LDRD
2015 Annual Report

BROOKHAVEN NATIONAL LABORATORY

Laboratory Directed Research & Development Program Activities

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BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES
UPTON, NEW YORK 11973-5000
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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 2015 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.

Introduction

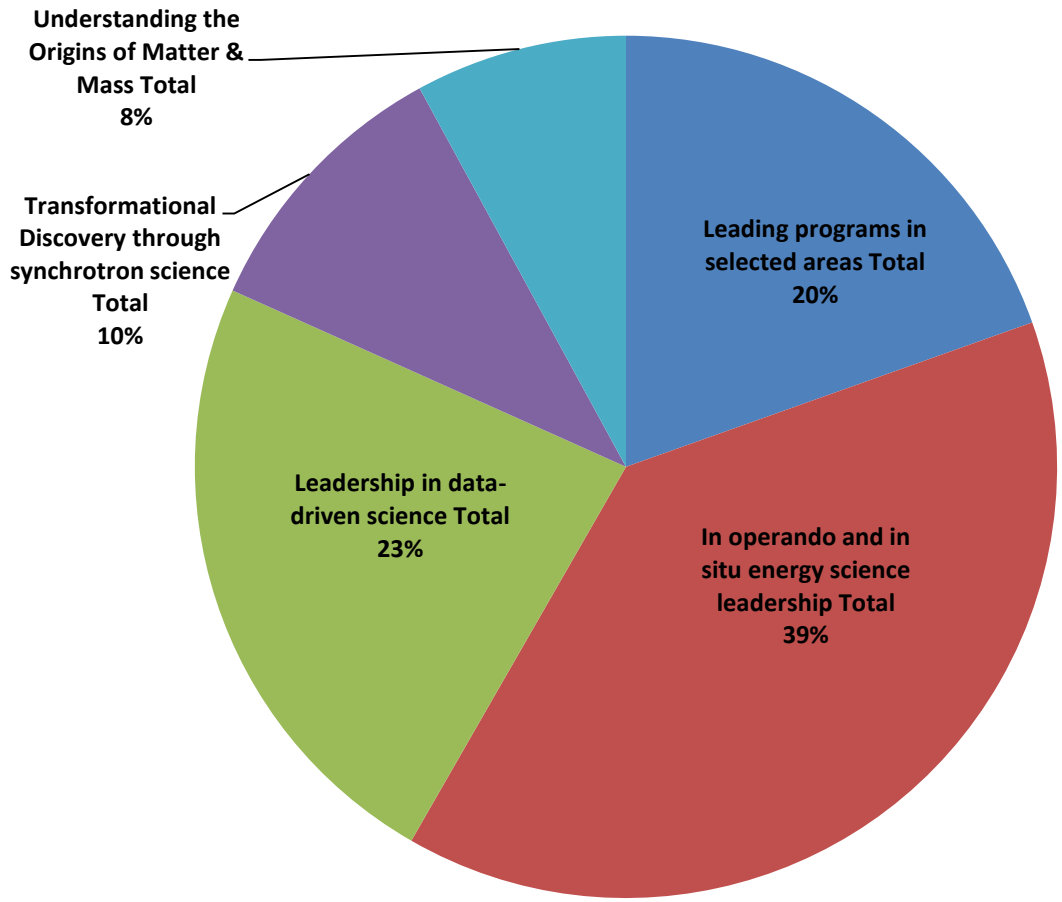
Each year, Brookhaven National Laboratory (BNL) is required to provide a program description and overview of its Laboratory Directed Research and Development Program (LDRD) to the Department of Energy (DOE) in accordance with DOE Order 413.2B dated April 19, 2006. This report provides a detailed look at the scientific and technical activities for each of the LDRD projects funded by BNL in FY 2015, as required. In FY 2015, the BNL LDRD Program funded 43 projects, 12 of which were new starts, at a total cost of $9.5M.

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 science discovery.

In addition, BNL leverages its unique resources to expand its scientific capability beyond the four scientific Critical Outcomes with leading programs in selected areas of high energy physics, biology and environmental science, 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 80% supported the four Critical Outcomes. In total, these LDRD investments supported 38 postdoctoral researchers and graduates students in whole or in part and resulted in 77 publications and 5 awards.

Figure 1 - Scientific Outcome



This Program 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

2015 PROJECT SUMMARIES

Complex Modeling of Nanostructures

LDRD Project # 12-007

S. Billinge

PURPOSE:

This project aims to develop data analysis algorithms and software for solving atomic structures of nanoparticles and locally disordered materials. Accurate knowledge of atomic structure is critical information for understanding, development and application of new materials. Structure determination of nanomaterials is considerably harder, because they have a more complicated structure (distortions at the surface) and at the same time produce weaker and less resolved signals in experimental measurements.

APPROACH:

We seek to overcome these difficulties, by combining multiple experimental and theoretical inputs in a single structure determination and/or structure refinement computational procedure. Besides the Principal Investigator, the project team included: Dr. Pavol Juhas, a staff scientist at BNL; Dr. Kevin Knox, a postdoctoral research associate at BNL; Xiaohao Yang, a graduate student at Columbia University; and Dr. Michael McKerns, a part-time consultant.

TECHNICAL PROGRESS AND RESULTS:

We have continued the maintenance and development of the DiffPy-CMI framework of Python and C++ libraries. Most new features have been added to the pyobjcryst Python library, which now provides functions for simulations of powder and single crystal X-ray diffraction data. The code repository for the libObjCryst C++ library has been reorganized to allow for a direct incorporation of code updates from the parent Fox-ObjCryst project. Another major development was porting of all framework components to installable packages for Anaconda Python, a leading Python distribution for scientific computations. The upcoming release of DiffPy-CMI will utilize Anaconda Python, which will greatly simplify the software installation for end-users and also ease the preparation and distribution of code updates. As an added benefit, the software deployment procedure has been unified on all supported platforms, i.e., on 32 and 64-bit Linux and Mac OS X. Another significant development has been adoption of the Travis CI service for automated software builds and testing. Updates to the DiffPy-CMI sources trigger building and testing of the codes on Linux and Mac platforms and several build configurations are available at the Travis CI service. Failed tests and build errors are immediately reported by email. The library sources are also analyzed for test coverage and the results are uploaded and comprehensively presented at Codecov, an online code-analysis service.

The Complex Modeling method and the DiffPy-CMI software have been described in our article published in 2015 in Acta Crystallographica. Since its release in March 2014, the DiffPy-CMI software has been downloaded over 1000 times and we estimate hundreds of independent users. We keep in touch with this community through the diffpy-users and diffpy-dev mailing lists, where we assist the users with software use and research questions. In addition to software development, we have applied the DiffPy-CMI framework to several science projects on nanostructure analysis.

Structure and shape determination of CdSe quantum dots

The CdSe quantum dots were synthesized by the group of Prof. Owen from Columbia University. These materials exhibit quantized growth and can be prepared in large amounts in a monodispersed form. Initial studies indicate the structure of these particles is based on a CdSe zinc-blende lattice, which is terminated by {111} faces to form nanosized tetrahedra. We have conducted a uniqueness and shape validation study by solving the particle shape from a combination of experimental data and theoretical assumptions. Overall four shape probes were included either on their own or combined to conduct shape analysis:

- Experimental X-ray pair distribution function (PDF)
- Experimental and simulated small angle X-ray scattering (SAXS)
- Requirement of low surface area expressed as a minimum of unoccupied neighbor sites per each Cd or Se atoms
- Experimentally determined stoichiometric ratio of the Cd and Se atoms in the quantum dot.

We found the available experimental scattering patterns (PDF and SAXS) are insufficient for a unique shape determination and yield degenerate structure solutions with similar, high-quality fit to the measured data. The correct shape was successfully determined from ideal SAXS data simulated over a wide Q-range to 5/A, but the solution degeneracy reappeared at a Q-range limited to 3/A. Optimization of the surface area showed preference for {111} facets, which maximize bonding of the surface atoms as they can have three nearest neighbors. Established shapes were also recovered after combining the requirement of low-surface area with the experimental Cd:Se stoichiometry.

Structure determination of molecular crystals from PDF

In collaboration with Prof. Schmidt from Goethe University, we have developed more accurate simulations of PDFs measured from organic crystals. In these materials, the atoms within the same molecule form rigid bonds with well-defined lengths, while atoms from different molecules are only weakly coupled and show much larger variation in their distance. The DiffPy-CMI software allowed us to easily adjust the PDF calculation procedure and account for variations in the PDF signal due to these non-uniform bonding strengths. In a follow up study, we used the more accurate PDF simulations to determine orientations and positions of molecules in several molecular crystals from PDF measurements alone. These results were published as two articles in Acta Crystallographica A and in the Journal of Applied Crystallography.

SrMise – algorithm and software for automated peak extraction from PDF

This work was to develop a way of extracting peaks from the PDF in a model independent way. If you have a structural model, it is straightforward to compute the positions of peaks in the PDF function. However, in the absence of a good model, this task becomes difficult because of the overlap of peaks in the function. This approach takes an information theoretical approach to extracting peaks in the sparsest way that is consistent with the data, using the Akaike information criterion. The work resulted in a paper that was published in Acta Crystallographica, A and also a software program, called SrMise, which was released on the diffpy.org website.

Inter-individual Variation in Radiation-Induced Epigenetics Modifications and Their Potential Impact on Carcinogenesis

LDRD Project # 12-012

P. Wilson

PURPOSE/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 ionizing radiation-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 National Aeronautics and Space Administration (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 2016, 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 (SOBP) ion irradiations, and test more promising charged particle radiosensitization strategies.

TECHNICAL PROGRESS AND RESULTS:

The following is a summary of our results for FY2014/15.

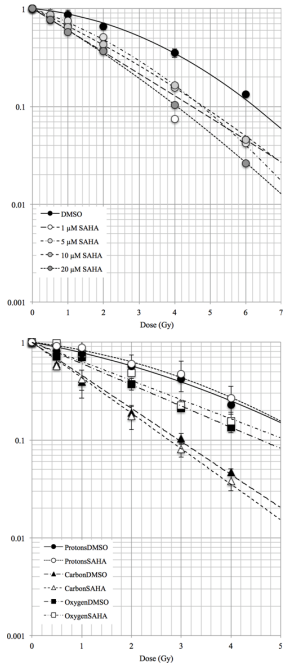


Figure 1. Survival (mean ± SEM) of A549 lung carcinoma cells treated with SAHA/vorinostat or DMSO (drug vehicle control) 18 h prior to irradiation with ^{137}Cs γ-rays (top panel) or 200 MeV protons, 290 MeV/n carbon ions, and 350 MeV/n oxygen ions (bottom panel). Dose-dependent relative biological effectiveness (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 (NHDF)	10 μM SAHA	1.24–1.83*	0.87–1.20	0.69–0.76	0.65–0.68
	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 (lung carcinoma)	10 μM SAHA	1.39–4.16*	0.66–0.96	0.86	0.27–1.13
	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 (osteosarcoma)	10 μM SAHA	1.20–1.75*	0.98–2.30*	0.40–1.07	1.11–1.64*
	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 (glioma)	10 μM SAHA	1.27–1.82*	1.11–1.31*	0.88	0.89–1.19
	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.

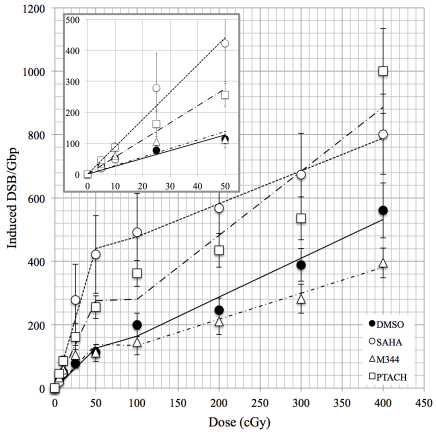


Figure 2. DSB induction in quiescent G0/G1-phase NFF28 normal fibroblasts (mean ± SEM) treated with 10 μM SAHA or M344, 5 μM PTACH or 0.2% DMSO after 200 MeV protons measured by contour-clamped homogeneous electric field gel electrophoresis. DSB induction after 5–50 cGy doses (see inset) was 8.5, 3.3, 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.

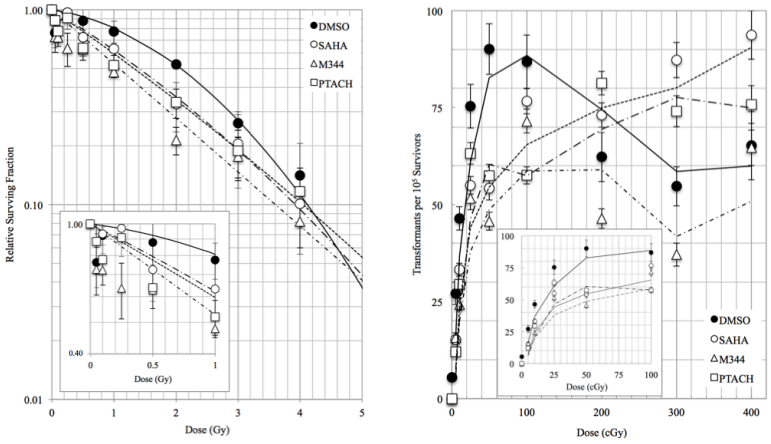


Figure 3. Left panel. Survival of log-phase NFF28 fibroblasts treated with 10 μM SAHA or M344, 5 μM PTACH or 0.2% DMSO (drug vehicle control) 18 h prior to irradiation with 200 MeV protons. HDAC inhibitor treatment resulted in significant radiosensitization similar to G0/G1-phase cultures. Inset shows 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).

In addition to reports published in 2015 and early 2016, several additional 2016 publications are being prepared, 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), perform clinically-relevant SOBP versus entrance irradiations, and to identify more promising charged particle radiotherapy strategies based on chromatin/DNA compaction modulation.

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 pattern, and ecosystem responsive behaviors such as photosynthesis and stomatal conductance. However, how the coupled atmosphere and land-surface-ecological system interact is still poorly understood. This project seeks to advance our understanding of the interactions 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 atmosphere-land-ecosystem modeling. This will give BNL a significant edge in competing for funding in 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 the 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 impacts of urban land use and land cover on regional climate variations over the U.S. Northeast; and 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 observations and the existing coupled Weather Research and Forecast (WRF) and Community Land Model (CLM) for the investigations; and 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); and 2) Luis Ortiz 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) had 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[1], entitled "Influences of soil moisture and vegetation on convective precipitation forecasts over the United States Great Plains", was published in August, 2014. A major finding is that vegetation changes have a greater impact on precipitation than soil moisture changes and removal of vegetation produced substantial drying. 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 had been established at BNL, including workstations, a computer server, and recent versions of the WRF and CLM coupled model. The new facility has been used to conduct several scientific studies. Another senior Ph.D. student (Luis Ortiz at CCNY) has been using the facility to model urban effects on the U.S. Northeast regional climate since his 2014 BNL summer internship. We are finalizing two papers for publication from further studies since the internship. Findings from the studies show that metropolitan land use and land cover can significantly impact temperature and precipitation distributions. Furthermore, we have also conducted studies to examine decadal cloud variations and model parameterizations on photosynthesis linked to carbon absorptions. Two papers[2-3] based on these were published in 2014, led by the Principal Investigator (PI) and the Co-Investigator, respectively. Although the project ended in February, 2015, by using the research accomplishments and facilities built through this project, in FY 2015 the PI wrote: 1) a FY 2015 DOE Early Career proposal on land-atmosphere feedbacks and a FY 2016 BNL Laboratory Directed Research and Development proposal on the U.S. Northeast urban-climate interactions; and 2) a FY 2016 DOE Early Career preproposal on human urban processes in Earth System Models. One poster about land-atmosphere interactions was presented at the 2015 DOE Atmospheric Radiation Measurement (ARM)/Atmospheric System Research Joint User Facility PI Meeting; two posters from the urban-climate studies were presented at the 9th International Conference on Urban Climate with extended abstracts published at the meeting website (http://www.meteo.fr/icuc9/), and one of the two urban-climate posters was presented at the 2015 New York Scientific Data Summit Conference. Luis Ortiz won the joint International Association for Urban Climate and American Meteorological Society Student Presentation Award by presenting his urban-climate research work (under Professor Jorge Gonzalez's and the PI's co-mentorship) at the 9th International Conference on Urban Climate, Toulouse, France, July 20-24, 2015.

