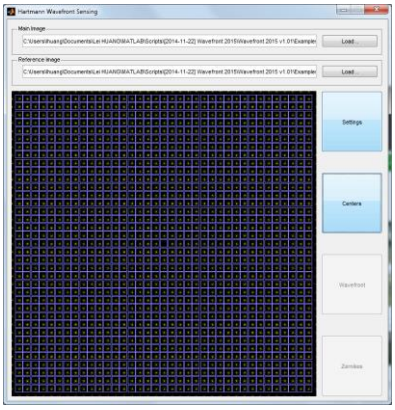
APPROACH:

The NSLS-II facility sets a new performance standard for Synchrotron Radiation optical components. From the beginning of the project, it was realized that 1 nm spatial or 0.1 meV spectral resolutions cannot be reached using existing optical technology, but require extensive and on-going innovations. Our LDRD proposal covers two important optical technology innovations. The first innovation is the development of the next generation of *at-wavelength metrology* tools for X-ray component characterization, alignment, and performance studies. This development extends visible light metrology but goes far beyond, as many X-ray components, such as high quality Kirkpatrick-Baez mirrors, multilayer crystals, and lenses can only be characterized at the energy at which they were designed to operate. *At-wavelength metrology* is far superior to visible light optical metrology in terms of sensitivity and accuracy. Our development effort will reduce beamline commissioning time and provide more optimized systems. For example, the X-ray microscopies being developed at the Hard X-ray Nanoprobe, Submicron Resolution X-ray Spectroscopy (SRX), and Full-Field X-ray Imaging beamlines require detailed knowledge of the optical transfer function (OTF), i.e. the spatial frequency response of a system of optical components to amplitude and phase modulation. As OTF is not just a product of the X-ray optics performance alone, but a mixture of the incoming radiation, mechanical stability, detector response and image processing, this measurement must be performed frequently, as conditions change. Our *at-wavelength metrology* tools will enable these measurements to ensure optimal performance.

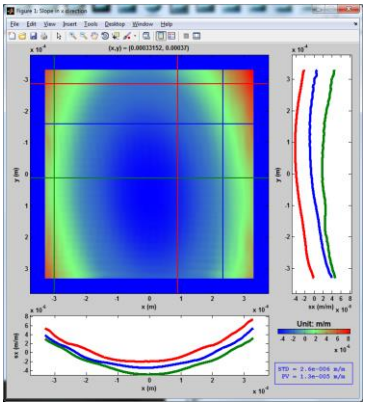
The second optical technology innovation of our LDRD proposal involves *wavefront phase characterization*, which is crucial to optimally utilize the highly coherent NSLS-II source. The importance of phase characterization is seen, for example, in biomedical imaging where the use of phase contrast dramatically enhances image quality and reduces radiation dose compared to conventional absorption-based imaging. This second phase uses the tools developed during the first phase. Our proposal is part of a Department of Energy (DOE) laboratory collaboration aimed at reducing duplicative efforts and building joint capabilities that would address future needs for the entire DOE complex.

TECHNICAL PROGRESS AND RESULTS:

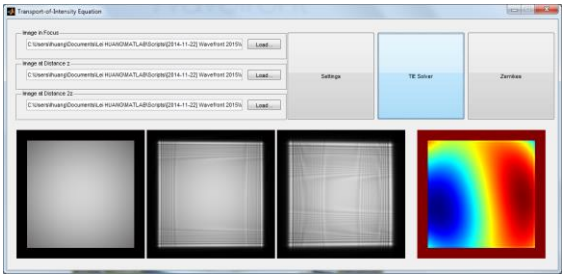
During our initial studies for at-wavelength metrology, we researched the methods for wavefront reconstruction from gradient data. A review and a new method have been already been completed. In order to double check the resultant wavefront in real experiments, we developed several different wavefront measurement techniques: Hartmann wavefront sensing, grating shearing interferometry, transport-of-intensity equation based phase retrieval method, etc...



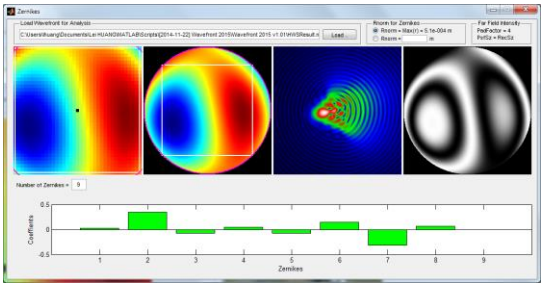
Simulation for Hartmann Wavefront Sensing



Simulation for Grating Shearing Interferometry



Simulation for Transport-of-intensity Equation



Zernike Analysis

So far many simulations are being carried out to verify the algorithms are accurate enough for their practical use. The next step would be the real wavefront measurement test in beam lines.

Some hardware has already been purchased to start the construction of our high resolution detectors and a dedicated Hartmann sensor for *at-wavelength metrology*.

The first test will be performed at the NSLS-II SRX beamline during the commissioning phase scheduled in late Feb and early March, 2015.

Multidimensional Imaging Data Analysis: From Images to Science

LDRD Project # 13-033
W. Lee

PURPOSE:
The original goal of this LDRD was to develop two tools that are broadly applicable to multidimensional data: (1) registration of 3D images from different techniques and (2) extraction of relevant scientific information from 3D images of heterogeneous porous media. Due to the strong interdependency and broad common goals of two other related LDRDs (#13-017 and #14-024), the PIs have agreed that it was crucial to first establish a robust common framework for the data workflow/management/analysis at the National Synchrotron Light Source II (NSLS-II).

APPROACH:
The original approach was to develop very specific image analysis tools focused on specific experiments. However, in light of the synergy with two related LDRDs and the goals of NSLS-II, a significant effort has been redirected to establishing a robust common framework for data workflow/management/analysis at NSLS-II and also to provide the proper tools for extracting data from the beamlines. It was recognized that in order for software analysis tools to be robust, generally useful, and have longevity, a coherent architecture/framework for data at NSLS-II is needed. Thus, the approach is to first establish such an architecture/framework and then to develop the specific tools.

TECHNICAL PROGRESS AND RESULTS:
The NSLS-II data analysis pipeline is intimately linked to the data acquisition architecture. Figure 1 shows the conceptual architecture of how NSLS-II data is acquired, stored, accessed and analyzed. The novel feature of this architecture is that the data storage is distributed; i.e., various data of interest may be stored at different physical locations at different time steps. For example, the detector data may be acquired and stored at a very high rate (> 10 Hz), as needed by the experiment. Other measurements, such as the storage ring current, which changes much more slowly, need not be stored at the same frequency. This distributed data storage allows one to optimize the data acquisition and storage. However, it complicates how the user can access data of interest. When this LDRD started, the technical details of this data acquisition architecture were not yet worked out and none of the red sections and almost none of the blue sections were implemented. Also, when this LDRD started, the workflow management system was also not yet defined. In summary, at the start of this LDRD, *all* of the dependencies that tie into the goals of this LDRD were not available and in most cases, not sufficiently defined.

Two postdocs, Gabriel Iltis and Thomas Caswell were hired on this LDRD. They collaborate closely with two related data management/workflow/analysis LDRDs: 13-017 and 14-024, and, with the beamline controls group (Bob Dalesio, group leader). Although the original goals for this LDRD reside in the red Data Analysis Tools box in Figure 1, it became clear that in order to achieve the broader goals of the facility, the data infrastructure and architecture (all the red boxes and some of the blue boxes) which did not exist then, needed to be established, developed and implemented. Due to their expertise, Thomas Caswell and Eric Dill (LDRD 14-024) have focused on working with the beamline controls/data acquisition to establish, develop and implement the proper protocols, framework and architecture. Gabriel Iltis has focused on implementing an image processing and visualization toolkit for 2D and 3D image data sets. The

implementation of the above architecture and the decision to utilize Python as the main programming language enables us to take advantage of the large numbers of scientific libraries that exist within the Python community. As such, although much effort has been spent on developing and implementing the architecture, the original goals of the LDRD remain on track.

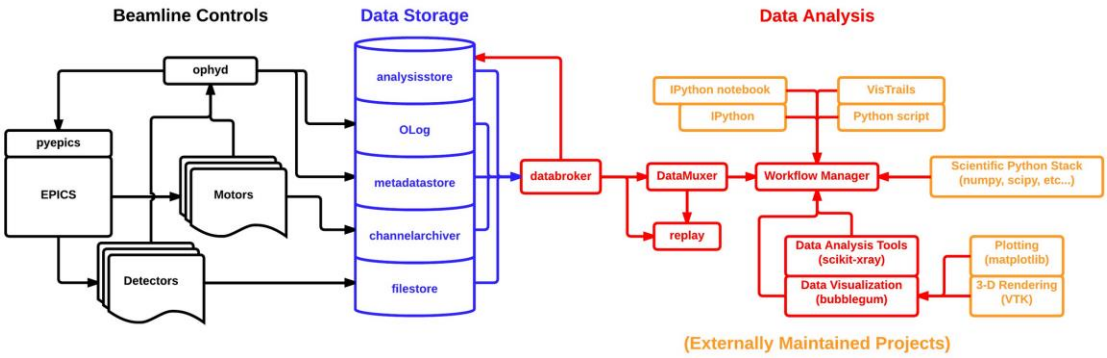


Figure 1 Data acquisition and analysis architecture for NSLS-II. The colors indicate the groups that are primarily responsible for that section: Black: Beamline Controls group, Red: This and other LDRDs; Blue: Shared. (Figure from Eric Dill).

FY14 Achievements:

- Established software development process and review procedure to make sure all software is robust, maintainable, and correct; i.e.; code review, documentation, testing and version control. Used GitHub as the platform for code review.
- Utilized, evaluated and reviewed competing Graphical Workflow Managers, with the final decision to use VisTrails
- Wrote an automatic application programming interface (API) generation for Python codes – all new codes are fully documented and html docs are automatically generated
- Set up infrastructure to automatically run a test suite when new code is added to the libraries
- Implemented binary source distribution system using Conda as a way to roll out the analysis software package to different beamlines
- Wrote and implemented wrapping tools to automatically expose all the analysis software into VisTrails by parsing the API documentation
- Wrote and implemented basic image arithmetic and segmentation tools for 2D and 3D image data sets
- Incorporated 2D visualization tools into the framework
- Collaborated to add differential phase contrast routines into the framework.

For FY15, we plan to:

- Add the image registration and 3D heterogeneous media image analysis tools into the established framework.
- Incorporate and customize the Visualization Toolkit (3D rendering/visualization) software into the framework.

Atomic Resolution Elemental Mapping Using X-ray Assisted STM

LDRD Project # 13-034
E. Nazaretski

PURPOSE:

Imperative for fundamental understanding of materials is the enhancement of our capability to design, manipulate, and control their ultimate functionalities. To develop materials by design, the determination of atomic level chemical composition and atomic scale imaging becomes critical. X-ray assisted scanning tunneling microscopy (STM) is a promising technique to achieve real space chemically specific atomic mapping. Absorption of X-rays gives rise to an additional STM current accompanied by a photoelectron current. A few attempts to combine the power of STM with synchrotron X-rays yielded sub 100 nm spatial resolution limited mainly by a high background photoelectron current. We propose to develop novel 'smart tips' based on carbon nanotubes (CNT) to reduce photoelectron currents and drastically improve spatial resolution. We will evaluate the performance of CNT-based tips using well defined samples and will conduct elemental mapping in the topological insulators $Bi_{2-x}Mn_xTe_3$ and $Ba(Fe_{1-x}Co_x)_2As_2$ superconductor crystals. By locating the position of substitutional Mn, X-ray assisted STM provides a direct visual method for examining the tendency to form clusters from the atomic to submicron scale, elucidating the effects of magnetic impurities and ferromagnetism on the topological surface states. For $Ba(Fe_{1-x}Co_x)_2As_2$ samples, we will monitor formation of Ba clusters and their influence on superconducting properties.

APPROACH:

We proposed a novel approach for development and fabrication of 'smart tips' suitable for X-ray assisted STM measurements at the NSLS-II. Multi-walled carbon nanotubes (CNT) have been used for scanning probe microscopy applications and demonstrated sub-nm resolution of topographic features when operated in tapping mode. We will utilize nanofabrication capabilities available at the Center for Functional Nanomaterials (CFN) at BNL and the Center for Nanoscale Materials at Argonne National Laboratory (ANL) to fabricate CNT-based STM tips and evaluate their performance utilizing the ID-26 beamline at the Advanced Photon Source (APS) at ANL.

TECHNICAL PROGRESS AND RESULTS:

The LDRD work related to X-ray assisted STM techniques is a two-step process. The first step, fiscal year one (FY14), involved nanofabrication, characterization, and initial evaluation of CNT-based smart tips; the second step, fiscal year two (FY15), involves further evaluation of CNT-based smart tips and sub-nm resolution elemental mapping of materials, such as the superconductor $Ba(Fe_{1-x}Co_x)_2As_2$ and Mn doped BiTe compounds.

One objective for FY14 was to develop and characterize the core component of the synchrotron X-ray-enhanced scanning tunneling microscopy (SXSTM) CNT-based smart tip. To develop the CNT-based smart tip, we had a user proposal approved for the CFN, for the usage of a number of fabrication and characterization techniques. We successfully implemented Plasma Enhanced Chemical Vapor Deposition (PECVD) to grow100 nm-3um SiO_2 on entire $Pt_{90}Ir_{10}$ tips with various radii of curvature. The films grown were uniform, as confirmed by scanning electron microscope (SEM) images of radial and vertical cross-sections of the tips. We then applied the FEI Helios dual beam focused ion beam (FIB)-SEM instrument to fabricate smart tips. First, we

removed the insulator at the apex of the tip to expose a desired amount of $Pt_{90}Ir_{10}$, for CNT attachment. We managed to expose ~1 um long $Pt_{90}Ir_{10}$ pillar out of SiO_2- insulated tips. Second, CNT was transferred to and "welded" to the tip apex. Finally, after CNT attachment, the exposed $Pt_{90}Ir_{10}$ pillar area was minimized by the localized growth of an insulating film through electron beam assisted chemical vapor deposition. A precursor molecule for SiO_2, tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS) was applied in situ through a nozzle in close proximity to the tip, along with H_2O. The interactions of the precursor with the Ga^+ ions caused the deposition of an insulating film in areas where the ions were hitting the tip. We have demonstrated that only ~300 nm long metal apex was exposed after the TEOS procedure. Two types of SiO_2, formed on one tip through PECVD and TEOS, respectively, were characterized by Energy-dispersive X-ray spectroscopy and showed similar chemical composition. Therefore, we demonstrated fabrication and characterization of CNT-based tips equipped with various thicknesses of SiO_2 and radii of the tip apex.

The other objective in FY14 and early FY15 was to evaluate performance of developed smart tips in a lab-based/off-beamline environment. We performed initial testing of uncoated and SiO_2 coated CNT-$Pt_{90}Ir_{10}$ tips using the Ambient Scanning Probe Microscope - VEECO Multimode V by imaging well defined samples, such as highly ordered pyrolytic graphite to allow pre-screening of tips. We then utilized RHK Variable Temperature UHV Scanning Tunneling /Atomic Force Microscope to determine the ultimate resolution of CNT-based uncoated tips. An Au(111) single crystal served as a model system to test the performance of the CNT-based smart tip. An CNT-$Pt_{90}Ir_{10}$ bare tip has been tested on the Au(111) crystal, and preliminary results show the characteristic herringbone structures of an Au(111) crystal surface, suggesting that the CNT-$Pt_{90}Ir_{10}$ bare tip works. In addition, we tested the 'survival rate' of CNT tips due to X-ray exposure at the X22A beamline before the shutdown of the National Synchrotron Light Source. Results of tests on five CNT tips showed that CNT survived exposure to 32.1 KeV X-ray radiation for at least 36 hours, with deposition of amorphous carbon from air (as expected).

For our initial experiments, we already evaluated the performance of CNT-based smart tips using SXSTM at the Nanoprobe beamline ID-26 by imaging Co clusters on Cu(111). We successfully aligned the system to the X-ray beam, and the x-y (in plane) tip scan was used to map the X-ray beam footprint in the sample plane. For SXSTM measurement, in spectroscopy mode and in the far field (350 nm tip-surface distance where no conventional tunneling takes place), a full energy scan from 7.5 to 10.0 KeV were acquired for the clean Cu(111) surface and Co clusters on Cu(111) surfaces, to confirm the surface cleanness of Cu(111) and the existence of Co on the Cu(111) surface. Then, the performance of CNT-based smart tips was evaluated on the characterized Co clusters on Cu(111) surface.

These measurements provided valuable information to perform further optimization of tip fabrication process to improve their robustness and spatial resolution.

In FY15, to perform actual X-ray measurements, we have an active (approved) proposal to access the ID-26 beamline for SXSTM experiments at the APS. Currently, the beamtime is scheduled for the last week of April 2015. We built up close collaborations with the SXSTM group of Dr. Volker Rose at ANL, for the ongoing evaluation of CNT-based smart tips and chemical mapping of $Ba(Fe_{1-x}Co_x)_2As_2$. and Mn-doped BiTe samples

Segmented Adaptive-Gap Undulator with Different Period Lengths in Segments for Production of High Flux and Brightness Hard X-Rays at NSLS-II

LDRD Project # 13-036

O. Chubar, C. Kitegi

PURPOSE:

The purpose of this project is to develop an innovative insertion device – a Segmented Adaptive-Gap Undulator – that will enable the most complete and efficient use of beam characteristics and magnet lattice properties of the National Synchrotron Light Source II (NSLS-II), in particular the low emittance of the electron beam, high brightness of the X-ray beam, and long straight sections available for insertion devices (IDs). The main concepts developed in the scope of this project are applicable to all known undulator technologies, in particular room-temperature and cryo-cooled In-Vacuum Undulators (IVU) and Superconducting Undulators, and significantly enhance spectral performance of these undulator types. Our project targets first of all the development and design of a room-temperature hybrid Segmented Adaptive-Gap In-Vacuum Undulator (SAGIVU). Such undulators can be used at many NSLS-II beamlines, resulting in improvement of their performance and more successful realization of their scientific programs.

APPROACH:

The project includes a large number of calculations in the areas of 3D magnetostatics, synchrotron radiation, heat conductivity, and mechanical stress analysis, many of which are already completed at the time of this writing. Based on results of these calculations, prototypes of two key SAGIVU sub-systems – magnet arrays and liner foil – will be designed and realized, and a number of magnetic and mechanical tests will be performed on them. To reduce costs of the project, several existing mechanical and magnetic parts will be used. This includes old mini-gap IVUs of the NSLS X-ray ring, in particular X9 and X13, which became available after the shut-down of the NSLS (Figure 1), and spare magnets for the turn-key IVUs purchased for NSLS-II. The planned magnetic and mechanical tests will be performed on a small (~1.5 m long) magnetic measurements bench of the NSLS-II ID group. Mr. Christopher Eng, a mechanical engineer hired recently for this project, has already made a significant contribution by the development of a detailed computer-assisted design model of a SAGIVU magnet system, including several versions of magnet keepers (Figure 2) and assistance in the preparation of the NSLS mini-gap IVU relocation plan.