Papers published:

[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

[2] Wu, W., Y. Liu, M. P. Jensen, T. Toto, M. J. Foster, and C. N. Long, 2014: A comparison of multiscale variations of decade-long cloud fractions from six different platforms over the Southern Great Plains in the United States, J. Geophys. Res. Atmos., 119, 3438–3459, doi: 10.1002/2013JD019813 (highlighted at the DOE's ARM web site)

[3] Rogers, A., 2014: The use and misuse of Vc,max in Earth System Models. Photosynthesis research. doi:10.1007/s11120-013-9818-1.

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 were 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 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 features and smaller gauge volumes, 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 the ability to produce smaller features, reducing the gauge volume probed.

TECHNICAL PROGRESS AND RESULTS:

In the past years, we have been working on the design of the slit system through a new ray tracing program we developed to evaluate requirements on slits designs, dimensions and placement with respect to the gauge volume of interest and energy of the X-rays. That work has been followed by the fabrication of a first prototype, its integration to the National Synchrotron Light Source X17A beamline set-up and testing of its capabilities in several standards case studies. Based on these results, our ray tracing program has been refined and a second version of the slit system has been fabricated for implementation at the NSLS-II X-ray Powder Diffraction beamline. The new slit system, called spiderweb slits, provides rapid depth-resolved X-ray powder diffraction. This design is far more versatile compared to previous methods, since the slits can select most of any diffraction cones from a gauge volume over a continuous range of diffraction angles, without the need for scanning any parts of the system. This capability is especially important for *in situ* and *operando* experiments. At the end of FY14 and the beginning of FY 15 (project ended the first week of January 2015), we have focused on demonstrating the slits performance on both standard and science case experiments (*In operando* diffraction measurements of Ag_xFeO_2 cathodes for Li ion batteries in collaboration with K. Kirshenbaum and E. Takeuchi of Stony Brook University/BNL, carried out at the Advanced Photon Source). The results have led to the submission of a patent application to the United States Patent and Trademark Organization and a publication.

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 (5 MeV, 100 pC, 100 fs) passes above a storage ring bunch (30 ps), it kicks a slice (150 fs) 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 (150 fs) is much shorter than the crab cavity method (1-2 ps). 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.

The low energy compressor developed during this study can also be used in ultra-fast diffraction (UED) and ultra-fast electron microscope (UEM) experiments to provide electron bunches focused to a beam size on the order of 50 microns and a bunch length on the order of 100 fs.

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 laser slicing method: 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 this perspective, but it needed an extensive feasibility study in order to quantify its advantages over laser slicing.

Clearly we need to study the brightness of this method by analytical work then by simulation. Then we need to study how to generate the short electron bunch focused to under a 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 conditions 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. 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, 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 150 fs 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 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 to reduce the bunch lengthening without significant loss of the kick angle; this makes it possible to reduce the bunch length to 100 fs. 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 much a shorter pulse length using a much shorter space in the storage ring.

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.

We presented and published the above results in workshops and international conferences. Recently we published 3 papers on the analysis in Physical Review:

- A. He, F. Willeke, and L. H. Yu, "Ultrashort x-ray pulse generation by electron beam slicing in storage rings", Physical Review Special Topics - Accelerators and Beams 17, 040701 (2014).
- A. He, F. Willeke, and L. H. Yu, "Dependence on crossing angle of electron beam slicing in storage rings", Phys. Rev. ST Accel. Beams 17, 120704 – Published 17 December 2014.
- A. He, F. Willeke, L. H. Yu, L. Yang, T. Shaftan, G. Wang, Y. Li, and Y. Hidaka, "Design of low energy bunch compressors with space charge effects", PRST 18, 014201 (2015).

These papers document our work in detail and can be used for future reference and guidance for proposal and development of experimental projects. Our work has achieved significant success, as it provides solid ground for the next steps in the development of electron beam slicing. During the study we found a connection of our work with UED and UEM experiments. The electron bunch generated by the low energy compressor in our electron beam slicing can also be used in UED and UEM experiments. As a byproduct, this new method can reduce the time jitter between the electron bunches and the laser pulses. Thus this LDRD has opened a new direction in the field of electron imaging.

Flow-Based Battery Architectures for Large Scale Electrical Energy Storage

LDRD Project # 12-025
C. Erdonmez

PURPOSE:

This project combines expertise in and tools from materials science and electrochemistry to study potential "low-cost" electrochemical systems targeting grid-scale energy storage. More specific goals of the project are: (a) demonstrate synchrotron methods as tools for studying, with greater rigor than before, promising alkaline battery chemistries; (b) establish connections between materials properties and electrochemical behavior; and (c) start answering scientific questions of engineering relevance. The specific battery chemistries chosen for this study are alkaline chemistries employing a highly basic aqueous environment. The project aims to build up capability at BNL in the areas of flow-assisted and/or aqueous battery systems, to launch collaborations with local institutions in these areas and to demonstrate BNL capabilities to the wider community. Synthesis, device fabrication and electrochemical characterization capabilities were pursued in collaborations involving groups both in and outside BNL.

APPROACH:

Stationary energy storage at large scales using batteries is an area of growing interest and could help integrate renewable energy sources into the electrical grid, as well as lower the significant costs associated with maintaining reliability. The most important challenges towards adoption of large-scale batteries in such roles are limited reliability, as well as relative high cost. High battery costs, e.g., for the dominant lithium-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 suitable for use in flow-assisted electrochemical systems. The bulk of technique development focuses on alkaline battery chemistries where the focus is on converting non-rechargeable or poorly rechargeable technologies into robust rechargeable technologies.

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 and 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 30 – 36, which fell in the first half of FY15. As detailed in previous reports, a number of capabilities had already been developed and a number of initial findings had been 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 a structural change which is likely associated with cathode capacity and lifetime improvements; (d) imaging and diffraction data established the impact of trace heavy metal dopants in modifying morphology, and (e) real time internal diffraction revealed a difference in the sequence of cathode phases formed under discharge than from those published earlier by other researchers.

In FY15, the greatest focus was on further rigorous study of the behavior of the MnO_2 alkaline cathode under differing electrolyte compositions. Through a combination of control experiments at the synchrotron and extended electrochemical studies, we 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. In the course of this work, we also synthesized high surface area ramsdellite-rich materials, which may find other uses as additives. This work was submitted for publication in FY15, and eventually published in FY16.

Another major activity in FY15 was *in situ* and *ex situ* structural studies of iron oxide anodes in alkaline media. We identified the major reaction pathways as a function of particle size (nanoscale vs. micron scale powders), the crystal structure of the starting material and the electrolyte composition. Results from the work were presented early in FY16 and a manuscript is under preparation. Other groups have also recently become interested in iron oxide particles as the basis of flowable electrodes.

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 a reasonable overall cost. The Collider-Accelerator Department selected a new approach to the solution of eRHIC using the non-scaling Fixed Field Alternating Gradient (NS-FFAG) arcs.

APPROACH:
The Principal Investigator of the project 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 in energy of the beam. This allows a reduction of the previous six rings that have fixed energy in the eRHIC design with two NS-FFAG rings that accept multiple energies. In addition, one of the major expenses is the superconducting linac, where the cost is proportional to the energy. By allowing more passes through the linac, energy can be reduced. To achieve an electron energy of 20 GeV with six rings of fixed energy, the total energy of the two linacs needs to be ~3.3 GeV. With 11 passes through the linac, the energy can be reduced to half.

TECHNICAL PROGRESS AND RESULTS:
With the financial support obtained from the LDRD, we have succeeded in developing NS-FFAG designs with a new tool "muon1" from our new member of BNL's scientific staff (S1). The advantage of this approach is a single ring in the tunnel to cover the whole energy range from injection to the maximum electron energy of 20 GeV.

A plan for Phase I of the LDRD was to provide a basic eRHIC NS-FFAG design with the preliminary magnet design. The PHASE I was extremely successful as it was accepted and supported by the International Advisory Committee during the eRHIC design review from November 25 – 27, 2013. Funding for this LDRD provided us with new tools to compare the results from five different programs: "SYNCH, MADX, ZGOUBI, muon1, and TRANSPORT, which were all in agreement. A major success was that results of the 3D magnet design by the OPERA magnet code showed excellent agreement with the predictions of the other codes. The LDRD plan for Phase II of the LDRD to build and test a permanent NS-FFAG magnet was successfully achieved.

The eRHIC concept of the electron-ion collider is in direct competition with the design promoted by JLab. BNL has an advantage over the latter in already having a high-energy proton/ion synchrotron. The electron energy recovery linac in the eRHIC design has been transformed by the application of the NS-FFAG concept. The six recirculating rings of the previous design are replaced with just two FFAG rings and the previous five sets of straight sections by just one. The new design is in principle more flexible as the FFAG arcs can accept a continuous range of energies. Specific achievements in 2015 are:

- Finalized two eRHIC magnet designs: one with adjusted Halbach design and the other is an iron dominated permanent magnet of radially displaced quadrupole design. The prototype of the iron-dominated design is presently being finalized, while five of the adjusted Halbach magnets have been built and measured.
- Continued the regular Cornell eRHIC prototype weekly meetings and finalized the full proposal for New York State follow-on funding
- Continued the preparation for the Conceptual Design Review (CDR) of the Cornell Brookhaven Electron Energy Recovery Test Accelerator (C-BETA) project, which is going very well
- Visited the Electron Energy Corporation to allow preparation for full permanent magnet production for the eRHIC prototype magnets and for the C-BETA magnets
- Updated the eRHIC lattice and the Pre-CDR report is being prepared
- Presented full cost estimate for the eRHIC FFAG at the February 2015 meeting of the Nuclear Science Advisory Committee.

The following excerpt, from the eRHIC Advisory Committee Project Review in November 2015, recognizes the impact of this research: "The Committee welcomes the imminent funding of the Cornell Brookhaven Electron Energy Recovery Test Accelerator (C-BETA) and congratulates BNL/Cornell management on a significant success. We note that some form of multi-pass linac [energy recovery linac (ERL) or recirculated linear accelerator (RLA)] is necessary for all design approaches thus C-BETA is now arguably the most critical R&D element in the program. The Committee considers some C-BETA results critical for a CD-1 review (2019)."

Time Resolved Imaging of X-rays and Charged Particles

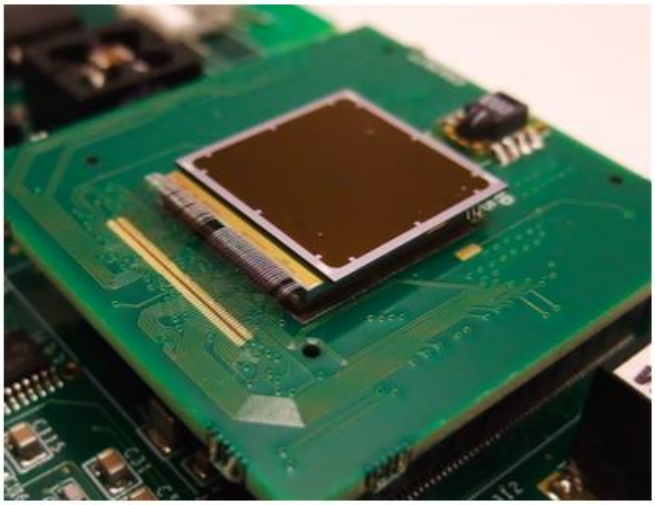
LDRD Project # 13-006
A. Nomerotski

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 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 mass 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, provides 10 ns time resolution and high quantum efficiency for photons with wavelength between 350 and 1050 nm. This resulted in an imager with characteristics far superior to cameras currently available commercially. We employed a commercially available readout system to characterize the new device and tested the new camera with several imaging MS groups. An improved camera prototype with faster frame rate, based on the new readout system eX, will be developed and the first prototype produced and tested.

TECHNICAL PROGRESS AND RESULTS:
We list below the main accomplishments in FY 2015:

- Six wafers with new sensors were completed in October 2014; post-processed and diced in February 2015. The first sensor assemblies and camera, shown below, were delivered to BNL in March 2015 and tested at the BNL Chemistry Department in April 2015. The full turnaround for the sensors from submission to the first results was less than one year.



(a) The new sensor in TimepixCam.

(b) Photograph of TimepixCam.

- Took ion imaging data with TimepixCam in FY 2015 at
  - BNL: M.White group: surface photochemistry
  - Stony Brook: T.Weinacht group: coincidence ion & electron imaging
  - Oxford: M.Brouard and C.Vallance groups: velocity mapping, coincidence ion imaging;
  - FLASH light source (Deutsches Elektronen-Synchrotron, also known as DESY): D.Rolles and T.Marchenko groups: femtosecond scale molecular dynamics.
- The data analysis and preparation of corresponding publications are in progress.
- We used the above camera at NSLS-II in August 2015 to acquire 8 keV x-rays and to perform a proof of principle demonstration of time correlations due to the abort gaps in the NSLS-II beam. The plot below shows the pixel autocorrelation function, g_2. The distribution is structured with the beam revolution period due to the absence of hits in the abort gap.

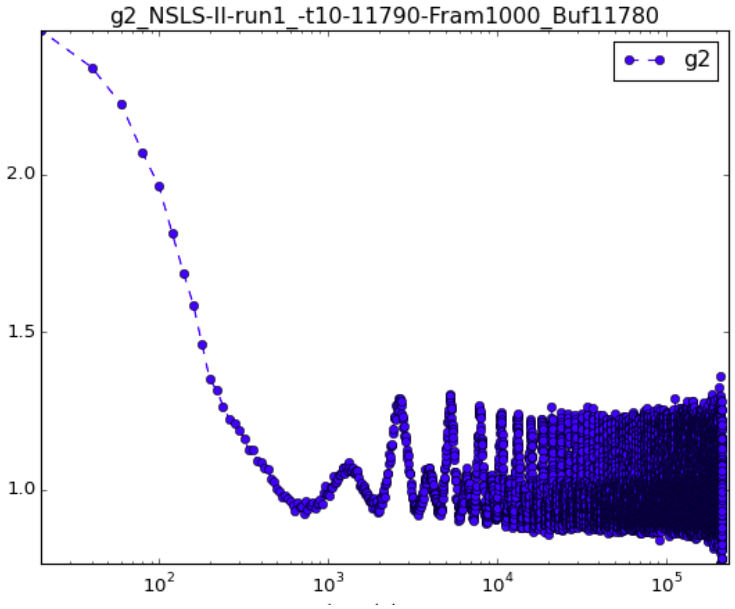


Figure 1. Plot of the pixel autocorrelation function, g2.

In summary, we completed all planned milestones for FY 2015.

The main milestones for FY 2016 are:

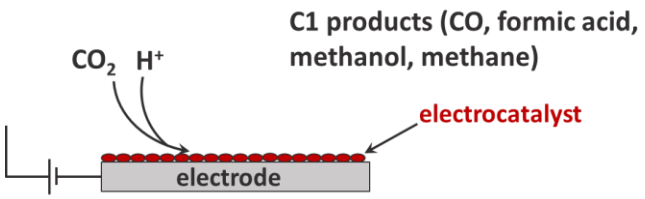
- Continue taking data with TimepixCam at BNL and other institutions and publish the results
- Conduct the first XPCS experiments at NSLS-II using the Timepix detector
- Characterize the eX camera with the optical sensor and take the first science data
- Characterize TimepixCam for applications, which require single photon sensitivity.

Electrochemical Reduction of Carbon Dioxide on Surface-Modified Metal Electrodes

LDRD Project # 13-013
D. Polyanskiy

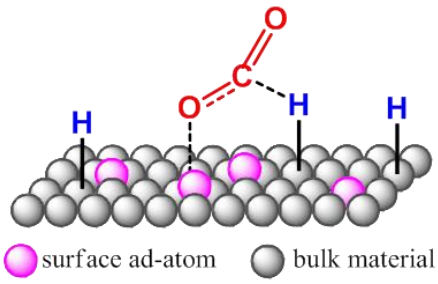
PURPOSE:

The long term goal of this project is to facilitate the design of new catalytic systems based on abundant metals for efficient electrochemical reduction of carbon dioxide (CO_2) in aqueous solution to generate carbon-based reduction products. 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 and through collaboration with other BNL groups will play a critical role in establishment of such mechanistic insights.