An on-going collaboration with The NewYork Structural Biology Center, which is constructing a Partner beamline at NSLS-II, may bring some follow-on funding for this project. With this funding, a segmented mechanical carriage (i.e. “strong-back”) and a vacuum system can be designed, an installable SAGIVU can be built, and necessary tests with an electron beam can be performed (based on a specially developed plan that doesn’t compromise the scientific program of the beamline). This will allow us to fully accomplish the development and realization of the SAGIVU for NSLS-II, after this project ends.

TECHNICAL PROGRESS AND RESULTS:

Photos of mini-gap NSLS IVUs that were chosen for relocation to the NSLS-II magnetic lab for use in this project are presented in Figure 1. After moving to the magnetic measurements lab, these undulators will be modified to accommodate new ~0.7 m long magnet girders and will be

used in the tests as prototype SAGIVU segments. Figure 2 shows three different options of one of the main modules of the SAGIVU prototype magnet system, which is currently in its final stage of development. Ordering of prototype magnet system parts, assembly of the segments and start of the magnetic and mechanical tests is planned for FY15 and continued in FY16.

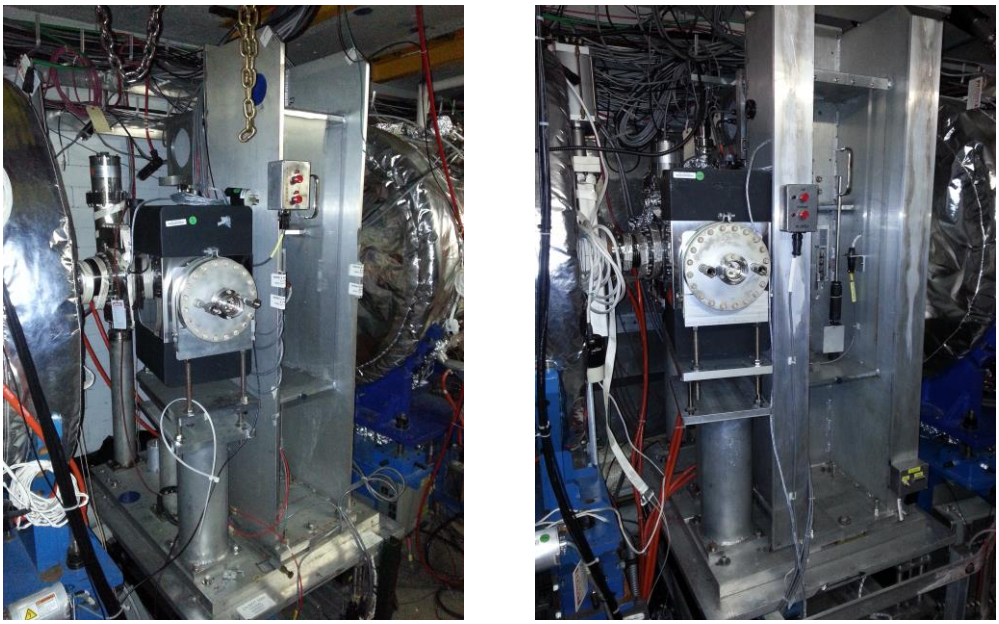


Figure 1 X9 and X13 mini-gap IVUs in the NSLS X-ray ring tunnel, prepared for extraction and relocation to the magnetic measurements lab of NSLS-II.

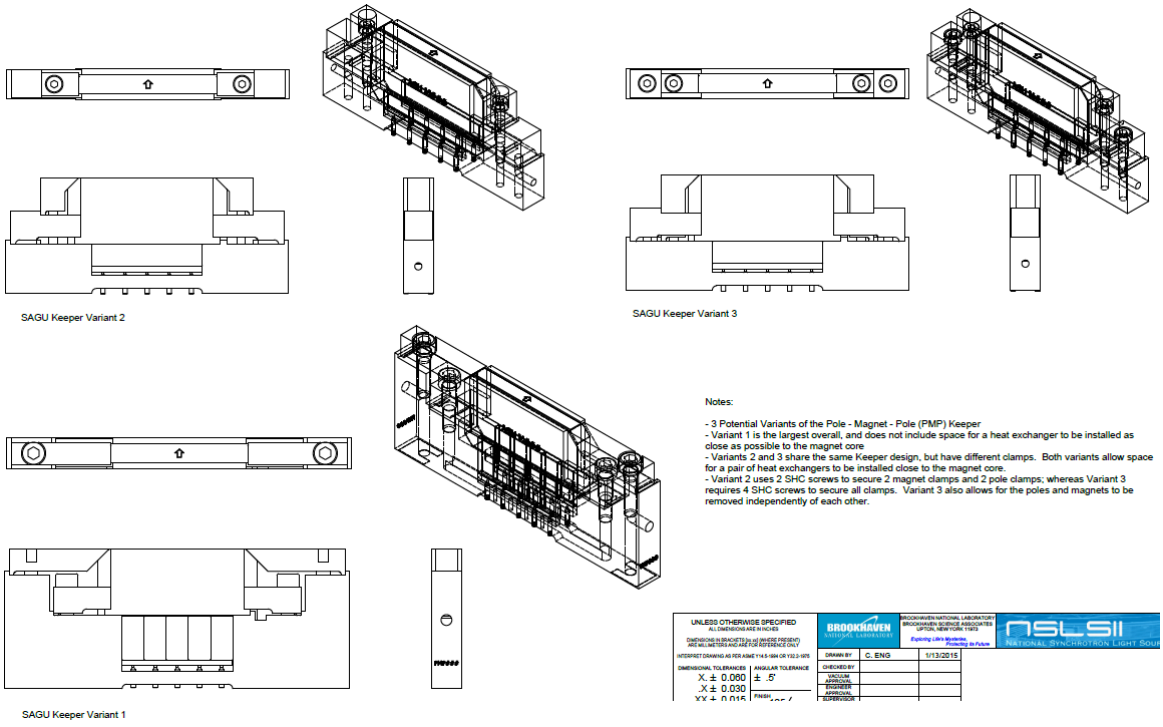


Figure 2 Assembly drawings (portions) of three different options of "Pole-Magnet-Pole" module – the key element of the SAGIVU magnet system.

Catalysis Program in Sustainable Fuels

LDRD Project # 13-038

J. Chen

PURPOSE:

This LDRD project established a research program led by Jingguang Chen as a Joint Appointee between BNL and Columbia University and provided starting research funding at both BNL and Columbia. The research program addresses the need for improved catalytic pathways for sustainable fuel synthesis. It focuses on chemical routes for the synthesis of fuels by recycling carbon dioxide, including catalytic processes to convert CO_2 into CO using H_2 as a source of energy and reduction equivalents. This is a sustainable path for incorporation of CO_2 into a fuel synthesis pathway, where CO may be combined with renewable sources of H_2 to form synthesis gas ($CO + H_2$) as the feed for Fischer-Tropsch synthesis of hydrocarbon fuels.

APPROACH:

Motivation: The primary energy source for transportation is currently the combustion of fossil fuel hydrocarbons. This contributes to rising atmospheric carbon dioxide levels and exacerbates problems of national dependence on foreign oil. Chemical routes for the synthesis of fuels by recycling carbon dioxide driven by renewable energy sources would reduce the net emission of carbon and could displace foreign oil. The research program specifically focuses on chemical routes for the synthesis of fuels by recycling carbon dioxide.

At BNL, the Chen group has initiated laboratory research, including hiring research staff, and is collaborating with the existing BNL catalysis and electrocatalysis research groups. At Columbia, a subcontract provided startup funding for laboratory research, including initial graduate student costs in FY2013 and FY2014. The FY2015 research effort under this LDRD will be carried out at BNL. The research efforts are linked under a common theme in sustainable processes for fuels synthesis. The project will strengthen the BNL catalysis science program through newly linked research thrusts. The projects will be carried out using a combination of theoretical and experimental work and in-situ techniques at the Center for Functional Nanomaterials and the National Synchrotron Light Source II.

TECHNICAL PROGRESS AND RESULTS:

During the past year of LDRD funding, the Chen group at Columbia University focused primarily on obtaining proof-of-principle results for CO_2 conversion using H_2. The combined theoretical and experimental results have identified the general trends, where the catalytic activity is related to the role of reducible oxide supports and the catalytic selectivity is controlled by formation of bimetallic alloys. Several transition metal carbides have been identified as highly active and selective catalysts for CO_2 conversion. These results were instrumental in receiving Department of Energy funding for ongoing support of the Chen group's efforts at BNL [1], and contributed to an initial publication [2]. The Chen group also investigated routes for conversion of C2 oxygenate fuels, which can be derived from biomass and are another path to sustainably recycle CO_2 into fuels [3], [4].

At BNL the Chen group members finished the installation and testing of several techniques, including an ultrahigh vacuum system for temperature programmed desorption, the CO

chemisorption equipment for measuring surface areas of catalysts, and an electrochemical system for electrocatalysis. The Chen Group members also worked with the Chemistry and BNL facility operations personnel to successfully obtain the certification and approval (Operational Readiness Evaluation) for performing experiments in these two laboratories.