APPROACH:

A wide variety of materials were studied for electrochemical reduction of CO_2 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 the 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 the 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:

Fiscal year 2015 was the final year of this project. Results for the entire project are presented.

- A manuscript detailing findings described below has been published in one of the world's leading catalysis journals *ACS Catalysis:* Hsieh, Y.-C.; Senanayake, S. D.; Zhang, Y.; Xu W.; Polyansky, D. E. "The effect of chloride anions on the formation and reactivity of nanoporous silver catalysts for CO_2 electroreduction" *ACS Catal.* **2015**, *5*, 5349−5356.
- The results were presented by the postdoctoral 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, Sanjay Senanayake, Yu Zhang, Dmitry Polyansky.

- An invited talk was delivered at the 250th ACS National Meeting, Boston, MA, August 16-20, 2015. Title: "The effect of chloride anions on the synthesis and activity of nanoporous silver catalysts for CO_2 electroreduction."
- The chloride-modified silver (Ag) electro-catalyst was studied in more detail. It was shown that this catalyst can be prepared by simple electro-oxidation of Ag foil in the presence of chloride (Cl) anions in aqueous solutions. The resulting electro-catalyst demonstrated a highly developed nanostructured surface (Figure 1).

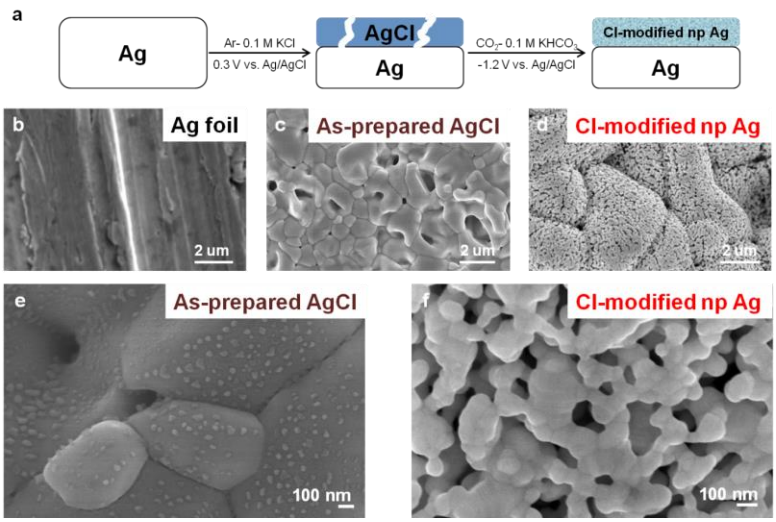


Figure 1. (a) Schematic illustration of the formation of as-prepared AgCl and in the presence of Cl. Scanning Electron Microscope (SEM) images of (b) untreated Ag foil, (c) as-prepared AgCl after 12 h oxidation, and (d) Cl-modified Ag. High-magnification SEM images of (e) as-prepared AgCl after 12 h oxidation and (f) Cl-modified Ag.

- 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 the current density of 2 mA cm^{-2}. A current density of 10mA cm^{-2} can be achieved at overpotential of only 0.53 V and 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 Ag atoms on the surface are catalytically active.
- 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.
- In addition to the effect of nanostructured surface morphology, adsorbed Cl anions contribute 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 Cl 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.
- The performance of Cl-modified Ag 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^+ on the catalyst surface from the $KHCO_3$ electrolyte. An oxidative treatment in the presence of Cl anions recovered the original catalytic performance, but resulted in the lower rate, due to the smaller surface area.
- Another manuscript is in preparation which describes more detailed mechanistic studies of the effect of other halides (bromide and iodide) on the catalytic performance of Ag electro-catalysts.

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

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

PURPOSE:
Modern scientific instruments are now generating data at unprecedented rates. In particular, Brookhaven's new synchrotron, the National Synchrotron Light Source II (NSLS-II) offers unprecedented X-ray brightness and high-speed detectors. The correspondingly large data-rate is beyond the ability of human experimenters to manually interpret and analyze. It is now evident that a crucial complement to high-throughput instruments is automated analysis methods and workflow, which can process, transform, and analyze scientific data without human manual intervention. 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 to extract scientifically relevant parameters and content from the large amount of experimental data.

APPROACH:
We leveraged the existing software from National Synchrotron Light Source 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:
This LDRD was completed September 30, 2015. During the past three years, we made four significant contributions that align with BNL's strategic goal in high performance computing and data analysis: 1) designing engineered solutions and software tools to enable early science at the Hard X-ray Nanoprobe (HXN), Sub-micron Resolution X-ray Spectroscopy (SRX) and other beamlines; 2) publishing scientific results in top-ranking journals (three journal papers) and computer science conferences (two conferences); 3) winning DOE Office of Advanced Scientific Computing Research (ASCR)/Small Business Innovation Research (SBIR) awards and secured external funding based on the preliminary research outcomes that are supported by this LDRD; and 4) participated in national collaborations, presented demos in national forums, and shared domain expertise and software development with the staff members on the data management LDRD to ensure quick adoption by NSLS-II.

We implemented three image analysis systems, 1) a Python-based Differential Phase Contrast (DPC) imaging tool that addresses the strong need for real-time data processing for DPC imaging during the experiment; it is two orders of magnitude faster than the original MATLAB-based implementation; 2) a Python-based X-ray Fluorescence Analysis Package (PyXRF) that contains a high-level fitting engine, a comprehensive command-line/Graphical User Interface (GUI) design, rigorous physics calculations, and a powerful visualization interface; and 3) Graphics Processing Unit (GPU)-Accelerated Tomography. We completed the technical commissioning of the DPC and PyXRF packages and used them to analyze data in real time during the first HXN

early science user experiment in July. Beamline scientist (Hanfei Yan) confirmed that DPC performed *in situ* image reconstruction and analysis during the July experiment.

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 DPC imaging tool to address the strong need for real-time data processing for DPC imaging during the experiment. 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 only takes six seconds, which is a hundred times faster than the original MATLAB code. It has a GUI for general parameter input, 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 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.

Fluorescence Analysis Package

We developed a sophisticated X-ray fluorescence analysis package (PyXRF) for two project beamlines (HXN and SRX) at NSLS-II. This software was handed over to the NSLS-II computing group and shared across all DOE light source facilities. PyXRF offers a method of automatically finding elements, so that users do not need to resort to the error-prone manual process of selecting elements. Moreover, PyXRF provides a convenient and interactive way of adjusting fitting parameters with physical constraints. This helps users perform sensitivity analysis, and find an appropriate initial guess for fitting. Furthermore, we also created an advanced mode for professional users to construct their own fitting strategies with full control of each fitting parameter. PyXRF runs single-pixel fitting at a fast speed, and enables the possibility of viewing the results of the fitting in (near) real time during experiments. A convenient I/O interface was designed to obtain data directly from BNL/NSLS-II's experimental database. PyXRF is under open-source development and designed to be an integral part of NSLS-II's scientific computation library. PyXRF is one of the most important analytical software packages used at HXN and SRX for their early science commissioning. This packaged has been installed at both NSLS-II beamline servers and user computers, and is recognized as a powerful analysis package in the field.

FY15 Milestones accomplished:

- Completed the Phase Contrast Image Processing Pipeline and the associated user interfaces
- Completed the Fluorescence Analysis Package and associated user interface
- Completed the two different types of tomography reconstruction algorithms: Filter-back projection and Iterative tomography
- Generated eleven science papers for image analysis conference and journal publications
- Received DOE ASCR funding for Science Flow, SBIR funding for GPU-accelerated tomography, and three LDRDs led by the personnel associated with this LDRD.

Synthetic Control of Lipid Biosynthesis in Plant Vegetative Tissue

LDRD Project # 13-020

J. Shanklin

PURPOSE:

This project 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 referred to as synthetic biology. This project is designed to produce proof-of-principle that synthetic biology 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:

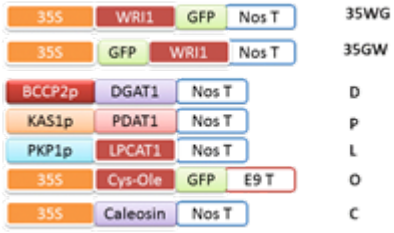
The project essentially involves two parts, 1) expanding the WRINKLED1 (WRI1) regulon and 2) controlling the expression of the WRI1 transcription factor.

WRI1 is the 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 project 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.

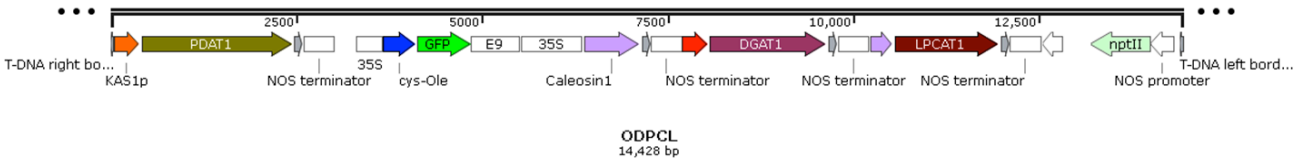
Examination of the *Arabidopsis* Information Resource expression database shows that WRI1 is not expressed to any significant level in vegetative tissues, and expression in leaves is specifically low. Thus, in order to turn on the expanded WRI1 regulon, we need to specifically express the WRI1 in leaf 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:

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.



In FY 2015, we 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. While TAG accumulated up to 3.5% of dry weight was detected in these plants, constitutive expression of WRI1 resulted in negative pleiotropic growth effects, resulting in small unhealthy growth compared to plants lacking WRI1. We therefore placed WRI1 under the control of the AlcR/AlcA alcohol-inducible constitutive promoter.

FY 2016 MILESTONES:

Analyze *Arabidopsis* lines expressing the AlcR/AlcA -inducible WRI1 construct created in FY 2015 using silica thin layer chromatography and gas chromatography coupled mass spectrometry. Preliminary results indicate that the growth rate and form of these plants is normal and we will analyze the TAG content of plants induced to express WRI1 at various stages of growth and compare TAG levels before induction, at 2- and 7- days after induction and at senescence.

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 (Li) transport and reactions in batteries with unprecedented spatial resolution. Tools and techniques will be made available for 'first light' experiments at 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 studying electrochemical reactions in bulk electrodes but have inadequate spatial resolution for exploring nanoscale morphological and structural changes and determining where and how new phases nucleate and propagate. TEM, capable of exceptional spatial resolution, has been unsuitable for *in situ* studies until recently, when specialized electrochemical cells were developed for it. It would be desirable to develop an electrochemical cell that allows for correlative *in situ* synchrotron and TEM studies of an electrochemical reaction of the same electrodes under real working conditions. In this effort, a novel sealed electrochemical cell with flexibility to use liquid electrolyte, along with a full suite of biasing systems, will be developed for TEM and synchrotron measurements (Figure 1a). Advanced *in situ* TEM techniques will be developed for direct observation of morphological and structural evolution of electrodes, and correlative *in situ, operando* measurements using nano beam X-ray diffraction/spectroscopy will be made on the same set of samples at NSLS-II. A previously developed solid-electrolyte based *in situ* cell (Fig. 1b) will be further modified for tracking Li reactions precisely *via* atomic imaging and spectroscopy. The developed *in situ* techniques and capabilities will be used to probe *real-time* electrochemical (de)lithiation of individual particles, and with computational modeling, to determine the kinetic transformation pathway during battery operation under *non-equilibrium* conditions.

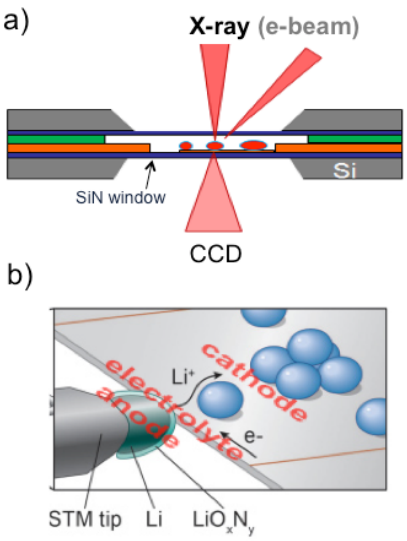


Figure 1. Schematic illustration of two types of *in situ* electrochemical cells, based on (a) liquid and (b) solid electrolyte, for measuring single-particle electrochemistry by TEM and synchrotron X-ray methods.

This project involves multidisciplinary collaboration with scientists at BNL including Eric Stach and Yimei Zhu on advanced electron microscopy, Yong Chu on nano-beam X-ray diffraction/spectroscopy, and Gerbrand Ceder (from Massachusetts Institute of Technology) on modeling. A collaboration with Hummingbird Scientific was established to develop and refine the *in situ* liquid cells for electrochemical applications.

TECHNICAL PROGRESS AND RESULTS:

Over the last two years, the state-of-the art liquid-cell design for electrochemical measurements in the TEM was advanced through collaboration with Hummingbird Scientific. In FY15, the solid electrolyte-based cell (Fig. 1b) was re-designed and new functions were added for simultaneous TEM-Electron Energy Loss Spectroscopy and electrochemical measurements on selected nanoparticles. This breakthrough allows correlating local structural evolution to electrode behaviors at the single-particle level during electrochemical cycling. Electrochemical tests for improving the functionality of the cell are under way, through collaboration with researchers in the m2M Energy Frontier Research Center (EFRC).

In a parallel effort, the electrode configuration of the cell was modified for probing Li intercalation dynamics in local regions within a single particle; this new capability was demonstrated in studying the model system, Li_xFePO_4 (LFP; one of the most interesting intercalation cathodes for high-power batteries). As illustrated in **Figure 2**a, within a specially designed electrode, isolated LFP nanoparticles can be selected for *in situ* electron diffraction and high-resolution TEM imaging with the electron-beam either parallel or perpendicular to the Li diffusion channel. In this study, the cell development is essential for access to local Li transport and intercalation at scales varying from a single nanometer to tens of nanometers, and up to the whole LFP nanoparticles. Details on the evolution of local Li concentration were revealed from this study, showing that fast lithiation in nano-sized LFP proceeds *via* kinetically favorable solid solution transformation, but dynamically inhomogeneous across the particle (Fig. 2b-d). This cell has been made available to the researchers in the m2M EFRC.

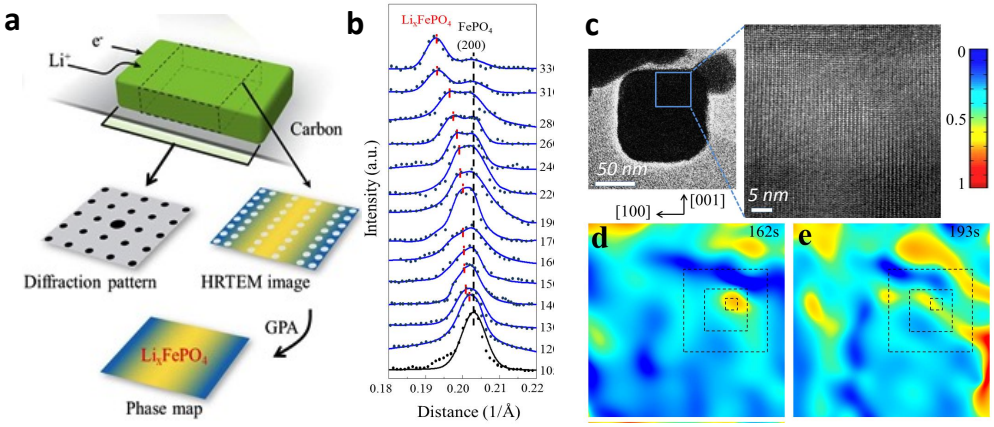


Figure 2. Real time tracking Li intercalation in a single LFP nanoparticle using a new *in situ* cell. (a) Schematic illustration of the setup. (b) Intensity profile of the electron diffraction recorded from a single LFP particle. (c) Bright-field and high-resolution TEM images of a single LFP particle selected for this study. (d, e) Maps of local Li concentration within the LFP particle at intermediate lithiated states.

Efforts on refining the cell design are ongoing, to make the cell best suited for studying different types of electrodes and electrochemical systems. More recently, utilization of the cell was extended to studying ionic transport in full-stack solid-state batteries and across Li-solid electrolyte interface through external collaborations. In FY16, the main efforts will focus on correlative *in situ* TEM/synchrotron measurements of single-particle electrochemistry at the Center for Functional Nanomaterials, NSLS-II, the dry room at the Interdisciplinary Science Building and other facilities, using in house-developed cells and the cells available at the facilities.

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%[i]), it is not cost-competitive with conventional silicon in part due to high manufacturing costs. CIGS is a direct bandgap semiconductor with a high absorption coefficient and a bandgap that can be tuned over a wide range (1.0 to 1.7 eV) by varying the Ga concentration within the cell.[ii,iii] The optimal overlap with the solar spectrum, and therefore the optimum efficiency, should occur for a CIGS bandgap of about 1.5 eV, corresponding to a Ga fraction of 0.6 - 0.7. However, the highest performing CIGS cells with efficiencies of 20% are found for Ga concentrations of about x = 0.3, with non-stoichiometric Cu concentrations.[iii] 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[iv] 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 as well as local chemical composition (i.e., the structure at the nanoscale). Transmission electron microscopy studies of CIGS films have shown strong chemical fluctuations at the nanoscale and the presence of Cu-rich and Cu-poor regions,[v] but have not correlated nanoscale measurement to local device performance. A key prediction of this model is the loss of intra-absorber charge separation in CIGS when the overall absorber composition becomes too enriched with gallium. Our goal is to connect regional device performance (microns) with nano-scale chemical and structural properties of the films to test the validity of this model.

APPROACH:

The approach we will take is to connect regional device performance (microns) with nano-scale chemical and structural properties of the films. Standard CIGS cells, with peak efficiencies of 17% or more, will be fabricated through co-evaporation at the University of Albany, with Ga concentrations varying from 0.1 to 0.6, and for different substrate processing temperatures. Standard techniques will be used to measure current-voltage (I-V) curves, open circuit voltage, and short-circuit current, fill factor, and overall device efficiency. Lithographic contact measurements will be pioneered to correlate structure and function at the single grain (few micron) level.

TECHNICAL PROGRESS AND RESULTS:

This past fiscal year, we made a major breakthrough. In testing out graphene-CIGS Schottky photovoltaic junctions, we discovered that the soda lime glass substrate on which the CIGS is grown provides graphene n-doping that is strong, low-cost, and not subject to degradation. Subsequently, we were able to achieve such doping without the CIGS, by just placing the graphene directly on the soda lime glass. This result may enable low-cost and scalable control over the electronic properties of graphene, with applications to consumer electronics (touch

screen Indium Tin Oxide replacement, for example) in addition to solar panels. This work is described in detail in the following publication:

- D. M. N. M. Dissanayake, A. Ashraf, D. Dwyer, K. Kisslinger, L. Zhang, Y. Pang, H. Efstathiadis & M. D. Eisaman, "Spontaneous and strong multi-layer graphene n-doping on soda-lime glass and its application in graphene-semiconductor junctions," *Scientific Reports*, **6** 21070 (2016) http://www.nature.com/articles/srep21070 and in two press releases (https://www.bnl.gov/newsroom/news.php?a=11814) and (http://sb.cc.stonybrook.edu/news/general/2016-02-12-using-glass-to-improve-graphenes-powerful-conductivity.php).

In addition to this work, by pioneering a new lithographically defined metal contact probe for CIGS photovoltaics, we were able to demonstrate grain-to-grain variation within CIGS to the degree that neighboring micron-scale grains may exhibit very different recombination dynamics due to different copper content. This work is being written up for *Physical Review Letters*.

Finally, we also reported on the results of varying Ga ratios in this paper:

- J. Claypoole, B. Peace, N. Sun, D. Dwyer, M. D. Eisaman, P. Haldar, and H. Efstathiadis, Characterization of Cu(In,Ga)Se2 (CIGS) films with varying gallium ratios, *Journal of Alloys and Compounds*, DOI: 10.1016 /j.jallcom. 2015.09.006 (2015).

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[i] I. Repins, M. A. Contreras, B. Egaas, C. DeHart, J. Scharf, C. L. Perkins, B. To, and R. Noufi, *Prog. Photovolt: Res. Appl.*, **16** (2008) 235.

[ii] S. Siebentritt, U. Rau, *Wide-Gap Chalcopyrites*, Springer (2006).

[iii] S. H. Song, "Structure optimization for a high efficiency CIGS solar cell," *Proceedings of the 35th IEEE Photovoltaic Specialists Conference* (IEEE, New York, 2010) 002488.

[iv] B.J. Stanbery, "Intra-Absorber Junction Model for the Device Physics of Copper Indium Selenide-Based Photovoltaics," *Proc. 31st IEEE Photovoltaics Specialist Conference* (IEEE, New York, 2005) 355.

[v] Y. Yan et al., *Appl. Phys. Lett.*, **87** (2005) 121904.

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 in order 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 particular 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 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 renewable energy systems, and this will also be analyzed using failure-modes-and-effects analysis (FMEA) and probabilistic safety assessment (PSA) 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 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:

A dynamic model of the battery associated photovoltaic (PV) generation system has been built up in the widely adopted commercial software package, PSS/E. In this development, the control blocks provided were leveraged and the frequency measurement was fed back through the user programmable .dll file. The dynamic performance of different control parameters was investigated to achieve a favorable performance for the battery system in provision of frequency support. Based on such assigned control system parameters, the impacts of different penetration levels of PV generation on the inertial response were investigated, as shown in Fig. 1. For the cases in which the inertial response was so deteriorated that the operational requirement was violated, e.g., frequency depression of more than 0.5 Hz, a battery system was integrated to provide frequency support. The performance of different capacity of battery systems on the inertial response is shown in Fig. 2. Further investigations were conducted to study the system performance with reduction of traditional stabilizers and the functionality of the battery in remediation of the severe situations. The results can be seen in Fig. 3. To investigate the dynamic performance of the PV system under different penetration levels and with different battery capacities, the dynamic simulation process was automated by using Python language, such that the PSS/E software can be used as a lower level 'calculator' in the probabilistic battery sizing approach.

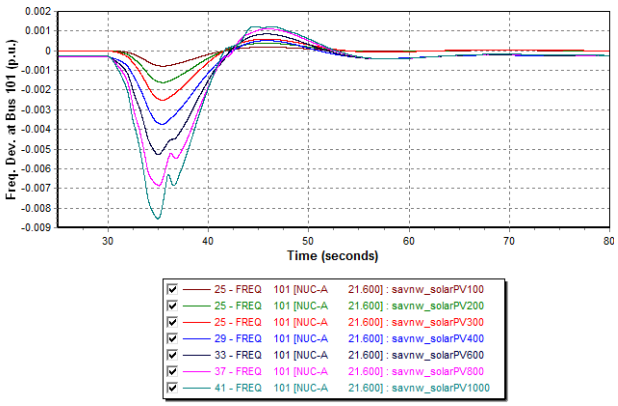


Figure 1. Impacts of different penetration levels of PV generation on the inertial response.

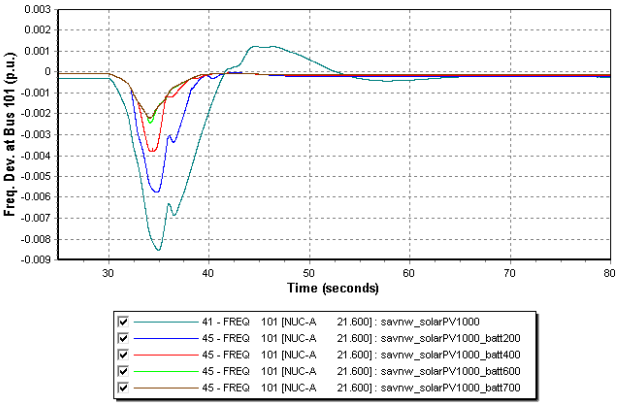


Figure 2. Performance of different capacity of battery systems on the inertial response.

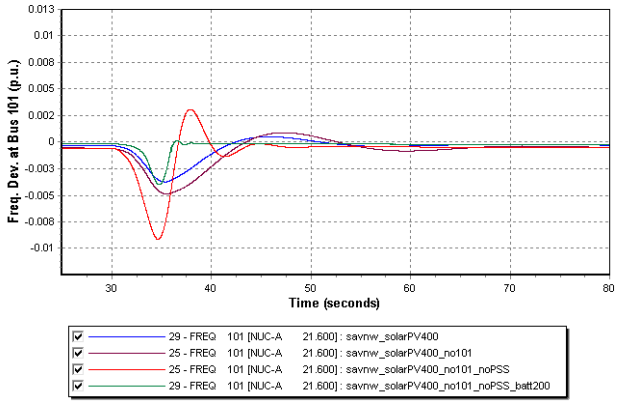


Figure 3. System performance with reduction of traditional stabilizers and the functionality of the battery in remediation of the severe situations.

In situ Studies of Interfaces Under Extreme Environments

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

PURPOSE:

Probing corrosion at the nuclear cladding-steam interface under extreme environments in nuclear reactors is critical to understand the performance of nuclear claddings and to design and develop advanced cladding materials for more economical and safer nuclear power. Our knowledge of kinetics and corrosion reaction mechanisms that occur at metal-alloy-fluid interfaces, such as the nuclear cladding-steam interface, remains far below the level needed to elucidate the underlying physics due to our lack of high-resolution, ultra-fast characterization tools. This project addresses the lack of high-resolution *in situ* characterization tools by developing a sample environment for *in situ* investigation of interfacial interactions at metal-alloy fluid interfaces under high-temperature conditions. 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 National Synchrotron Light Source II (NSLS-II) will be studied. Such studies will elucidate the phase and structural changes associated with corrosion of nuclear claddings, which will aid in designing next generation corrosion-resistant claddings. Successful demonstration of the proposed *in situ* capability will make high impact science opportunities available at NSLS-II and pave the way at BNL towards the development of advanced synchrotron-based X-Ray methods for *in situ* studies of materials under extreme environments. Development of such a capability will also help realize 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. The acceleration of corrosion, also known as breakaway oxidation, that occurs during severe accidents, such as Loss of Coolant Accidents conditions, 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 during the Fukushima accident were caused by hydrogen produced by the Zr-water reaction.

The *in situ* sample environment directly observes and measures corrosion film formation at metal-alloy interfaces in a steam environment using synchrotron based XRD and XRF methods. Direct observation of interfacial reactions at metal-alloy interfaces will provide structural and chemical information on the oxide layer formed at metal-alloy interfaces due to corrosion in real time. For *in situ* studies, we have successfully developed and commissioned the proposed *in situ* reaction at NSLS and the Advanced Photon Source. In FY16, *in situ* studies of Zr alloy and advanced steel claddings in a steam environment at 400°C are planned using XRD. *Ex situ* studies under a range of temperatures, weight gain and electron microscopy measurements will be performed to help support the *in situ* studies. Such *in situ* investigation of nuclear claddings under steam will help understand the structure of the oxide layer formed as a function of alloy composition and structure, which will further help optimize the design of corrosion resistant next generation cladding materials. This work was done in collaboration with Eric Dooryhee, Sanjit Ghose and the XPD team.

TECHNICAL PROGRESS AND RESULTS:

1. **Commissioning the *in situ* sample environment at the XPD beamline was done in three steps**:

I) Optimizing reflection mode set-up at XPD: To optimize data collection from the metal-alloy interface, a wavelength of 0.290765Å (42.64 keV) was used and the beam size was reduced to 200x200 microns. The *in situ* sample environment was positioned on an eulerian cradle with four degrees of freedom to give flexibility for sample alignment in the X-ray beam to monitor oxide formation at the metal-alloy interface.

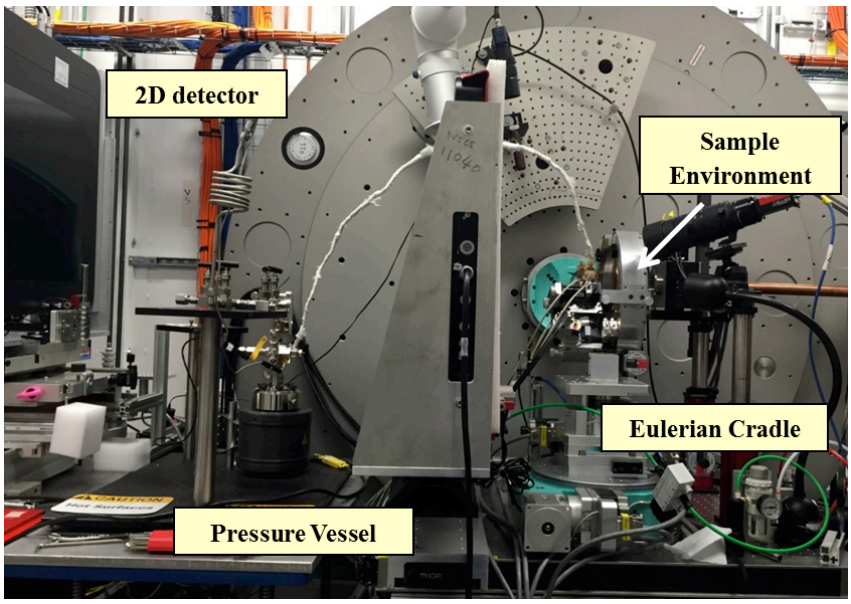


Figure 1. The *in situ* cell at XPD in an *in situ* corrosion study.

II) Preliminary measurements on thin film samples: To assure that the setup is able to measure the thin oxide layer *in situ* relative to the bulk, two preliminary measurements were performed. First a 100 µm gold thin film deposited on a Si wafer was measured to optimize the beam size and the sample tilt and maximize the Au signal relative to the Si wafer. The second was to measure a thin oxide film (1 µm) on a Zr metal substrate *ex situ* where the sample was oxidized in the same fashion as the intended *in situ* test for sample environment commissioning. After successful testing of the optimized reflection mode set-up by collecting XRD data on gold and Zr oxide thin films on these samples, the *in situ* study was carried out.

III) *In situ* corrosion study at XPD: The *in situ* sample environment was successfully commissioned at the XPD beamline in November 2015 (Figure 1). The *in situ* corrosion data was collected on a pre-oxidized Zr metal sample (exposed to steam for 40 hours at 350°C) prior to the beamtime to utilize the beamtime efficiently. An eulerian cradle with four degrees of freedom was used to mount the sample environment as shown in Figure 1. After total 52 hours of exposure to steam, development of monoclinic ZrO_2 was observed at the Zr metal surface.

2. ***Ex situ* corrosion studies on Alloy-33**: Corrosion studies of advanced steels using Grazing Incidence X-ray Diffraction, XPS and XRF were carried out. Results on alloy-33 showed an oxide scale was formed, consisting of two layers, chromium oxide and spinel phase ($FeCr_2O_4$) oxides.
3. **Copyright for *in situ* sample environment**: design was filed for the new technology developed.

In conclusion, the *in situ* sample environment was successfully commissioned at the XPD beam line and mechanistic corrosion studies of advanced steels such as APMT and Alloy-33, which are candidates for nuclear claddings, were performed. A copyright on the *in situ* sample environment was filed and results on Alloy-33 were submitted for publication. In FY16, NSLS-II users studying *in situ* corrosion of materials for nuclear applications will be able to access the sample environment through the NSLS-II proposal system.

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 *operando* time-dependent diffraction capabilities at the X-ray Powder Diffraction (XPD) beamline and at other diffraction and scattering beamlines at Brookhaven's 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 course of this project, we have demonstrated that MED introduces structural selectivity into time-dependent diffraction experiments in a range of catalytic, physical and chemical processes.

APPROACH:
MED is a technique allowing the dynamic structural characterization of crystalline materials subjected to an external stimulus (temperature, pressure, gas…). Contributions from the (active) part of the crystal that varies synchronously with the stimulus can be extracted. The team has been active in developing the MED technique through an aggressive experimental program at several facilities and beamlines: National Synchrotron Light Source (NSLS) X17A, X7B and X14A, the Advanced Photon Source 11-ID-C and 17-BM. A large variety of systems were examined, under the effect of a periodically alternated parameter like temperature and pulsing gas environment: Cu/CeO_2 catalysts, Gd doped ceria, $CuFe_2O_4$, FeCrAl, Ni-Pd, Metal Organic Frameworks (see for example, Figure 1). 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, polypropyl compounds and WO_{3-x} nanotubes. A MED-based proposal is submitted that requests General User time for the summer run cycle of NSLS-II. 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 or strongly asymmetric. The technique proves to be very accurate and informative in a number of cases, but it requires a periodic stimulus and a linear response of the crystal system.