Future milestones at BNL:

Oct. 2014 – Sept. 2015: The future research efforts will focus on two areas: (1) generation of CO_2-free H_2 through water electrolysis and (2) conversion of CO_2 using hydrocarbons instead of H_2. In the first area, we will focus on identifying low-cost electrocatalysts to replace the state-of-the-art platinum (Pt) for the hydrogen evolution reaction (HER). We will explore the possibility of using non-precious bimetallic alloys to achieve Pt-like HER activity through combined density functional theory calculations and electrochemical measurements. In the second area, we will investigate the feasibility of converting CO_2 to CO by hydrocarbon, such as ethane (C_2H_6) through the following reaction: $2CO_2 + C_2H_6 \rightarrow 4CO + 3H_2$. One of the advantages of this reaction scheme is the utilization of light alkanes, which are becoming more abundant from shale gas. We plan to perform experimental and theoretical studies to understand the reaction mechanism and identify promising catalysts.

[1] 'Converting CO_2 to CO Through Heterogeneous Catalysis'; PI Jingguang Chen; Submitted 5/14/2013 to DOE Office of Science under the Office of Basic Energy Sciences, Chemical Sciences, Biosciences and Geosciences Division in the Catalysis Science Program; Funded starting FY2014 as FWP CO-035; $650k/year FY14-FY16 renewable.

[2] "Molybdenum Carbide as Alternative Catalysts to Precious Metals for Highly Selective Reduction of CO2 to CO", MD Porosoff, XF Yang, JA Boscoboinik, and JG Chen, Angewandte Chemie Int. Ed., 53 (2014) 6705-6709.

[3] "A New Class of Electrocatalysts of Supporting Pt on Engel-Brewer Alloy Substrates", XF Yang, B Koel and JG Chen, Chemical Communications, 85 (2014) 12981-12984.

[4] "Decomposition Pathways of C2 Oxygenates on Rh-modified Tungsten Carbide Surfaces", TG Kelly and JG Chen, Surface Science, submitted.

Boron Arsenide ($B_{12}As_2$) Thin Films for Next-Generation Thermal Neutron Detectors

LDRD Project # 14-003

Y. Cui, R. James

PURPOSE:

The goal of this project is to determine the feasibility of using boron arsenide ($B_{12}As_2$) crystals as a transformational thermal neutron detector. Detecting neutrons is important to safeguard fissile materials; the primary method has been use of ^{3}He-based gas counters, but this approach is limited by the weight and cost of the pressure vessels containing the gas. The problem is greatly compounded by the global shortage of ^{3}He gas. There is a high demand for a new class of neutron detection and imaging instruments for nonproliferation and national security applications. Semiconductor materials based on high-reaction cross-sections of a few isotopes, e.g. ^{10}B and ^{6}Li, are of great interest because of their potential high efficiency in neutron detection. At the same time, such materials could be light weight, easy to maintain, and potentially low cost, making them suitable for hand-held and portable devices in field applications.

In this project, we investigate the characteristics for $B_{12}As_2$ as a material for detecting neutrons and photons. By demonstrating the photo-sensing capability, we can verify the transport of free carriers of this material. The success of this work will lead to increased availability of new neutron-detection devices for many applications.

APPROACH:

We are testing $B_{12}As_2$ thin films as a new radiation detector. This semiconductor is attractive for neutron detection due to several excellent properties: the large absorption cross-section of ^{10}B for thermal neutrons enabling high detection efficiency; the high charge-carrier mobility ensuring full collection of the ionization charge generated by secondary particles in the interaction of the neutron with the ^{10}B nuclei; the solid-state form of the material allowing for fabrication of compact detectors and easy integration with CMOS technology for electronic readout; and the low atomic number making the material relatively insensitive to gamma-rays, which normally appear as background and may interfere with neutron measurements of nuclear materials.

This is a two-year LDRD project to characterize and develop $B_{12}As_2$ materials for neutron detectors by conducting experiments in the following three areas:

(1) Material growth - We work with Kansas State University to obtain materials grown by the metal-flux method and by chemical vapor deposition (CVD). In parallel, we conduct material growth experiments internally with other approaches to explore alternative means for efficient material growth and to establish our capability in this area.

(2) Materials characterization - We systematically characterize the materials using techniques available in our group and at the National Synchrotron Light Source and Center for Functional Nanomaterials. The characterization methods include I-V measurements to determine the resistivity of materials; scanning electron microscopy (SEM) to take topographic images of the sample surfaces and analyze their elemental composition (via energy dispersive X-ray analysis); white-beam X-ray diffraction topography to determine the crystalline structure of the crystals; high-resolution X-ray diffraction to measure the state of strain in the $B_{12}As_2$ epitaxial films; and, Hall effect measurements to determine the carrier mobilities and lifetimes in the crystals.

(3) Detector fabrication - We prepare surfaces and deposit electrodes on $B_{12}As_2$ thin films using sputtering of different contact materials, with an initial focus on use of Au and Pt. We exposed the fabricated devices to LED light and neutron sources to measure the photo-sensitivity and response to neutrons.

Other investigators involved in this project include A. E. Bolotnikov, G. S. Camarda, A. Hossain, U. Roy, G. Yang, and guest scientist, R. Gul.

TECHNICAL PROGRESS AND RESULTS:

2014 was the first year of this project. We conducted research in all three area mentioned above.

(1) Material growth - We acquired $B_{12}As_2$ crystals by both metal-flux and CVD methods. We characterized these materials to establish the baseline for the project. In parallel, we used a portion of the acquired crystals as target materials for in-house crystal growth experiments and conducted thermal evaporation and electron beam evaporation for thin-film deposition. Fig. 1(a) shows the crystals from the metal-flux method (left) and the thin-film material from electron beam evaporation (right).

(2) Materials characterization - With the acquired materials, we conducted SEM measurement to investigate the impurities in the materials (Fig. 1b) and X-ray topography to determine the crystalline structure. With selected materials, we fabricated detector devices by depositing contacts onto crystal surfaces (Figs. 1a and 1c). We conducted I-V measurements; the results show the as-grown material has low resistivity (Fig. 1c). We also carried out Hall-effect measurements and found the hole mobility to be 150 $cm^2/V{\cdot}s$. We fed back the data to the crystal growers to improve the growth process.

(3) Detector fabrication - We measured the photoconductivity of $B_{12}As_2$ detectors by exposing them to 470-nm LED light. The experimental result (Fig. 1d) shows that this material is sensitive to light. This result supports our hypothesis that $B_{12}As_2$ could be used as a radiation detector. We also exposed detectors to a neutron source. However, because of the high leakage current in the current material and the low flux of neutrons, we were not able to get a neutron response from the detectors. We plan to redo the experiments with better material and use a nuclear reactor (for much higher neutron flux) in year two.

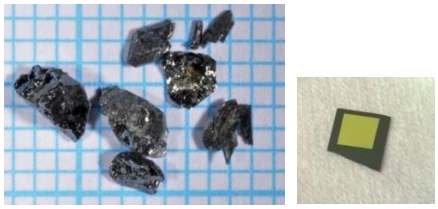


Fig. 1(a)

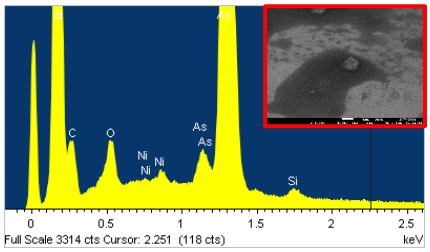


Fig. 1(b)

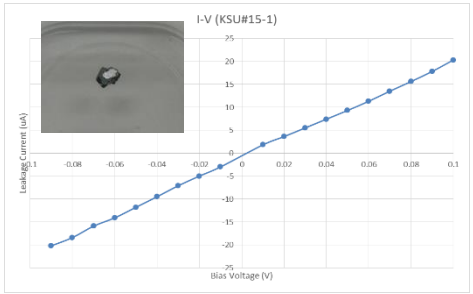


Fig. 1(c)

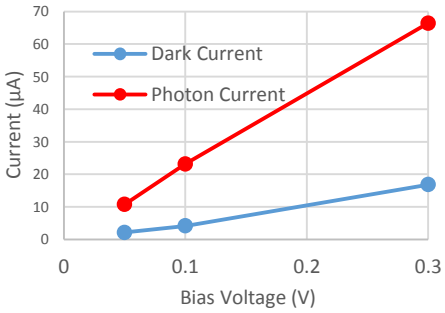


Fig. 1(d)

High Performance Direct Wind Superconducting Magnets

LDRD Project # 14-011
B. Parker

PURPOSE:
The purpose of this LDRD is to investigate extending BNL Direct Wind superconducting magnet capabilities in order to be able to produce coil structures suitable for use as eRHIC Interaction Region (IR) magnets. The eRHIC IR magnets are especially challenging to produce because they involve complex coil structures that must simultaneously have strong fields for focusing and deflecting hadron beams while providing nearby low field "protected regions" to pass the electron beam. For this we must develop new high performance superconducting cable to reach the required B-field strengths and develop new more efficient coil geometries that have low field protected regions. Finally we must also learn how to ensure precise conductor placement in the context of having to deal with stiffer, larger-diameter superconducting cable. Note that the advances arising from this LDRD are directly applicable to future BNL Direct Wind work (e.g. an improved International Linear Collider (ILC) IR magnet design, a new inflector magnet for g-2 at Fermilab and new superconducting gantry magnet designs for cancer therapy).