TECHNICAL PROGRESS AND RESULTS:
The goal was two-fold: i) to develop an algorithm for data analysis and ii) to implement the hardware to conduct MED measurements at NSLS-II XPD. 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.

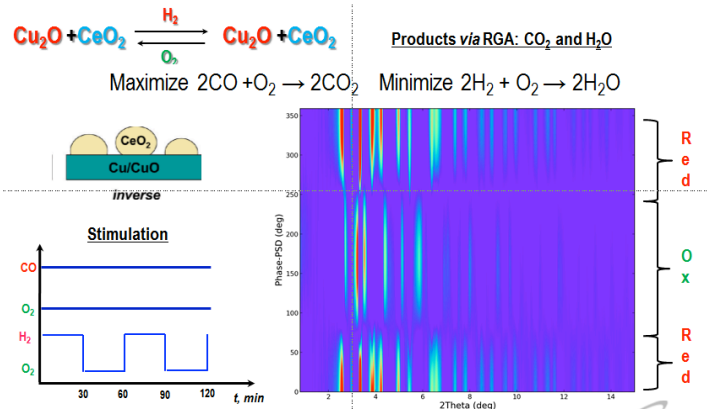


Figure 1. Oxidation-reduction of $Cu_{60}Ce_{40}$ in a H_2/O_2 flow at 250°C in a CO/O_2 stream.

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-II/XPD.

Tasks	Status (accomplished)	Next Actions
Sample screening and Tests	High-impact science cases selected through approved peer-reviewed proposals. Reach-out at conferences.	Extend MED to other important experimental systems. Extend MED to pair distribution function.
Setting-up Experiment controls	Instrumentation and set-up at NSLS finished. Implementation at NSLS-II XPD finished. Purchased a fast switching valve and a Residual Gas Analysis system.	Continue to develop the MED hard/software for science at NSLS-II. Science commissioning of the system is due to happen in the 2nd run cycle of 2016 at the NSLS-II XPD beamline (proposal submitted).
Experiment	MED benchmarked in real-case studies and test applicability. • *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	1st experiments at XPD: proposals were reviewed and well received. Measurements have been postponed until the Experimental Safety Envelope of NSLS-II XPD can accommodate them. A comprehensive Gas Handling System (with cabinets and gas supply regulators) is in the procurement phase and will directly serve this project.
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 (paper in preparation for submission to *J. Appl. Crystallography*). Extend the use of Principal Component Analysis to the treatment of MED.

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:

Worldwide, the trend of increased synchrotron brightness has far outpaced advances in the quality and *in situ optimal tuning and alignment* of beamline optical components. Using the existing alignment methods, beamline optics suffer from unnecessary extra aberration and beamline scientists struggle with time-consuming and ambiguous qualitative alignment feedback methods. The photons produced by next-generation light sources must be transported by state-of-the-art beamlines to the installed and fully equipped end-stations. This photon transport cannot be developed to the right level without adequate *ex situ* and *in situ* metrology.

The development of *in situ metrology* tools for X-ray component characterization, alignment and beamline performance studies is a necessary complementary method of visible light metrology. Availability of adequate measurement tools and adjustments directly at the beamlines is crucial for thorough *optimization* of operational performance of individual beamline components and entire beamline systems. One of the major missions of *in situ* at-wavelength metrology is to provide the required instrumentation and measurement techniques to fulfill these requirements.

APPROACH:

The next generation of mirror measurement tools must target sensitivity and accuracy values well below the actual current level and will need to meet the optimal quality of the new X-ray sources (diffraction limited). It has become apparent that without the development of effective, broadly applicable *in situ* metrology techniques, costly increases in source brightness may hardly be noticed in endstation sample chambers. There are literally orders of magnitude in metrology performance to be gained by the development of new measurement techniques, instrumentation and procedures, to satisfy the ever-increasing demand for greater accuracy, increased reliability and rapidity of measurements with super high quality X-ray optics. The unavoidable use of adaptive optics or an adaptive cooling scheme makes the quest for a perfect beam diagnostic a priority. For example, the major obstacles in focusing X-ray beams to ultimate sizes below 100 nm are the requirements for unprecedented levels of alignment and quality of optics. An effective way to overcome these obstacles is to analyze the output wave-front and use this as a feedback to perform the ultimate alignment.

This LDRD project 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 (HXN), 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 project involves *wave-front phase characterization*, which is crucial to optimally utilize the highly coherent National Synchrotron Light Source II (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 project 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 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.

So far many simulations have been carried out to verify the algorithms are accurate enough for 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.

Figure 1. Grating Shearing Wavefront Sensor.

The first test will be performed at the SRX or HXN beamline of NSLS-II before the end of the summer in 2016. .

The possibility of measuring absolute diffraction limited wavefronts has been addressed during this project. The main issue preventing the development of such capabilities is the lack of absolute calibration in the hard X-ray regime. Calibration of any type of wavefront sensors is always required to improve the accuracy. A proper theoretical calibration method has been proposed (paper submitted) in the X-ray domain.

This method will be tested in collaboration with SLAC National Accelerator Laboratory and the Advanced Photon Source (APS) on the APS Test Beamline.

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 image data: (1) registration of 3D images from different techniques and/or resolution and (2) extraction of relevant scientific information from 3D images of heterogeneous porous media. These original goals have since been changed, at the request of the National Synchrotron Light Source II (NSLS-II) management. The new goals are to develop and deploy a common framework for the data acquisition/workflow/management/analysis at NSLS-II. This new goal is a collaborative effort with two other related LDRDs (13-017 and 14-024) and the NSLS-II Controls group.

APPROACH:
The original approach was to develop very specific image analysis tools focused on specific experiments. Two postdocs, Gabriel Iltis and Thomas Caswell were hired under this LDRD. However, at the request of the NSLS-II management, the effort was redirected to establish a robust common framework for data acquisition/workflow/management/analysis at NSLS-II. This new goal is a collaborative effort with two other related LDRDs (13-017 and 14-024) and the NSLS-II Controls group.

TECHNICAL PROGRESS AND RESULTS:
When this LDRD started, the NSLS-II data infrastructure architecture was not yet defined and only basic EPICs control of hardware was implemented. That was primarily why the goals of this LDRD were changed - because of the urgent need to define and deploy the underlying architecture and infrastructure. Over the last two years, the team has worked to define, develop and implement a data architecture and infrastructure for the NSLS-II.

Figure 1 shows the architecture of the NSLS-II data acquisition, management and analysis infrastructure, as is currently implemented on the beamlines. 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, but 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. A database (e.g., MongodB) is used to catalog all the data; but the architecture and implementation is not wedded to the specific database. Another novel feature is the idea of a Data Broker Application Programming Interface. This component acts as a unified gateway for the user to access the data from all of the collection and storage systems. Another key aspect is the focus on good software practices and on the development of libraries instead specific applications. A considerable amount of effort has also been dedicated to rollout packaging, version control and documentation. As a result of this (and the two other related) LDRDs and the close collaboration with the NSLS-II Controls group, the NSLS-II currently has a new advanced data acquisition, management and analysis architecture that is suited to the requirements of the facility.

FY15 Achievements:

- Started active collaboration with Linear Coherent Light Source on scikit-beam
- Wrote reference implementation of meta-data + scalar data store (metadatastore)
- Wrote reference implementation of file abstraction layer (filestore)
- Formalized document model (event based collection)
- Implemented new data acquisition software (bluesky + callbacks)
- Implemented basic data export functionality (suitcase)
- Implemented synchronizing code for merging asynchronous data (datamuxer)
- Implemented unifying interface for metadata store/file store access + search (databroker)
- Implemented streaming 1 and 2 time multi-tau correlation analysis (scikit-beam)
- Fluorescence fitting Graphical User Interface front-end for scikit-beam (pyxrf)
- Made significant improvements to dev-ops infrastructure
- Deployed Jupyter hub internally to provide computation resources to users.

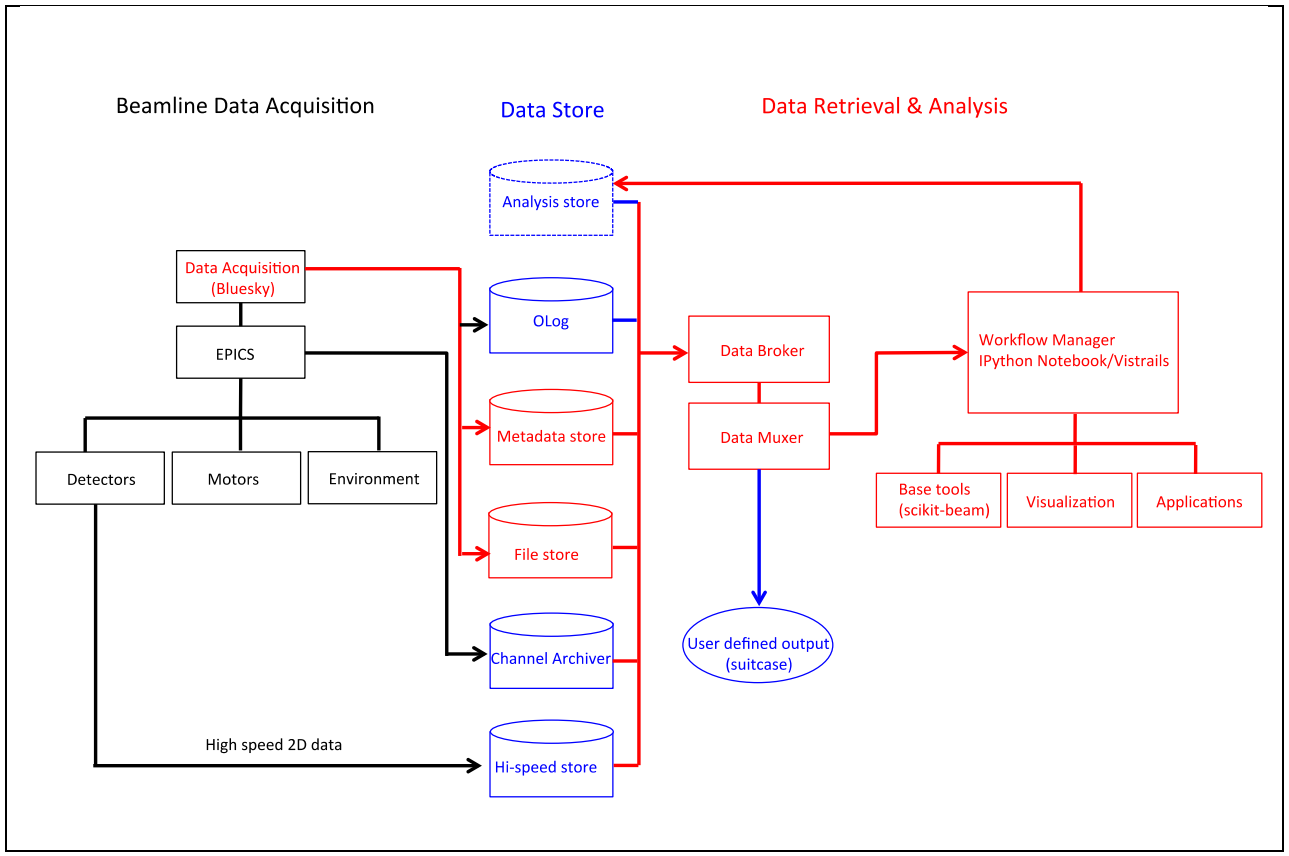


Figure 1. Data architecture implemented at NSLS-II. Items in black were implemented prior to this LDRD. LDRD funded effort has led or made significant contributions to all the components in red. Items in blue are developments by non-LDRD staff. Dashed item has not been implemented yet.

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 the photoelectron current. A few attempts yielded sub 100 nm spatial resolution, but were limited mainly by the high background photoelectron current. We propose to develop novel 'smart tips' based on carbon nanotubes (CNT) to reduce the photoelectron current 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 insulator $Bi_{2-x}Mn_xTe_3$. 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 the submicron scale, elucidating the effects of magnetic impurities and ferromagnetism on the topological surface states.

APPROACH:

We proposed a novel approach for development and fabrication of 'smart tips' suitable for X-ray assisted STM measurements at the National Synchrotron Light Source II (NSLS-II). Multi-walled carbon nanotubes 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 Mn doped BiTe compounds.

One objective for FY15 was to finalize development and characterization of 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 microscopy (SEM) images of radial and vertical cross-sections of the tips. We then applied FEI Helios dual beam focused ion beam-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 a $Pt_{90}Ir_{10}$ pillar that was ~1 um long out of the SiO_2-insulated tips. Then, the 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 a metal apex ~300 nm long 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 FY15 was to evaluate the performance of the smart tips that were developed in a lab-based/off-beamline environment and also to verifiy the performance with the X-ray beam. 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 the Variable Temperature Ultra High Vacuum Scanning Tunneling / Atomic Force Microscope from RHK Technology to determine the ultimate resolution of the CNT-based uncoated tips. An Au(111) single crystal served as a model system to test the performance of the CNT-based smart tip. A CNT-$Pt_{90}Ir_{10}$ bare tip was tested on the Au(111) crystal, and preliminary results show the characteristic herringbone structures of the Au(111) crystal surface, suggesting that the CNT-$Pt_{90}Ir_{10}$ bare tip works.

For our initial experiments, we evaluated the performance of the CNT-based smart tips using SXSTM at the Nanoprobe beamline ID-26 at the APS. 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. Characteristics of the tip and photoelectron shielding were inferred from these measurements. Results of the fabrication and characterization of CNT-based tips were presented at the Synchrotron Radiation Instrumentation conference in New York City and were also published in the Journal of Nanomaterials ('Fabrication and characterization of CNT-based smart tips for synchrotron assisted STM', Hui Yan, Marvin Cummings, Fernando Camilo, Weihe Xu, Ming Lu, Xiao Tong, Nozomi Shirato, Daniel Rosenmann, Volker Rose, and **E. Nazaretski**, Journal of Nanomaterials, **2015**, 492657, (2015)).

In FY15, measurements on Mn-doped BiTe samples were scheduled at the 26-ID beamline of APS. A beamtime proposal was submitted and approved. Unfortunately the SXSTM system was down during the scheduled beamtime and therefore actual measurements were delayed until the first quarter of CY16. A manuscript on BiTe samples was prepared and we expect to submit it after we acquire X-ray SXSTM data.

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. The LDRD program provides 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 started to obtain results. The Chen group is also 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 - FY2015. 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 new 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 National Synchrotron Light Source II.

TECHNICAL PROGRESS AND RESULTS:

During the past year of LDRD funding the Chen group at both BNL and Columbia University focused primarily on obtaining proof-of-principle results for CO_2 conversion using H_2 and light alkanes. 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 and bimetallic catalysts have been identified as highly active and selective catalysts for CO_2 conversion. These results were instrumental in receiving DOE field work proposals (FWP) funding for ongoing support of the Chen group efforts at BNL [1].

In addition to CO_2 conversion using H_2, we continued to explore other areas of catalysis and electrocatalysis to expand our efforts in Sustainable Fuels. These efforts have led to three publications acknowledging the current LDRD [2-4]. In Publication [2] we 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. In Publication [3] we explored the conversion of a

hemicellulose-derived oxygenate, furfural, to 2-methyl furan that can be used as gasoline range molecules. In Publication [4] we explored the utilization of cellulose-derived oxygenates (ethylene glycol and glucose) as fuels for fuel cells to generate electricity. Overall these efforts have identified new and complementary research areas to those sponsored by the FWP.

At BNL the Chen group members finished the installation and testing of several techniques, including CO chemisorption equipment for measuring active surface areas of catalysts, Brunauer–Emmett–Teller (BET) physisorption equipment to measure the total surface areas and pore volumes of catalysts, a flow reactor to perform steady-state evaluation of catalysts, and an electrochemical system for electrocatalysis.

The initial research in this LDRD focused on conversion of CO_2 to CO using H_2 as a co-reactant. That research served as the foundation for a new DOE FWP [1] that will fund studies in that area.

[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] T.G. Kelly and J.G. Chen, "Decomposition Pathways of C2 Oxygenates on Rh-modified Tungsten Carbide Surfaces", Surface Science, 640 (2015) 89-95.

[3] K. Xiong, W. Wan and J.G. Chen, "Reaction Pathways of Furfural, Furfuryl Alcohol and 2-methylfuran on Cu(111) and NiCu Bimetallic Surfaces", Surface Science, accepted (2016).

[4] E.G. Mahoney, W, Sheng, M. Cheng, K.X. Lee, Y. Yan and J.G. Chen, "Analyzing the electrooxidation of ethylene glycol and glucose over platinum-modified gold electrocatalysts in alkaline electrolyte using in-situ infrared spectroscopy", Journal of Power Sources, 305 (2016) 89-96.

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

LDRD Project # 14-003

Y. Cui

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. We investigated the characteristics of $B_{12}As_2$ as a material for detecting neutrons and photons. By demonstrating the photo-sensing capability, we verified the transport of free carriers in this material. The success of this work is expected to lead to increased availability of new solid-state neutron-detection devices for many applications.

APPROACH:

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 further 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 the 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 for neutron detection. In this project, we tested $B_{12}As_2$ 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 complementary metal-oxide semiconductor (known as 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.

We carried out a two-year 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 worked with Kansas State University to obtain materials grown by the metal-flux method and by chemical vapor deposition (CVD). In parallel, we conducted material growth experiments (e.g., laser ablation) 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 characterized the materials using techniques available in our group and at the National Synchrotron Light Source and the Center for Functional Nanomaterials. The characterization methods included current-voltage (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; and Hall effect measurements to determine the carrier mobilities and lifetimes in the crystals.

(3) Detector fabrication - We deposited 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 ultraviolet (UV) light, alpha- and neutron-sources to measure the photo-sensitivity and response to neutrons. Other investigators involved in this project include R. B. James, A. E. Bolotnikov, G. S. Camarda, A. Hossain, U. Roy, G. Yang, and R. Gul.

TECHNICAL PROGRESS AND RESULTS:

(1) Material growth - We deposited $B_{12}As_2$ thin film samples by a CVD method. We also acquired $B_{12}As_2$ crystals by a metal-flux method and used the material to conduct electron beam evaporation experiments for thin-film deposition. Using the latter method, we grew samples on both p-doped and n-doped SiC substrates. Samples produced in this task were used in the following studies of material characterization, detector fabrication and device performance evaluations.

(2) Materials characterization - With the $B_{12}As_2$ materials, we carried out Hall-effect experiments to measure the type and mobility of the charge carriers in the material. Table 1 shows the results of these measurements for the CVD-deposited samples. We also conducted I-V measurements to determine the resistivity of the samples and used the same setup to measure the photocurrent response of the material to UV irradiation. The results (Fig. 2) show that $B_{12}As_2$ is very sensitive to UV light. We generated a record of invention based on this finding.

(3) Detector fabrication and testing - We measured the response of the $B_{12}As_2$ samples to an alpha source, ^{241}Am. We were able to obtain spectra of alpha particles with the $B_{12}As_2$ materials (Fig. 3). This encouraged us to pursue further studies with this material in order to optimize the growth process for better material properties and to design better electronic circuits with lower noise to read out the thin-film detectors. We will propose our ideas to the Department of Energy/National Nuclear Security Agency/Defense Nuclear Nonproliferation and other federal agencies when appropriate calls are announced.

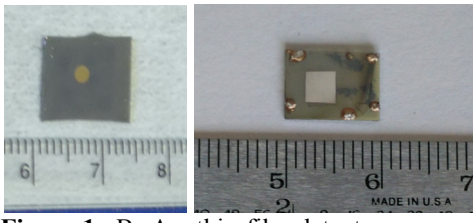


Figure 1. $B_{12}As_2$ thin-film detectors produced by E-beam evaporation (left) and CVD process (right).

	Mean value
Mobility [m²/V·s]	1.49E-4
Carrier type	P
Carrier concentration [1/m³]	N/A
Sheet carrier concentration [1/m²]	1.23E16
Sheet Hall coefficient [m²/C]	5.06E2
Resistivity [Ω·m]	N/A
Sheet resistivity [Ω/□]	3.41E6
Hall voltage [V]	4.7084E-6

Table 1. Results of Hall-effect measurements with CVD sample.

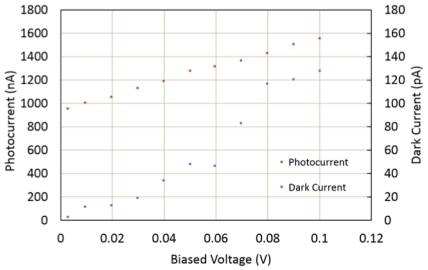


Figure 2. I-V measurement results from a $B_{12}As_2$ sample.

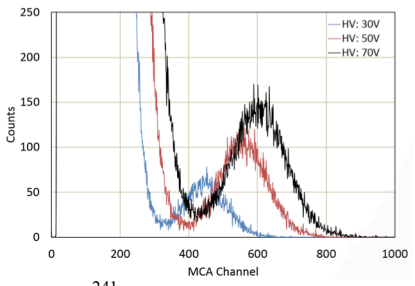


Figure 3. ^{241}Am spectra obtained with a $B_{12}As_2$ thin-film detector.

1st Light: Elucidating Solid-Solid Interfaces in Energy Storage Systems

LDRD Project # 14-005
E. Takeuchi

PURPOSE:
This LDRD project will establish an important and unique infrastructure for the energy storage community allowing probing of mechanistic information under application relevant working conditions. Bimetallic cathode compounds, including metal oxides and phosphorous oxides, are of significant interest as energy storage materials, as they provide theoretically high voltage and high capacity. At the anode interface, surface deposits can form, leading to cell impedance rise resulting in premature device failure. The proposed research will develop the methodology and then characterize the solid-solid interfaces of bimetallic cathodes and of anode surfaces.

APPROACH:
Under this LDRD, a cell will be fabricated which will be used to characterize active materials in a cell environment, *in situ* and *operando*. The cell will be compatible with sub-micron resolution X-ray absorption spectroscopy appropriate for elemental imaging. Using hard X-ray absorption spectroscopy, we will develop the necessary characterization tools to visualize the various intermediates in a working battery environment. The techniques will provide fundamental information regarding the structures necessary to mediate electrical transport and conductivity within an energy storage system.

TECHNICAL PROGRESS AND RESULTS:
In situ X-ray diffraction (XRD) or X-ray absorption spectroscopy (XAS) on electrochemical systems can provide valuable information on the structural changes occurring (or not occurring) on an electroactive material. However, due to the complex nature and necessary components of an electrochemical cell, *in situ* measurements are typically difficult due to absorption effects, particularly for laboratory based XRD measurements utilizing Cu K-α wavelength X-rays, which have limited penetrating power due to its relatively low energy (ca. 8 keV).

During the previous phase of work, detailed studies of the anode interface were completed using a beryllium window cell and X-ray absorption spectroscopy measurements at the National Synchrotron Light Source. The data resulted in a new conceptual model for the surface-electrolyte interphase, which was published in the journal *ACS Applied Materials and Interfaces.*

Modified coin-type electrochemical cells are typically employed for *in situ* measurements; however these modified cells can create reduced stack pressure over the area interacting with incoming X-rays and possibly reduce the electroactivity in this region of the electrode, leading to incomplete reactions in the measured region. In addition, thin Kapton is typically used to create an X-ray window on the cell, which may be permeable to moisture/oxygen over time.

In order to create an inexpensive experimental cell with electrochemical performance identical to standard coin-type cells, a plastic pouch cell design developed during this phase of work, was employed as shown in Figure 1. By using inexpensive heat-sealable plastic, X-ray attenuation is minimized while homogeneous stack pressure is applied over the entire electrode via a vacuum sealing process. Unlike many specially designed *in situ* XRD cells, electrodes that are utilized in

coin-type cells can be directly used in this *in situ* pouch cell, eliminating the ambiguity of comparing fundamentally different electrode geometries and fabrication processes.

Over long exposures to atmosphere (ca. 3-7 days), the plastic pouch material is permeable to moisture/oxygen. To eliminate any possible contamination, an *in situ* enclosure was developed to mount the pouch cell while flowing an inert gas through to ensure the pouch cell remains under inert atmosphere with minimal X-ray beam attenuation (Figure 1b). This experimental design enables utilization for a variety of X-ray based techniques. The small Kapton cover (Figure 1b) facilitates transmission measurements, such as those used by synchrotron techniques (XAS and Debye-Scherrer XRD) along with fluorescence measurements.

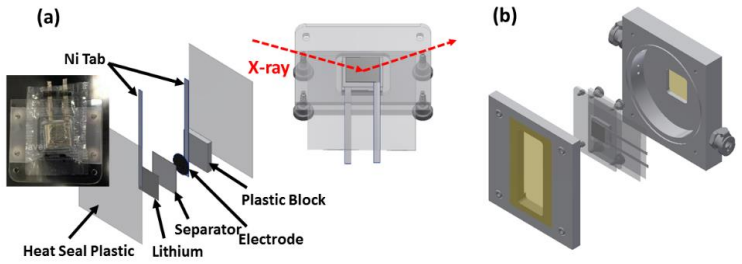


Figure 1. (a) *In situ* plastic pouch cell schematic and (b) *in situ* enclosure to ensure the pouch cell is measured under inert atmosphere.

These experimental designs were successfully utilized to collect *in situ* XRD measurements (Cu K-α radiation) on a variety of lithium ion battery electrodes in Bragg-Brentano geometry. With minimal X-ray beam attenuation, XRD scans were measured at 2-3°/min with excellent data quality (Figure 2). With fast data acquisition times, detailed XRD studies can be performed while the electrochemical cell (dis)charges utilizing realistic C-rates (0.1 C or faster). With the increased flux of the X-ray beam and advanced detector systems available at synchrotron sources, detailed *in situ* structural investigations using a variety of experimental techniques are feasible.

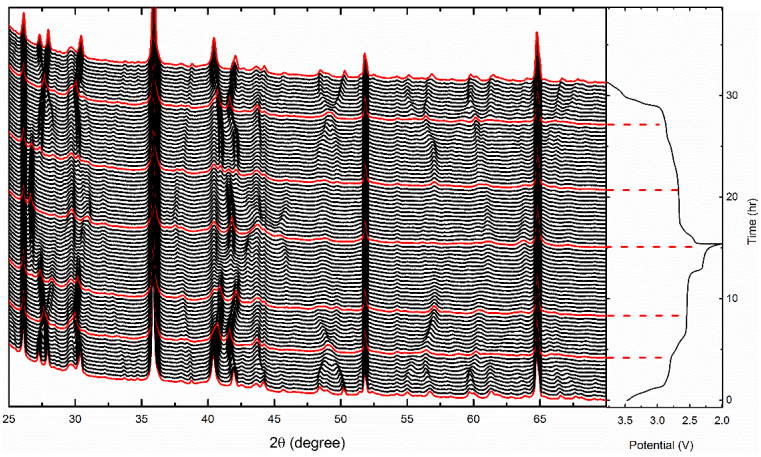


Figure 2. *In situ* XRD measurements on LiV_3O_8 electrode using laboratory based diffractometer. Data was continuously collected over a complete discharge and charge of the LiV_3O_8 electrode.

Milestones

- Assembly and feasibility test of *in situ* cell at the Submicron Resolution X-ray Spectroscopy (SRX) beamline – FY16
- Correlate *in situ* XRD data with feasibility XAS data – FY16
- Utilize cell for *in situ* demonstration experiment at the SRX beamline – FY17
- Correlate *in situ* XRD data with demonstration experiment XAS data – FY17.

High Performance Direct Wind Superconducting Magnets

LDRD Project # 14-011
B. Parker

PURPOSE:

This LDRD extended BNL Direct Wind superconducting magnet capabilities to produce complex coil structures for use in eRHIC Interaction Region (IR) magnets. Such magnets need strong fields for focusing and deflecting hadron beams while providing low field "protected regions" to pass the electron beam. To support eRHIC, we developed high performance superconducting cable, invented new coil geometries, made extensive winding machine modifications and developed procedures to wind with stiff larger-diameter cable. The advances in superconducting coil winding technology arising from this LDRD along with the development of new coil geometries are directly applicable to other BNL Direct Wind work.

APPROACH:

A key feature for eRHIC IR magnets is using nested coils to create a low field "sweet spot" region as illustrated in Figure 1. Inside both coils, fields add constructively to provide the strong bending or focusing. Between the coils, the fields cancel and leave a low field area where the electron beam can pass close by undisturbed. The inner aperture size is determined by eRHIC experimental requirements and leads to large coil peak fields and forces; however, the sweet spot configuration needs the inner coil to be largely self-supporting. BNL Direct Wind accomplishes this by having compressive force, to counter the magnet coil's Lorentz force, integrated with the coil structure during production. Past BNL Direct Wind magnets have performed well, but eRHIC coil parameters are very challenging and for this LDRD we set ourselves the task of making the short prototype coil winding shown in Figure 2.

TECHNICAL PROGRESS AND RESULTS:

There are two principal components of the semiautomatic Direct Wind facility. One of them feeds insulated superconducting cable from a spool to the cylinder on which the coil is being wound and, using a combination of heat from an ultrasonic generator and an air jet, bonds the cable to the cylinder. The other moves the cylinder so that the cable is bonded in the desired pattern. In all, eleven quantities are needed to control this process.

Producing the LDRD prototype shown in Figure 2 was more challenging than anticipated and a

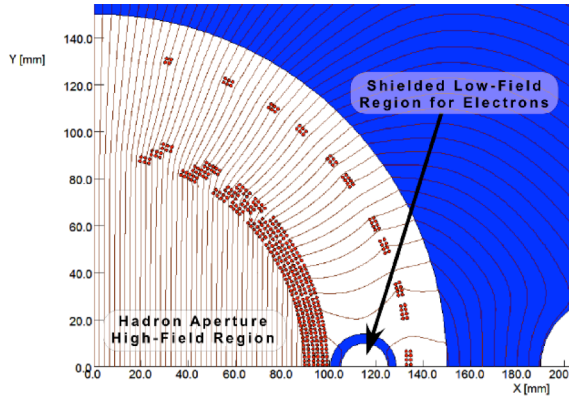


Figure 1. eRHIC IR dipole sweet spot concept.

Figure 2. Picture of the second coil layer of the LDRD short prototype dipole winding.

major benefit of this LDRD has been developing winding machine hardware and software upgrades to deal with the new challenges. With these lessons learned, we have a path forward to producing eRHIC IR magnets, which we are implementing.

From the start, we had to provide a bigger opening for the cable as it passed through the feed tube of the automatic winding machine, but soon discovered that we also had to revise the capstan design and improve the feed tube bearing design when parts wore out too quickly. Even with said improvements, we burned out motors and had to made adaptations to use more powerful capstan motors. The spools used to hold the cable needed attention as a large magnet diameter means more cable length than we dealt with before. The size and weight of the new superconducting cable made it easy to break standard mounting spools.

Larger diameter cable also needs greater ultrasonic power (i.e., heating for epoxy bonding), which can be partially compensated for by winding at a slower rate; however, it was then found necessary to improve the post-deposition cable cooling. Ultimately we learned that we must upgrade and increase the available ultrasonic power as a combination of a slower winding speed. Longer eRHIC magnet cable coil pattern lengths would imply that a machine operator would have to closely, and continuously, monitor winding over several days to complete a full length eRHIC coil layer (rather than just a few hours as needed for previous projects).

We have also improved our ultrasonic stylus design and calibration procedures in many ways. We now manufacture the ultrasonic stylus with harder materials (to keep the stylus from bending during winding) and implemented an extensive calibration procedure to ensure that greater ultrasonic energy goes to bonding. We also came up with additional software and winding geometry control tricks to better fight the cable spring-back and to ensure correct conductor placement.

Potentially the most significant place for improvement is in the superconducting cable itself. During the course of this LDRD, we maintained contact with the superconducting cable vendor and investigated ways to reduce the cable stiffness that was making coil winding so difficult. The vendor produced additional superconducting cable, using superconducting wire from our LDRD material minimum purchase, but this time with the cable twist pitch greatly reduced. By inspection, this new less tightly twisted cable is more flexible and should be easier to wind. This new cable was not available until after the LDRD ended, but we are looking to make short test windings to see if it will allow winding coils faster at the present power levels.

In conclusion, to successfully wind the present LDRD eRHIC prototype dipole coil, we had to overcome many technical challenges that eventually would have been unwelcome surprises for actual eRHIC IR magnet production. Now we have a much better basis for winding superconducting magnets with larger diameter cables and can build from this experience in our future work.