APPROACH:
Our initial eRHIC IR magnet designs were extensions of earlier work on active external field cancelation used for the ILC IR magnets and subsequent external field cancel coil designs for the SuperKEKB IR upgrade at KEK, Japan. However, it soon became apparent that in order to maintain adequate experimental acceptance in the forward/rear side of an eRHIC detector that brute force scaling of these earlier designs was not going to work. So in addition to looking to produce higher performance superconducting cable (along with associated winding machine modifications to use a new cable), we came up with a new sweet spot coil concept.

In the sweet spot coil geometry, we actually bring the e-beam directly through the coil structure since there is a natural zero-field crossing point somewhere at the midplane of standard coil structures. The trick is to carefully move the coil conductors apart in a way that leaves a physical gap for the e-beam while keeping the zero field point fixed. Unlike the direct field cancelation geometries alluded to earlier, which have coil currents fighting each other by flowing in opposite directions, all currents in a sweet spot coil structure flow in the same direction and this leads to greater efficiency at creating field in the main hadron aperture.

TECHNICAL PROGRESS AND RESULTS:
Before invention of the sweet spot concept, a lot of effort went into trying to get brute force coil field cancellation to work. While we argue that some type of low-field sweet spot arises naturally in any coil, there has nevertheless been a steep learning curve to figure out how to design and optimize practical coil solutions with such untraditional coil structures. For this the development of new codes and the adoption of new design approaches were critical. Fortunately much of the new software development was synergistic to ongoing work for SuperKEKB and g-2 so that the present LDRD has benefited greatly.

Over the course of time, the eRHIC IR coil designs have changed in a series of iterations as we came to better understanding of sweet spot coil possibilities and were challenged to meet (ever

more) demanding experimental and accelerator Machine Detector Interface requirements. Coil cross sections for the present, Version 2.1, eRHIC forward quadrupole and dipole magnets are shown in Figures 1 and 2. While there is interest in a new Version 3.0 IR optics layout to soften some accelerator physics design challenges, for the purpose of this LDRD we intend to procure cable and make winding machine modifications appropriate to validate the Version 2.1 magnet designs. It is necessary to first wind a series of test patterns, to learn how to handle a stiffer large diameter cable, before we can then proceed to wind and test a short prototype coil.

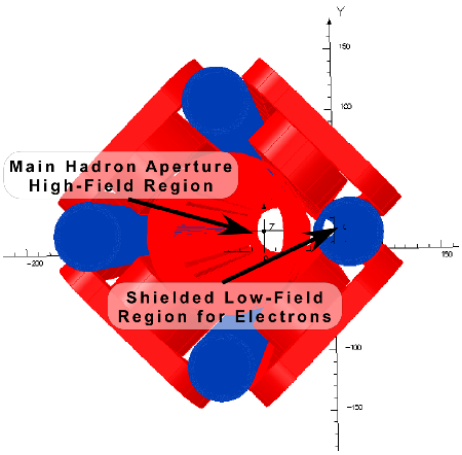


Figure 1 eRHIC IR quadrupole sweet spot concept.

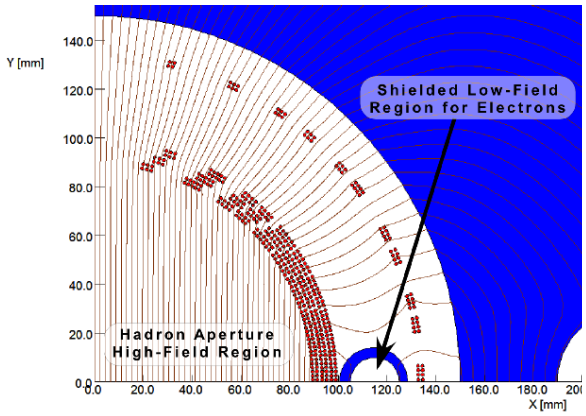


Figure 2 eRHIC IR dipole sweet spot concept.

Some 2015 LDRD Milestones

Date	**LDRD Milestones for 2015**
30 January	Finalize superconducting cable parameters and place order for new larger diameter conductor.
15 May	Start winding short coil patterns with new cable.
15 June	Start winding coil sets for R&D demonstration coil.
28 September	Perform warm magnetic field measurements.

In situ Investigation of the Strain Distribution in Next-Generation 3D Transistors using X-ray Nanodiffraction

LDRD Project # 14-021
H. Yan

PURPOSE:

Currently, microchip fabrication has evolved from the conventional 2D planar CMOS architecture to the 3D 22-nm technology node. In such a FinFET structure, a volumetric silicon (Si) fin is used as the channel between source and drain regions. A key issue in its design and fabrication is control of the strain, because the electron/hole mobilities are strongly linked to strain within the Si, and hence device performance. However, due to the lack of a characterization technique that noninvasively measures strain at such small length scales, the actual strain in a transistor remains unknown, in particular when the device is in operation. This challenging problem can be tackled at the hard x-ray nanoprobe beamline (HXN) of National Synchrotron Light Source II (NSLS-II), which provides a unique tool to noninvasively image strain at the nanometer scale. There are two objectives in this proposal. First, we will develop the appropriate inverse technique based on coherent diffractive imaging for 3D strain mapping. Second, we will design and fabricate a special FinFET for *in operando* measurement of strain using the technique we developed.

APPROACH:

We propose to use the nanodiffraction capability at HXN of NSLS-II to map the strain within FinFETs *in operando* and to correlate it with their mechanical and electrical properties. Owing to its penetration power and sensitivity to strain, x-ray micro/nano-diffraction techniques have been widely used for strain mapping in semiconductor materials. However, for the conventional method, the resolution is limited to the focused beam size and the measured strain is an "average" over the illumination volume, which is not sufficient to address our scientific question. Therefore, new techniques have to be developed. We pursue Bragg ptychography for 3D strain imaging. It is done by analyzing the Bragg diffraction intensity change on a flat 2D detector from pixel to pixel using an iterative phase-retrieval algorithm. Previous work has shown that 2D strain distributions with a resolution better than the focus size could be obtained. In this work we will extend this technique to a 3D case to obtain a resolution substantially below 10 nm, and then apply it to study the strain in the Si fin of a FinFET *in operando*. There are four phases of research during the lifetime of this project:

1. Develop a forward diffraction modeling tool to generate synthetic diffraction data and then apply the inverse technique to obtain the strain field in the crystal. By comparing the input and output strain fields, we can explore the limitation and accuracy of existing inverse algorithms, and determine the optimum experimental condition for the best result. It also greatly helps us to develop new algorithms.
2. Carry out a proof-of-concept experiment using a simple sample with a known strain field for a preliminary test. This will help us to better understand the nature of the problem. The experiment will be conducted at beamline 2ID-D of the Advanced Photon Source (APS) as a collaborative effort with the local beamline scientist Zhonghou Cai.
3. Design and fabricate a FinFET suitable for a nanodiffraction experiment at HXN. The device will be fabricated at IBM.

4. Conduct the experiment at HXN of NSLS-II for 3D strain imaging *in operando* at nanometer resolution.

TECHNICAL PROGRESS AND RESULTS:

Since the beginning of the project in June 2014, we have made a lot of progress. We have developed the forward diffraction model, written a C code for simulation and parallelized it for CPU & GPU acceleration. This simulation tool will be published and made available to the whole x-ray crystallography community in the near future. We have tested extensively the Bragg ptychography algorithm for inverse strain field reconstruction on the synthetic data to understand its limitation and accuracy. Alternative algorithms are being studied to improve the convergence and accuracy of this technique. We have conducted the first proof-of-concept experiment at beamline 2ID-D of the APS. The experimental data is being studied for strain field reconstruction. A conference poster was presented in the Coherence conference held in Chicago, Sept 2-5, 2014. In the 2014 Young Researcher Symposium (YRS) held at BNL, Nov. 20th, 2014, the poster titled "Dynamical artifacts in Bragg coherent diffractive imaging" won the "People's Choice" YRS Poster Award.

This year, we plan to achieve the following milestones:

1. Publish the software package for forward diffraction simulation
2. Publish the first experimental result obtained at APS
3. Design and fabricate the FinFET device suitable for the nanodiffraction experiment at HXN
4. Conduct the first experiment at HXN of NSLS-II for strain imaging at sub-10 nm spatial resolution.

Enable Early Sciences in NSLS-II with Experiment-Driven Big Data Stream System

LDRD Project # 14-024
R. Harrison

PURPOSE:
The purpose of the project is to develop prototype and pre-production capabilities for the integrated scientific computing and data management at the National Synchrotron Light Source II (NSLS-II). Our primary goals are to enable successful early science on the initial six beamlines, to lay the foundation for a long-term solution, and to inform and provide leadership that will develop and deploy the production tools.