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 Complementary metal-oxide semiconductor (known as CMOS) architecture to the 3D 22-nm 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 (HXN) Beamline at National Synchrotron Light Source II (NSLS-II), which provides a unique tool to noninvasively image the strain at the nanometer scale. There are two objectives in this project. 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 the HXN beamline at 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, with conventional methods, 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 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 the HXN beamline at NSLS-II for 3D strain imaging *in operando* at nanometer resolution.

TECHNICAL PROGRESS AND RESULTS:

In the past fiscal year, we have done a few proof-of-concept experiments at the 2ID-D beamline at the APS. The main goal was to understand the effects of coherence, beam instability and thermal drift on the Bragg ptychography reconstruction. We tested the data analysis code and investigated the key factors in the experiment that would affect the reconstruction. The knowledge gained is critical to ensure the success of the future experiment at NSLS-II. We also did a systematic study on the effect of dynamical diffraction in Bragg coherent diffractive imaging (BCDI), both theoretically and experimentally. Dynamical diffraction occurs in a nearly perfect crystal with a size close to or larger than a micron. Kinematical diffraction, which is the mathematical basis of BCDI, is only an approximation to the former and is not valid in many cases. In order to extend the application range of BCDI, it is very important to understand the type, magnitude and extent of dynamical diffraction artifacts in BCDI reconstruction. A successful experiment was conducted at the 34ID-C beamline at APS. The data showed a good agreement with the theoretical calculation. A paper based on the experimental results is in preparation for publication.

A FinFET device designed for this project has been fabricated at IBM. However, due to the delay in commissioning of the diffraction capability at the HXN beamline at NSLS-II, we were not able to conduct our first experiment on FinFET in the past year. HXN is the only beamline that provides the resolution needed, so no other place is an option. We plan to do the experiment in the summer. A data analysis package has been fully tested and is ready to be used for analyzing the diffraction data.

In parallel, the effort to complete a forward simulation software package for single crystal diffraction (kinematical and dynamical diffraction) is ongoing. The program is fully parallelized for Central Processing Unit and Graphics Processing Unit acceleration. A Graphical User Interface has been partially developed by a part-time student, hired through this project. We will continuous this development, in collaboration with Columbia University. Upon completion, it will be released to the crystallography community.

Our main tasks in this fiscal year are:

1. Conduct the experiment on a real FinFET device at the HXN beamline at NSLS-II
2. Release the forward simulation package to the community
3. Publish results of the completed studies. The publication of our very first paper was delayed, because of the significant amount of work required to make progress on the project, but it will be submitted in two weeks.

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

LDRD Project # 14-024
K. Kleese van Dam

PURPOSE:
The purpose of the project is to develop prototype and pre-production capabilities for the integrated scientific computing and data management at 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 is to develop a detailed scope and requirements analysis for the computational, data-management and scientific analysis needs of NSLS-II. 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. Also included 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.

TECHNICAL PROGRESS AND RESULTS:
After focusing in year one on requirement analysis and conceptual design, year two of the project moved on to advanced prototype design, pre-production tools and tool evaluation in real life scenarios. The project developed a substantive body of software tools for three principle functions: data acquisition, data management and data analysis. Specifically:

Data Acquisition –
1) ophyd: Python/EPICS-based device abstractions for NSLS-II
2) bluesky: a data collection interface

Data Management – Complete tool suite for the data storage, description, discovery and access –
1) metadatastore: MongoDB-backed metadata storage
2) filestore: storage for non-scalar data
3) databroker: externally facing application programming interface for data
4) datamuxer: tools for accessing data in a convenient, workable format
5) suitcase: data export facilities for NSLS-II

Data Analysis –
1) X-ray photon correlation spectroscopy – skbeam/correlation module
2) X-ray speckle visibility spectroscopy – skbeam/speckle module
3) Manual masking tool – xray-vision/mask.py
4) Statistical tests for speckle patters – skbeam/roi module including circular average, kymograph, mean intensity, region of interest pixel values, region of interest maximum counts
5) Create different shape labeled arrays – skbeam/roi module

6) Plotting tools for speckle analysis – xray-vision/speckle.py
7) xray-vision: visualization widgets and plotting helpers targeted at X-Ray sciences
8) pyXRF: fluorescence fitting graphical user interface
9) replay: live data view for beamlines at NSLS-II
10) album: a simple web app for browsing experiments

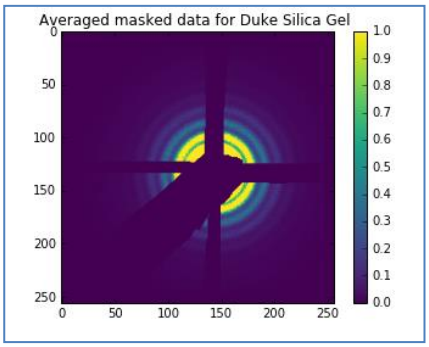


Figure 1. The image is an average over 5000 measurements with 1 ms integration time. The dark shadow of the beam stop and the dark columns in the scattering pattern were masked out for analysis.

The majority of the software was developed into production versions by NSLS-II staff in FY15 and FY16 as the tools reached a sufficient maturity level. All of the software is openly accessible on GitHub under - https://github.com/scikit-beam; it has been taken up by the wider DOE Basic Energy Sciences Facilities community for reuse at other facilities.

In addition to the foundational data acquisition, management and analysis tools, the project also explored streaming analysis frameworks that would enable the fast analysis and interpretation of results to support *in situ* experimental steering. The efforts focused on a Spark and EPICS V4 solution that was significantly adapted and enhanced to meet the specific high performance needs of the NSLS-II. In particular, the ability to integrate C++ and Python code as well as the ability to use graphics processing units was critical. Usage tests and further evaluations are planned for FY16. The work led to a Small Business Innovation Research proposal with Real-Time Innovation in 2015.

As the initial tool set has been developed and handed over to NSLS-II staff for further maturation and operational use, the project will focus in its coming year in particular on approaches and methods for high performance streaming analysis.

FY16 Milestones:
1) Detailed requirement gathering and documentation of NSLS-II beamline analysis requirements for the coming five years, with a particular focus on streaming analysis and steering
2) Development and testing of streaming analysis algorithms and workflows for the Coherent Hard X-ray Scattering and Coherent Soft X-ray Scattering beamlines
3) Further evaluation of the Spark / EPICS V4 streaming framework
4) Complex modeling, development of an integrated experimental data analysis and numerical modeling support for experimental planning and steering
5) Research of high performance, data intensive programming models that are particularly suitable for streaming, high volume, high velocity data analysis
6) Analysis on the wire - exploration of the feasibility to analyze data as it is transferred from the beamline to the central computing cluster for further analysis.

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

LDRD Project # 14-026
B. Babst

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, 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 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., coexpression 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:

In FY2014, we developed computational tools, mainly relying on coexpression analysis using metabolic genes known to be involved in nitrogen remobilization, to identify transporter-encoding genes that may be involved nitrogen remobilization. In FY2015, we identified 28

additional candidate nitrogen recycling transporter genes in *Arabidopsis*, based on the coexpression scores and gene structure, completing *milestone 1.1*.

In FY 2014, we made significant progress on *milestone 1.2*. We obtained seed for 37 nitrate transporter (NRT) and ammonium transporter mutant lines in *Arabidopsis*, and propagated seed for screening by ^{13}N assays. We optimized our ^{13}N assay of N export from leaves with a throughput of 6-12 mature *Arabidopsis* plants at one time. In FY2015, we genotyped about 50 nitrogen transporter mutant lines in *Arabidopsis*, and confirmed that 20 of those lines were homozygous for the mutation. We screened 15 mutant lines using ^{13}N radiotracer assays by administrating $[^{13}N]NH_3$ as a gas to leaves and identified 3 lines that exhibited altered nitrogen transport compared to wild type plants, when grown with low soil nitrogen (Figure 1). We are conducting a more detailed characterization of those 3 mutant lines, toward *milestone 2.2*.

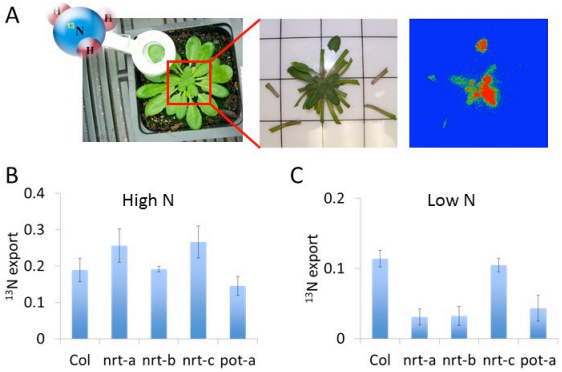


Figure 1. Custom leaf cuvette for small plants and imaging of dissected *Arabidopsis* plant (A). Export of ^{13}N from leaves of wildtype and mutant plants grown with high N (B) and low N availability (C).

We applied cross-species co-expression network mapping to identify relevant functional homologs of NRT genes in poplar, toward *milestone 1.3*.

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 in FY2014. We measured growth and photosynthesis and archived frozen tissue samples from 50 day-old sorghum plants, which will be used for transcriptomic analysis. In FY2015, we quantified soluble sugars for leaves and internodes and generated RNA sequencing data (by contract) for global gene expression profiling, which we are now analyzing. This project ended with the termination of the BNL Imaging Program and the loss of the scientific expertise to perform this work. Results were communicated at several meetings and in one publication.

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 Biosciences 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 DOE biofuels objectives. The 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 become 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 became the workhorse of predictive biology at the scale of metabolic networks.

While plants are multicellular organisms with different tissues like leafs, 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 (RNAseq).

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).

TECHNICAL PROGRESS AND RESULTS:

Aim 1, Genome scale metabolic network reconstruction:

The current version of the genome scale metabolic network includes 11 compartments, 3848 metabolites, 5759 reactions and 1183 annotated genes encoding the catalyzing proteins with catalytic and transport activity. The model was tested for functionality. Our model is referenced to the genome of *Arabidopsis*, the preeminent model organism in plant science. The most complex metabolic subsystem we reconstructed was that of glycerolipid metabolism. This is because each glycerolipid compound that one would consider as a discrete metabolite species is actually defined as an entire class of molecule structures. For example, for phosphatidylcholine, a glycerolipid with two fatty acids attached to the glycerol backbone-structure, there are 196 molecule species due to permutations of the 14 different fatty acid chains present in lipids. While genome scale models typically represent such compound classes as one molecule species (e.g., by averaged elemental composition), we decided to fully and explicitly represent the diversity of glycerol-lipid molecule species in our model. The large number of molecule species resulted in more than 3000 individual enzymes steps in the glycerolipid subnetwork that had to be encoded.
Currently our genome scale models are developed and maintained within the widely used COBRA toolbox (Schellenberger et al. 2011, Nature Protocols 6: 1290-1307). We tested the upload and simulation of our model in the KBase environment. In our tests the KBase Flux Balance Analysis environment seemed to not be adequate because various required methods, available in the COBRA toolbox, were not present in KBase.

Aim 2: Construction of tissue-specific metabolic models

Four tissue specific models were derived representing leaf, stem, seed and root cells. The models were constrained by cell specific biomass composition as derived from data mined in the literature, including tissue specific lipid profiles. A goal of the project is to use information about whether enzymes in a pathway in a specific cell type are highly expressed or not, in order to make predictions of pathway flux more precise and realistic. In this context, we realized that the flux prediction itself might be too unrealistic. While computationally convenient, the problem with linear programming, the widely used method for prediction of individual flux states, is that the sampling of only one optimal point in the solution space represents a rather arbitrary solution and yields too little information about the entire solution space. Therefore a random sampling procedure of the solution space in our model was needed. However, such approaches do not scale easily with network size. Although algorithms/methods already exist in the COBRA toolbox and in the Sybil toolbox (Gelius-Dietrich et al., BMC Systems Biology, 2013. 7:125), application to our model turned out to be difficult to control and computationally unstable.

Milestones for FY16:

- Due to the size of the glycerolipid network, we will derive an algorithm for the generation of the reaction equations based on automatized generation of the permutations of fatty acid chains that define the metabolite species
- Connect tissue specific models to simulate whole plant growth
- Conduct further work on code adjustments in order to have a reliable and computationally stable sampling of the model solution space
- Test ways to integrate results of differential expression analysis with probability distribution of flux predictions.

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 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 at BNL 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 Advanced Light Source (ALS):

Experiments have been conducted at the ALS at Berkeley examining the interaction of CO, water, CO_2 or hydrogen with metal/oxide catalysts useful for the MS and WGS reactions (Figure 1). These experiments allowed us to establish basic reaction parameters for future experiments of AP-XPS at the CSX-2 beamline of the NSLS-II, which will be carried out starting in March of 2016.

Preliminary AP-STM Experiments in Chemistry Department:

At the Chemistry Department, we are now in the process of correlating these studies with images of ambient-pressure scanning tunneling microscopy (STM) obtained at the Chemistry Department. Since no experiments have ever been reported on the *in situ* study of metal-oxide interfaces by STM, our initial work was carried on CuO_x/Cu(111) and CeO_x/CuO_x/Cu(111) surfaces, which will be used as reference systems because they are precursors for catalysts active for the WGS and the MS reactions. We observed in these STM studies that the surface of CuO_x can be dynamically modified by reduction in either hydrogen or CO, a fact that is relevant for both the WGS and MS reactions.

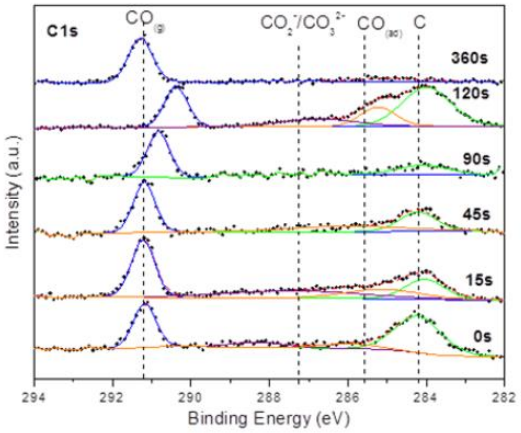


Figure 1. Preliminary AP-XPS experiments obtained at the ALS for the exposure of TiOx/Au(111) to ~ 0.1 Torr of CO.

Moving of instrumentation from NSLS and setting of AP-XPS and AP-XAS at the CSX-2 beamline of the NSLS II:

We have been extremely active in setting up and commissioning the end stations for AP-XPS and AP-XAS at the NSLS-II. The AP-XPS is almost ready for user operations and actual studies for the hydrogenation of CO_2 will start early in March of 2016. In the next two-three months, we expect to finish the assembly and testing of equipment at the AP-XAS end-station, and we will carry out experiments on it during the next six months.

Milestones for future funding:

The main objective for the rest of the funded year is to finish the set-up of the end station for AP-XAS at CSX-2 and then perform systematic mechanistic studies combining AP-XPS and AP-XAS.

Correlative Microscopy, Spectroscopy and Diffraction with a Micro-Reactor

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

PURPOSE: The purpose of this effort 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) as well as X-ray spectroscopy, diffraction and imaging at the National Synchrotron Light Source (NSLS/NSLS-II), and at other synchrotrons during the transition from NSLS to NSLS-II. The measurement of reaction products during the data acquisition allows '*operando'* characterization, i.e., characterization of the catalysts as they are 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. The capabilities being developed 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 Department, as well as the Synchrotron Catalysis Consortium: in short, they are well-aligned with the overall Laboratory strategy.