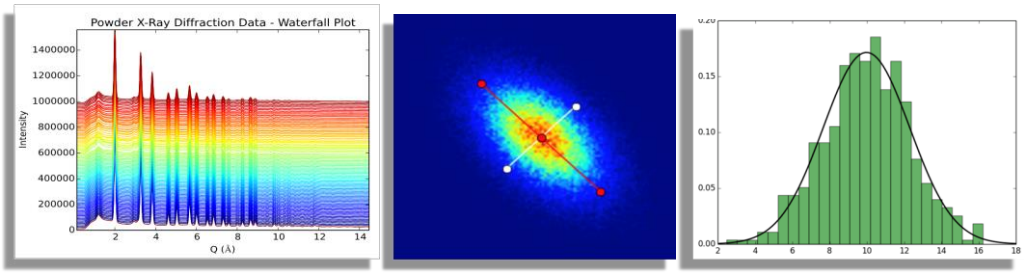
APPROACH:
The approach, which is to develop a detailed scope and requirements analysis for the computational, data-management, and scientific analysis needs of NSLS-II will be provided early in the project. Prototype and pre-production capabilities will be developed and deployed for efficient and effective storage, retrieval, search, and analysis of scientific data focusing on enabling early science. Included will be a flexible programming interface to various data formats and processing engines to facilitate integration of a variety of beamlines and their workflow engines into a streamlined data solution, and virtual experiments for experiment design and analysis. Another key feature is support for high throughput data reading and writing for compatibility with the capacity of modem detectors, and high reliability to work with existing or legacy hardware. This project has synergies with two other LDRDs: 13-017 a "NSLS-II Workflow Prototype System for Supporting Data Intensive Beamline Experiments" and 13-033 "Multidimensional Imaging Data Analysis: From Images to Science." All three LDRDs are managed together with personnel attending weekly meetings.

TECHNICAL PROGRESS AND RESULTS:
Data rates at NSLS-II will be > 90 Tb/day driven by use of high speed 2D detectors and the brightness of NSLS-II, allowing for faster data collection. This results in total storage requirements of > 18Pb if data is stored for 1 year, being accessed by > 3000 users. At the same time, the synchrotron user community has transitioned from "expert" users to scientists who use the synchrotron as a "tool." Currently most users do not have the hardware at home to analyze complex data or the analysis software to properly analyze the data. Full utilization of NSLS-II will require the facility to store and manage the data and provide analysis and visualization tools for the users.

In the present fiscal year, progress has been made on several fronts. Specifically,

1. Scientific use cases were collected for data analysis needs across the project beamlines
2. The basic approach for data analysis was determined, specifically a Python-based modular approach was selected
3. The Application Program Interface with the data acquisition was defined
4. The basic architecture behind data and meta data storage was refined
5. A toolkit of x-ray analysis code was written, meeting the early science use cases. Named "Nikea," it represents an end to end solution for x-ray data analysis and visualization.

6. A workflow manager, VisTrails, was selected, which allows users to graphically select Python code modules and string them together to accomplish a particular workflow. Standard workflows were written and made available for trial use at two beamlines (Coherent Soft X-ray Scatterings and X-ray Powder Diffraction).



Data Visualization & Analysis Graphical User Interface for Live Data

Milestones for FY15 and FY16:

FY15

1) Develop real-time data analysis, integrating analysis code with Data Acquisitions
2) Develop the "data broker" allowing data to be stored in variety of locations with different latencies as determined by the frequency of access and, in a way, that is transparent to the user
3) Roll out the pre-production analysis codes to the six project beamlines
4) Collect use cases for the NSLS-II Experimental Tools "NEXT" beamlines
5) Collect use cases for the Advanced Beamlines for Biological Investigations with X-rays (ABBIX) beamlines
6) Carry out external review of the approach.

FY16

1) Roll out production code to the project beamlines
2) Roll out pre-production code to ABBIX
3) Data broker is functioning for all operating beamlines
4) Data is stored non-locally.

Increasing Efficiency of Nitrogen Use by Plants: A Prerequisite for Bioenergy Crops on Marginal Lands

LDRD Project # 14-026
B. Babst, S. Maslov, W. Qu

PURPOSE:

Since nitrogen is often the most limiting nutrient on marginal soils, efficient use of nitrogen by bioenergy crops will improve the economic viability and the carbon dioxide savings of bioenergy. Efficient use of nitrogen for growth requires balancing nitrogen needs in photosynthetic tissues with needs in growing and developing tissues, which involves transport of nitrogen to appropriate tissues. A major knowledge gap is our limited understanding of nitrogen transport mechanisms and how they are regulated. We will use a combination of computational approaches and experimental genetic screening to identify genes involved in nitrogen transport within the plant. The practical outcome of this work will be a predictive model of whole-plant nitrogen regulation that can be used to improve nitrogen use efficiency of bioenergy crops, such as poplar and sorghum, for sustainable biomass production on marginal lands.

APPROACH:

Vascular transport of nitrogen is dependent on transporter proteins moving nitrogen-containing molecules across cell membranes into vascular tissue. Several genes that encode transporters important to nitrogen uptake from soil have been identified in the model plant, *Arabidopsis* (e.g., NRT1.1). Yet, overall nitrogen transport and its regulation are poorly understood, in large part because there has not been a means to measure transport at the whole-plant scale.

This project will lay the genetics foundation to understand the role of transport in plant nitrogen use efficiency. Our immediate objectives are to (1) identify and characterize key nitrogen transporters in a genetically tractable model system (*Arabidopsis*) by a combination of computational methods and mutant screening; (2) demonstrate our ability to translate from *Arabidopsis* to a bioenergy crop, by identifying and characterizing the functional homolog of the known nitrogen transporter, NRT1.7, in poplar; and (3) use computational modeling to identify the genes in bioenergy species most likely to have similar functions as each of the nitrogen transporters identified by our *Arabidopsis* mutant screens.

Our strategy is to use a combination of network modeling (Maslov) and live plant experimentation (Babst, Qu) that will feed back and inform each other in an iterative process. We will measure nitrogen transport in real-time using nitrogen-13 (^{13}N) tracers (Babst). This is the only means of measuring nitrogen transport, and is only possible at several labs world-wide. A fast screening assay of the plant genetics model *Arabidopsis* will identify mutants affected in nitrogen transport, supplying the "parts list" of genes needed to reconstruct and manipulate the system. The screening will be targeted using computational methods (e.g., co-expression analysis) to identify a small subset of genes likely to encode nitrogen-related transporters (Maslov). More refined experiments on nitrogen transport mutants (Babst, Qu) will be complemented by computational modeling to streamline translation of knowledge from *Arabidopsis* to bioenergy crop species, such as poplar and sorghum (Maslov).

TECHNICAL PROGRESS AND RESULTS:

We carried out several iterations of computational analysis to refine our approach. We conducted co-expression analysis using metabolic genes known to be involved in nitrogen remobilization to identify transporter-encoding genes that may be involved in nitrogen remobilization. In addition

to identifying several known nitrogen transport genes, our efforts have predicted other relevant genes for further study via our mutant screening pipeline, completing ***milestone 1.1***.

We made significant progress on ***milestone 1.2***. We obtained seed for 37 nitrate transporter (NRT) and ammonium transporter mutant lines in *Arabidopsis*, and are currently propagating enough seed for screening by ^{13}N assays. Based on computational analysis, we identified 10 additional mutant lines for screening, many of which are from gene families not previously associated with nitrogen transport. These latter candidates represent the highest risk and reward, as they may be "false leads" or may lead to the identification of novel functionality in previously uncharacterized gene families.

We made improvements and increased the efficiency of our ^{13}N assay infrastructure, such as designing a small leaf cuvette for the administration of $^{13}NH_3$ gas to an individual *Arabidopsis* leaf (Figure 1). With this cuvette that is easy to mass-produce, and other minor modifications to our system, we will increase the throughput of our assays from 2 plants to 6-12 mature *Arabidopsis* plants at one time. This and the hiring of a new postdoc (Dr. Fei Gao) in December 2014 will significantly accelerate progress on ***milestone 1.2***.

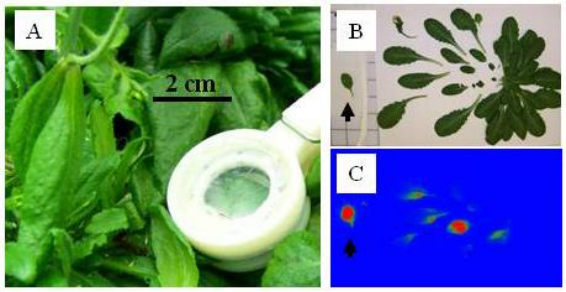


Figure 1 Custom leaf cuvette for small plants (A). Dissected *Arabidopsis* plant (B) and radiographic image of ^{13}N distribution in the same plant (C). Black arrows indicate the leaf to which $^{13}NH_3$ was administered in B & C.

The NRT1.7 gene encodes a transporter in *Arabidopsis* that is involved in nitrogen remobilization from leaves during reproduction. We applied cross-species co-expression network mapping to identify functional homologs of the *Arabidopsis* NRT1.7 gene in poplar. We predicted 6 functional ortholog candidates that are likely to have the same function in poplar, based on similarity of expression patterns in leaves, completing ***milestone 1.3***. Most of these candidate genes would not have been predicted based on sequence similarity alone.

To provide relevant transcriptome data for future translation of knowledge to the bioenergy crop sorghum (***milestone 1.4***), we performed a nitrogen limitation experiment with several sorghum genotypes. We measured growth and photosynthesis, and archived frozen tissue samples from 50 day-old sorghum plants which will be used for transcriptomic analysis.

MILESTONES

Year 1	1.1	Co-expression network based prediction of gene candidates	Maslov
	1.2	Nitrogen transport mutant screening	Babst
	1.3	Identify NRT1.7 homolog in *Populus* and begin transformation	Babst
	1.4	Perform sorghum experiment for gene expression analysis	Babst
Year 2	2.1	Assembly and analysis of sorghum gene expression data	Maslov
	2.2	Detailed functional analysis of key nitrogen transport mutants	Babst, Qu
	2.3	Phenotyping to validate function of *Populus* NRT1.7 homolog	Babst
	2.4	Apply for DOE funding for translation to bioenergy crops	Babst, Maslov, Qu
Year 3	3.1	Identify functional homologs in bioenergy crops	Maslov
	3.2	Verification of biochemical function of bioenergy crop genes by heterologous functional complementation	Babst, Qu
	3.3	Begin transformation of *Populus*/*Sorghum* for key genes	Babst

Tissue-Specific Metabolic Models in Plants

LDRD Project # 14-028
J. Schwender

PURPOSE:

Compared to the advanced state of genome-scale metabolic modeling of microbes, methodology and application of such modeling techniques in plants is lagging behind. Metabolic models of plants still fail to capture variations found in different tissues. Therefore, in addition to the master metabolic network derived from the genome, tissue-specific metabolic models need to incorporate information on gene expression patterns in different tissues. The objective of this project is to derive high-quality master and tissue-specific metabolic networks in plants. For this purpose, we will develop computational methods allowing one to integrate gene expression and network data with genome-wide metabolic networks. This project is synergistic to future efforts in the Biological, Environmental & Climate Sciences Department to create an integrated program in quantitative plant sciences with the ultimate goal of combining tissue-specific metabolic modeling with radiotracer metabolic transport measurements across tissues in plants relevant for Department of Energy (DOE) biofuels objectives. This project will provide a valuable contribution to the DOE Systems Biology Knowledgebase (KBase) which is the flagship computational systems biology project funded by the DOE Office of Biological and Environmental Research.

APPROACH:

With the amount of –omics data increasing exponentially, predictive models converting these data into biological knowledge becomes progressively more important. Genome-scale metabolic flux analysis is the gold standard of predictive modeling in systems biology. With the enormous increase in the amount of genome sequence information, an ever increasing number of organism-specific metabolic models are being constructed based on the information about genes and enzymes encoded in genomes. Based on such genome scale metabolic networks, Flux Balance Analysis (FBA) became the workhorse of predictive biology at the scale of metabolic networks. While plants are multicellular organisms with different tissues like leaves, flowers or roots, genome scale reconstructions are a superset of the metabolic reactions that are functioning at any time in its development, under any environmental condition, and in any possible cell type. Not all reactions of the superset of reactions ("master network") are active at the same time and in the same cell type. Thus, we have to derive tissue-specific sub-networks, which can be done based on gene expression data, in particular, considering comprehensive and quantitative expression datasets that can be obtained from microarray technology and next generation sequencing.

In this project, we aimed at construction and refinement of a genome-scale master metabolic model of the model plant *Arabidopsis thaliana*, taking into account subcellular compartmentalization of metabolic reactions. Then, a genome-scale model of a DOE relevant plant was to be derived (Aim 1). Based on the master networks, tissue-specific sub-networks had to be derived (tissue-specific metabolic models). This is done based on integration of tissue-specific gene expression data and by adjustment of the biomass equation of the model according to the biomass composition specific to the tissue (Aim 2). In addition, the development of Metabolic-Expression (ME) models for plants was planned (Aim 3). In ME models, the processes of gene transcription, RNA processing, translation and protein maturation are represented in much more realistic detail than in the classical constraint-based approach.

TECHNICAL PROGRESS AND RESULTS:

Aim 1. Genome scale metabolic network reconstruction: We constructed a high-quality genome-scale metabolic network for the model plant *Arabidopsis thaliana* based on a model on central metabolism previously developed for *Brassica napus*, but referenced to the *A. thaliana* genome. The model was extended by adding the pathways for cell wall biosynthesis, photosynthetic pigments, phenylpropanoids, and membrane lipids. Lipid metabolism reactions were added to the model by explicit representation of the structural diversity of glycerolipids, which is given by many possible combinations of different fatty acid chains that are linked to the glycerol backbone. This expansion greatly increased the total number of metabolites and reactions. For the reconstruction of phenylpropanoid and lignin metabolism, we conducted co-expression analysis based on *A. thaliana* expression data, in order to identify possible unknown genes that participate in the pathway. The latest version of the genome scale metabolic network includes 11 compartments, 1,388 metabolites, 1,990 reactions and 1,450 annotated genes encoding the catalyzing enzymes or transporters. The model was tested for functionality.

Aim 2. Construction of tissue-specific metabolic models: A leaf-specific functional metabolic model was derived. This was done by considering the composition of biomass as well as the macromolecules that constitute leaf biomass. Contents in protein, lipid, DNA, RNA, cell wall, etc. were defined based on the literature data on leaf composition. Transcript data were applied to verify the existence of all the reactions of the general metabolic network in leaves. The model was successfully run by simulation of FBA under autotrophic condition. The model can simulate biomass growth by CO_2 fixation through photoautotrophy and predict sucrose consumption as the carbon source under dark conditions.

We tested the E-flux method for integration of transcript data with FBA models. The boundaries of fluxes were re-set by the transcript data. The reaction that has the highest gene expression level would have the largest boundary (i.e., lower and/or upper boundary are set to 1,000). Other reaction boundaries were scaled to the largest boundary in proportion to its gene expression level. The flux variability analysis shows the solution space of the E-flux modified FBA model was decreased.

Aim 3. Development of ME models for plants: Not yet started. The ME method was prototyped with a microorganism. Our further evaluation of the task to set up a ME model in a complex eukaryote (plant) led us to conclude that this goal cannot be accomplished within this project.

Milestones for FY 2015:

- Using the *A. thaliana* model as a template, we will start constructing a model for Field Pennycress (*Thlaspi arvense*). *T. arvense* has been described by others as a new potential bioenergy feedstock plant. Model construction will be done by defining gene orthology between the two closely related organisms, which is now possible due to an available complete genome sequence of *T. arvense*.
- We will integrate the two genome scale models into the KBase modeling framework. Currently, our genome scale models are developed and maintained within the widely used COBRA toolbox.
- We will further explore different methods of integration of transcriptome data with the models to derive tissue-specific models. For this purpose, we specifically will test methods that are based on differential expression instead of absolute expression values.

Operando Studies of C1 Catalytic Reactions: Probing Model and Technical Catalysts at High Pressures Using Soft X-rays

LDRD Project # 14-035
J. Rodriguez

PURPOSE:

This LDRD will yield fundamental insights into catalysis, gained from the ability to perform spectroscopic studies at unprecedented gas pressures using the Coherent Soft X-ray Scattering-2 (CSX-2) beamline, a world-class soft X-ray beamline at the National Synchrotron Light Source II (NSLS-II). The planned experiments will demonstrate a novel paradigm for probing the active components and reaction mechanisms on both planar and high surface area catalysts *in operando* under relevant reaction conditions. For the water-gas shift (WGS, $CO + H_2O \rightarrow H_2 + CO_2$) and methanol synthesis (MS, $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) reactions primarily targeted here, both carried out on reducible oxides such a ceria and titania, such a mechanistic understanding for a set of highly active catalyst materials will provide the basis for engineering the next-generation catalysts for Cl chemistry.

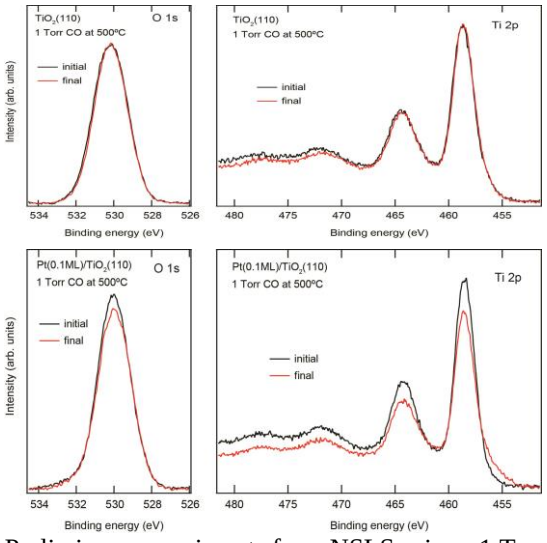
APPROACH:

Historically, fossil fuels have been the predominant sources of energy. The WGS reaction is used to remove CO present as an impurity in the reforming of hydrocarbons and to deliver high purity H_2. Within an overall focus on Cl conversion, we will target a second reaction, the synthesis of methanol from CO_2 hydrogenation, a conversion that shows great promise for the sustainable production of liquid fuels (alcohols). In industry, the most common catalyst materials used for this reaction are Cu based (low temperature). However, these materials suffer from issues related to deactivation, sintering and poisoning. Combined theoretical and experimental research at BNL has shown that composite oxide nanocatalysts of the type M/CeO./TiOx(M: Au, Cu, Pt) can provide catalytic activity 15 – 20 times higher than that of the standard industrial CuZnO catalyst. The source of this remarkable enhancement is not fully understood and requires the investigation of both model and powder catalysts (bridging the materials gap) by experiments from ultra-high vacuum to realistic reaction pressure.

Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and X-ray absorption spectroscopy (AP-XAS) can provide the ability to probe catalysts dynamically at pressures that are typically in the ~Torr regime, revealing the chemical state of the active phase of catalysts in the presence of weakly adsorbed or unstable critical intermediates. AP-XAS is the latest variant, adaptable to bridge the materials gap from model systems to powder materials. The combination of the AP-XPS end station proposed by the Center for Functional Nanomaterials (CFN) to be also installed at CSX-2, with the Catalysis Group at BNL as contributors, with the AP-XAS could become the worldwide standard for catalytic studies by soft x-rays under *operando* (~atm) conditions.

TECHNICAL PROGRESS AND RESULTS:

Preliminary AP-XPS Experiments at X1A: The environment for both chemical reactions to be studied, MS and WGS, is overall reducing. As a first step towards the study of our target reactions on Pt nanoparticles supported on ceria modified TiO_2, we carried preliminary experiments at the X1A beamline to study the effect of Pt nanoparticles on the reducibility of a TiO_2(110) surface. It is clearly observed that the presence of Pt significantly enhances the reducibility of TiO_2(110) in the presence of ~1 Torr of CO (see Figure). This is a fact that was hypothesized in the literature, but not directly corroborated before.



Preliminary experiments from NSLS using ~1 Torr of reactants

Preliminary AP-STM Experiments at the CFN: We are in the process of correlating this observation with microscopic studies in the reactor scanning tunneling microscope (STM) at the CFN. Since no experiments have ever been reported on the *in situ* study of oxide single crystals by STM, our initial work was carried on a nano-pitted Cu(111) surface, which is used as a reference system because is the industrial catalyst for the WGS reaction and is also active for MS. We observed in this case that the surface of Cu metals can be dynamically modified by the presence of either hydrogen or CO in the environment, both reactants in the WGS and MS reactions.

Preliminary AP-Infrared (IR) Experiments at Chemistry: We correlated our ambient pressure STM results with AP-XPS results also from the X1A beamline, and complementary AP-infrared reflection absorption spectroscopy carried in the Chemistry Department. These combined experiments led to a publication in the journal *Physical Chemistry Chemical Physics*. Using the experience gained in the simplified system, we will now proceed to study our target catalysts prepared in TiO_2(110) samples. We have been in parallel characterizing powder Pt/Ceria, Pt/Titania and Pt/Ceria/Titania catalysts *in situ* by IR spectroscopy. We have been able to unequivocally assign Ce cationic sites which have been the source of longstanding controversy in the literature, by correlating our experiments on planar and powder catalysts.

Moving of instrumentation from NSLS and setting up of AP-XPS and AP-XAS: Based on the above results, we expect to finish the assembly and testing of equipment at the AP-XPS and AP-XAS end-stations at NSLS-II, and carry out preliminary experiments during the first semester of 2015. We will in this way been able to directly compare IR and soft X-ray *in situ* experiments from planar and powder catalysts under working conditions.

Milestones

This year: The first objective for this year is to finish with the set-up of the end stations for AP-XPS and AP-XAS at NSLS-II. Then, experiments will start using model and powder catalysts.

Next year: Systematic mechanistic studies will be performed using AP-XPS and AP-XAS. These studies need a beam current and intensity that will not be available at NSLS-II until next year.

Correlative Microscopy, Spectroscopy and Diffraction with a Microreactor

LDRD Project # 14-036
E. Stach, A. Frenkel

PURPOSE:

The purpose of this LDRD is to develop and utilize a novel correlative characterization approach based on microfabricated catalytic reactors. This approach allows the acquisition of data from heterogeneous catalysis systems at atmospheric pressure, using advanced analytical electron microscopes at the Center for Functional Nanomaterials (CFN) and x-ray spectroscopy, diffraction and imaging at the National Synchrotron Light Source (NSLS/NSLS-II). The measurement of reaction products during the data acquisition allows *operando* characterization, i.e. characterization of the catalysts as they are actively working to catalyze the chemical reaction. By obtaining the data in an *operando* condition, it becomes possible to directly correlate the information about the system obtained from the measurements using each technique. Our work to date clearly demonstrates the value of this approach: our first experiments – using the probe reaction of ethylene hydrogenation mediated by Pt nanoparticles on SiO_2 supports – have shown that this correlative approach reveals complex changes in the distribution of nanoparticle sizes that could not be detected by either technique alone. The experiments have relied upon the microfocusing capabilities of NSLS Beamline X27A; our next experiments are scheduled as First Light experiments in April 2015 on the Submicrometer Resolution X-ray Spectroscopy (SRX) beamline at NSLS-II. The capabilities being developed through this LDRD effort are intimately linked to the proposed efforts of the Integrated Center for Energy Sciences for Catalysis Science, the core research programs at the CFN and Chemistry and the Synchrotron Catalysis Consortium and are well-aligned with the overall Laboratory strategy.

APPROACH:

Understanding the structure-property relationship has been the most significant challenge of investigating different catalytic reactions. Features such as cluster size and shape, state of atomic order, bond strain, the support, facet orientation, and metal composition have all been shown to affect catalytic activity, selectivity and stability. Some reactions cause structure or size changes in the catalysts. The nature of such correlations, and mechanisms responsible for them are not well understood. Coexistence of different particle sizes, shapes and compositions within the catalyst population may happen even in model catalysts. This heterogeneity posed a challenge to many "ensemble-averaging" techniques such as X-ray Absorption Fine Structure (XAFS) spectroscopy, which may neglect this structural heterogeneity into a single average measurement. Techniques such as electron microscopy, on the other hand, can be used to directly measure the structural heterogeneity in a sample, but is known to suffer from statistical limitations and experimental artifacts. Thus it is important to utilize a combination of complementary experimental methods to unambiguously describe the structural complexities that are inherent in these nanoscale systems, and do it in working conditions (*in operando*).

We are confronting this significant challenge through the use of microfabricated catalytic reactors that are compatible with a broad range of photon and electron based characterization methods based on imaging, spectroscopy and diffraction. These reactors allow provision of reactant streams at temperatures of up to 500°C and pressure in excess of 1 atmosphere, and which can measure reactant streams to confirm that the system is in a working condition. This allows us to make direct comparison between the measurements in an unprecedented fashion. Our experimental setup consisted of a microreactor system based on silicon micromachining. The catalysts are confined between two thin SiN windows by 250 nm at their closest point,

separated by an integrated spacer. Such a system is integrated within a Transmission Electron Microscope (TEM) sample holder so that gases can be provisioned to the sample in a sequential fashion. Different mixture of reactant gases (He, H_2, C_2H_4) were controlled by mass flow controllers, and the product analysis was done through a mass spectrometer. Measurements were taken at the CFN FEI Titan Environmental TEM and the NSLS microfocusing beamline X27A. Both series of measurements were done in identical reaction conditions using the identical setup. Different stages of reactions were synchronized across the two experiments for analysis purposes by correlating the data obtained on gaseous products.

TECHNICAL PROGRESS AND RESULTS:

We have obtained correlated, *operando* measurements from Pt/SiO_2 heterogeneous catalysts during the process of ethylene hydrogenation (Figure 1), in collaboration with Ralph Nuzzo at the University of Illinois at Urbana-Champaign. These results clearly demonstrate the ability to obtain high quality X-ray Absorption Spectroscopy (XAS) and Scanning Transmission Electron Microscope (STEM) data from the microreactor system. We have also demonstrated that we can obtain high quality infrared spectroscopy data (beamline U10B) – this allows determination of the molecular species on the active catalysts, and recently (using gas chromatography) that we can measure the reaction products quantitatively. These are significant accomplishments, as they allow direct links to be made between the actively reacting species, the reactant products, and

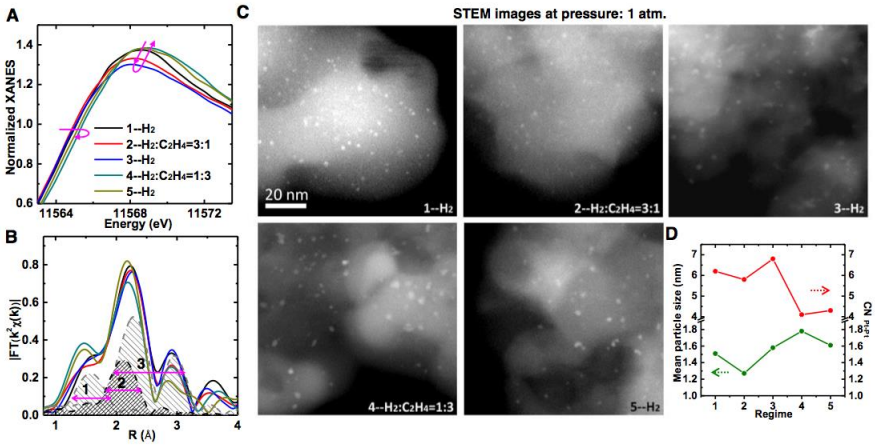


Figure 1 Experimental results from operando XAFS and STEM. (A) X-ray absorption near edge spectroscopy, (B) Fourier transform magnitudes of Pt L_3 edge EXAFS spectra, and (C) STEM images, all measured *in operando*, during different reaction regimes. EXAFS and STEM results are displayed in (D) for all regimes. The green line indicates the mean particle sizes, as obtained by the STEM image analysis. The red line shows the change of Pt-Pt coordination number obtained from XAFS analysis.

physical and electronic structure characterization.

During the past year, we developed a quantitatively robust method to link the direct (but resolution-limited) measurements of particle size distribution from STEM images and the comprehensive, but average measurements of EXAFS. The results clearly reveal the benefit of the correlative approach: we can track change in different particle morphologies throughout the entire reaction sequence.

We will extend this approach to the characterization of bimetallic nanoparticles (in collaboration with Jingguang Chen at BNL Chemistry / Columbia University) and the SRX beamline team, to understand the elemental redistribution that occurs in NiPt catalysts when exposed to oxidative and reductive conditions. We also submitted a proposal, approved for 2 years, for beamtime at the Advanced Light Source microspectroscopy beamline, to conduct *operando* studies of catalytic oligomerization of olefins over Pt and Pd catalysts in the microreactor. In addition to the core scientific questions in these systems, we will expand the range of experimental probes (electron, x-ray and optical) that can exploit this approach, thereby developing a robust platform for operando experimentation.