APPROACH: Supported metal nanoparticles are commonly used in heterogeneous catalysis, and are critically important to myriad industrial processes. They generally possess a large variety of three-dimensional structures, which are known to directly affect their catalytic function. Effects due to features such as cluster size, state of atomic order, bond strain, facet orientation, the support, and bimetallic composition have been shown to affect catalytic activity, selectivity and stability. Importantly – even when considering model catalysts – there may be a coexistence of different particle sizes, shapes, compositions and degrees of crystalline order within the catalyst population. This heterogeneity poses a formidable challenge to commonly used ensemble averaging characterization techniques such as X-ray absorption structure (XAS) spectroscopy, which collapses this structural heterogeneity into a single average measurement. Techniques such as electron microscopy can be used to directly measure the structural heterogeneity in a sample, but can suffer from limited statistics and experimental artifacts associated with beam damage and insufficient resolution. Thus it is increasingly common to utilize a combination of multiple experimental and theoretical methods to more accurately describe the structural complexities that are inherent in these nanoscale systems. Further complications arise when considering the structure of supported nanoparticles subjected to reaction conditions. It has become increasingly apparent that they can exhibit substantial structural changes when they are in a working (*operando*) state and that these structural changes may no longer be apparent when the sample is returned to a non-working state or examined *ex situ*. A variety of characterization techniques have been developed in recent years that allow these structural changes to be inferred or directly observed *in situ* (i.e., when subjected to approximate working conditions through the application of temperature and pressure) or under *operando* conditions. We are confronting this significant challenge by using 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 800°C and pressure in excess of 1 atmosphere, and which can measure reactant streams to confirm that the system is in a working condition - allowing us to make direct comparison between the measurements in an unprecedented fashion.

TECHNICAL PROGRESS AND RESULTS:

During the past year, we completed two studies on ethylene hydrogenation by Pt/SiO2 heterogeneous catalysts. The first was reported in last year's Status Report, and was published this year.[1] In that paper, we demonstrated how correlation of *operando* scanning transmission electron microscopy (STEM) and XAS data allows one to *quantify* the changes in nanoparticle size that occur during reaction. Specifically, we showed how different species (oxidized Pt, single atom clusters, 1-nm sized nanoparticles, and sintered agglomerates) changed throughout the process. It is in marked contrast to what has been the state-of-the-art, where all the changes were attributed to a single type of species, a "representative" nanoparticle. This paper was highlighted by BNL and the DOE Office of Science.[2] In our second journal article this year, multiple electron and photon probes are compatible with this approach, including micro-infrared spectroscopy, Raman spectroscopy, electron energy loss spectroscopy, as well as product measurement with gas-chromatography/mass spectroscopy (Figure 1).[3] By combining these different experimental approaches it becomes possible to probe nearly all of the important processes in catalysis, including the conversion of reactants to products, the nature of surface-bound species on the catalysts, the charge, size, shape and structure of the nanoparticles, characteristics of the support, and the particle/support interaction.

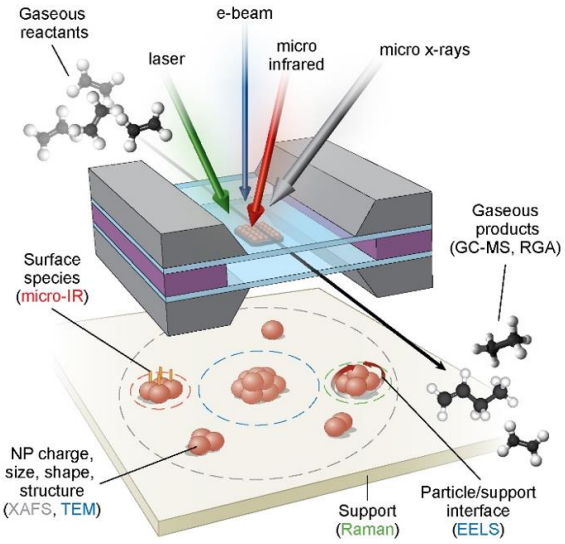


Figure 1. Combining multiple approaches to probe important catalytic processes during reaction.

We expanded this approach towards utilizing the advanced capabilities of NSLS-II. We worked with J. Thieme and his group at the Submicron Resolution X-ray Spectroscopy (SRX) Beamline to obtain micro-focused X-ray absorption spectra (Figure 2) from a NiPt bimetallic catalyst, prepared by J. Chen (BNL/Columbia). We are using this system to explore how bimetallic catalysts undergo reaction-driven structural and compositional changes when exposed to oxidative and reductive environments – a long-standing and important question in the field of heterogeneous catalysis. These studies are complemented by bulk XAS data at the Stanford Synchrotron Radiation Laboratory, and nanoscale compositional studies using energy dispersive X-ray spectroscopy in the *operando* STEM at the CFN. Exploring Ni/CeOx catalysts with the Rodriguez group in Chemistry, utilizing the X-ray Powder Diffraction beamline is also planned.

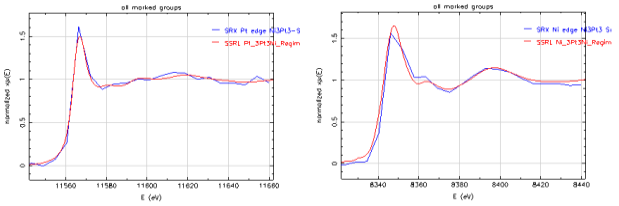


Figure 2. Spectroscopy + imaging of bimetallic catalysts in *operando* conditions Pt L_3 edge (left) and Ni K edge (right) data in $Pt3Ni3/SiO_2$ nanocatalysts (J. Chen's group). Data acquisition time at SRX: 5-10 min (blue). Similar data at X27A (red): 2 hours of averaging!

[1] Y. Li, et al., Nat. Comm., **6**, 7583, 2015.
[2] https://www.bnl.gov/newsroom/news.php?a=24446 and http://1.usa.gov/1dsI8rY
[3] S. Zhao, et al. ChemCatChem, **7**, 3683-3691, 2015.

Imaging Electronic Texture in High-Temperature Superconductors

LDRD Project # 14-037

S. Wilkins

PURPOSE:

The goal is to take advantage of the coherence and energy tunability of the X-rays available at the Coherent Soft X-ray (CSX) beam line at the National Synchrotron Light Source II (NSLS-II) to image various electronic textures found in high-temperature superconductors. A particular target of this research is the charge stripe order found in the copper-oxide system $La_{2-x}Ba_xCuO_4$. The objective is to detect time-dependent fluctuations and, ideally, to image the stripes in real space. Success in this endeavor would establish an important approach for experimentally characterizing the various electronic textures that appear to be common to strongly-correlated electron systems.

APPROACH:

The existence of charge stripe order in $La_{2-x}Ba_xCuO_4$ was originally discovered at Brookhaven by neutron diffraction. Neutrons directly detect atomic displacements, from which the charge modulation must be inferred. The possibility of directly probing the charge modulation through resonant soft X-ray scattering was first demonstrated at NSLS. The development of a scattering chamber for the X-1 beam line at NSLS by the X-ray Scattering Group made possible a detailed study of the charge stripe diffraction using incoherent soft X-rays resonant at the O K edge and the Cu L_3 edge.

One of the initial beam lines at NSLS II is CSX, which incorporates the X-1 scattering chamber. Besides the enhanced beam brightness at CSX, the X-ray beam is also highly coherent. This makes possible techniques such as X-ray Photon Correlation Spectroscopy (XPCS) and Coherent Diffractive Imaging (CDI). In XPCS, one measures the interference pattern that results from scattering by many different regions of the sample. By monitoring this pattern as a function of time, one can test for time-dependent fluctuations. In CDI, one attempts to invert the interference pattern to determine the microscopic pattern of the scattering objects.

This project was initiated when the Principal Investigator (PI) was in the X-ray Scattering Group, then headed by John Hill; Wilkins has since moved to NSLS-II. It has continued as a collaboration involving Mark Dean and John Tranquada (interim leader) of the X-ray Scattering Group working with the PI.

TECHNICAL PROGRESS AND RESULTS:

Postdoctoral research associate Xiaoqian Chen successfully detected the soft X-ray speckle pattern associated with diffraction from the charge-stripe order in a single-crystal of $La_{1.875}Ba_{0.125}CuO_4$ and measured its temperature dependence. Initial measurements were completed in the last fiscal year. Progress this year has been achieved in the analysis of these patterns. Dealing with noise in the detected signal has been a significant challenge. The X-rays are detected with a two-dimensional, position-sensitive charge-coupled device (CCD). To study the time-dependence of the X-ray speckle pattern, one attempts to read the signal from the CCD as quickly as possible; however, the fast read out increases the noise level. Chen has now learned how to analyze the data in a fashion that yields a meaningful interpretation of the signal while taking proper account of the noise. She reached the conclusion that no significant change in the speckle pattern has been observed with time, where the time step is of order 1 sec and the

total measurement time is several hours. Nevertheless, she noted that the contrast in the X-ray speckle pattern is significantly lower than that measured in specular scattering from the sample. The conclusion is that there must be some dynamic fluctuations of the stripes on a faster time scale than 1 sec that causes the reduced contrast. A research paper describing the data and analysis is in preparation.

In upcoming measurements, the plan is to see whether speckle can be observed in scattering that would measure a rotational-symmetry breaking (nematic) character of the electronic texture in $La_{2-x}Ba_xCuO_4$.

Bunch-by-Bunch Beam Position Monitor for eRHIC

LDRD Project # 15-003

M. Minty, P. Thieberger, W. Dawson, D. Gassner, R. Hulsart, K. Hamdi, R. Michnoff

PURPOSE:

The technical objective of this work is to develop a beam position monitor (BPM) capable of resolving closely spaced bunches ("packets" of particles; e.g., protons or ions) as motivated by the BNL-based initiative for a future electron-ion collider, eRHIC. The eRHIC design entails a novel cost-effective approach that transports multiple bunches of different energies in a common vacuum chamber. This LDRD aims to develop a method to accurately measure the beam trajectories to ensure optimal collider performance. Various engineering solutions have been evaluated. If successful, this development will reduce risk and cost in the eRHIC project.

APPROACH:

While conventional approaches to beam positon monitoring may be used for detection of time-isolated "diagnostic bunches" for eRHIC, the properties of these bunches could differ from the closely-spaced bunches destined for collisions. The aim of this LDRD is to develop a BPM capable of resolving the positions of closely spaced bunches.

Initially we considered BPMs with two parallel diamond-shaped striplines, which offered decreased sensitivity to pulse sample time fluctuations. As the eRHIC design was further optimized, it became clear that the BPMs should allow measurement of beam trajectories over a range of transverse displacements much wider than initially anticipated. We then proposed and developed a design, based on a commonly used approach for detection of beam current referred to as a wall-current monitor, which was adapted for application as a BPM and optimized for the envisioned range of eRHIC beam trajectories. Mechanical engineering design work has been supported by K. Hamdi. Electrical engineering support is being provided by C. Dawson.

The BPM pickup consists of narrow gaps in the upper and lower walls of the vacuum chamber through which the beams pass (Figure 1, left). The gaps will be bridged by low-value (~ 2 Ohm) resistors and coupled out using fast pulse transformers (Figure 1, right). Simulations of this design were carried out to determine the signal strength generated by the beam's image currents and to analyze the signal transport through the resistor/transformer network.

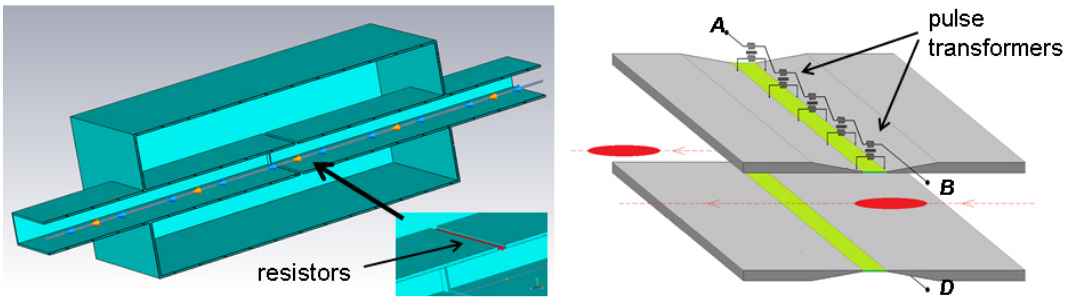


Figure 1. Conceptual view of the BPM showing beam traversing the small gap spanned by resistors (left) which are read out using pulse transformers (right).

TECHNICAL PROGRESS AND RESULTS:

During this first year of the project (one of two years supported by this LDRD):

- A BPM design approach has been selected, that can accommodate possible further changes in the eRHIC accelerator design (specifically, vacuum chamber dimensions)
- Simulations were carried out to refine the design and minimize the beam impedance
- A method for processing the output signals utilizing fast pulse transformers was developed and simulated
- Mechanical engineering aspects (e.g., fabrication methods) were evaluated and optimized
- Engineering drawings were developed, adapted to the geometry of the vacuum chambers of the BNL Accelerator Test Facility (ATF), where beam tests are to take place
- A beam time request was presented at the ATF Users' Meeting (October 2015)
- The ATF Program Advisory Committee advised to " … [move] this project from a feasibility project to an experiment"
- Engineering drawings were submitted to Central Shops for fabrication (December 2015)
- An experimental proposal for beam time at the ATF was submitted (February 2016).

The assembly drawing of the proposed BPM as adapted to the geometry of the ATF is shown in Figure 2. The detector proper consists of the central region with cross-sectional dimensions appropriate for eRHIC (60 mm width by 16 mm height) with 2.1 mm gaps on the top and bottom. This volume is adapted to the circular ATF beamline (35 mm ID) using slotted transition tapers. The total length of the insertion is 15" (381 mm) with 2 ¾" flanges at each end. The detector is composed of copper-coated stainless steel. The signals will be read out through SubMiniature version A (SMA) connectors.

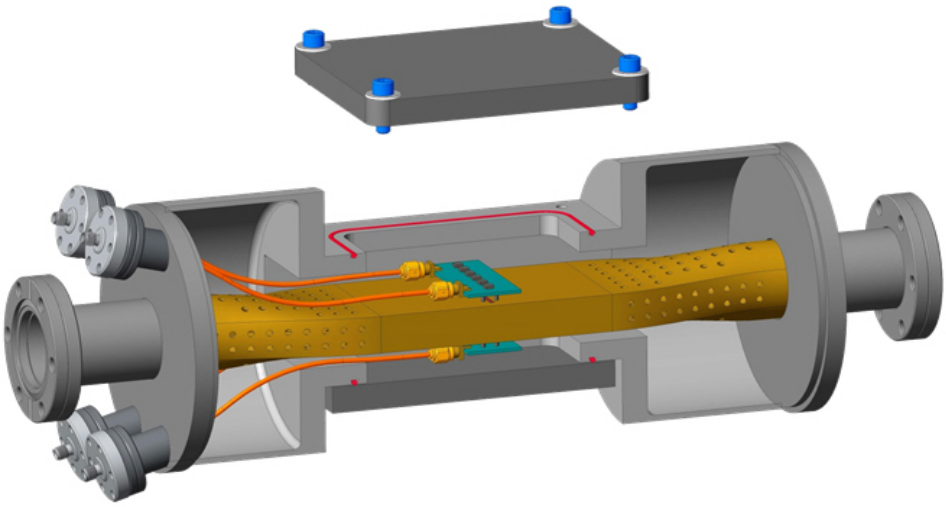


Figure 2. Assembly drawing of the proposed eRHIC time and space resolving BPM as adapted to the geometry of the ATF.

During the second year, the fabrication of this BPM will be completed. The detector performance will be tested at the ATF. Based on the outcome of the beam tests, a second BPM may be fabricated with the goals of improving performance if needed and/or streamlining fabrication procedures for cost optimization. If necessary, a second round of measurements at the ATF will be conducted to compare the results of the two BPMs.

Advanced Coherent Electron Cooling

LDRD Project # 15-005

V. Litvinenko

PURPOSE:

This LDRD project focuses on theoretical and experimental studies of Advanced Coherent electron Cooling (ACeC or Micro-Bunching e-Cooling), an approach that promises to be superior to any of the current cooling or proposed schemes. Specifically, its cooling rate readily will allow for cooling intense proton beams in the Relativistic Heavy Ion Collider (RHIC)/eRHIC within a few seconds.

Our goals include in-depth theoretical studies of the proposed phenomena, including assessing the sensitivities of the processes to realistic beam parameters and to various errors therein. We are preparing to verify experimentally the key component of the process: enhanced micro-bunching, i.e., the amplification of the system's response to external density perturbations.

APPROACH:

This technique undergoes the same detailed theoretical and computational scrutiny, as did the classical CeC scheme. We use the well-developed and tested VORPAL code (from Tech X Inc.) to simulate the electrostatic interaction between the ions and electron beam in the modulator. We are pursuing the use of the SPACE code to evaluate self-consistently the evolution of induced modulation in the buncher (chicane). Currently we simulate the interaction in the modulator to benchmark the SPACE code. The relativistic nature of the motion of particles inside the buncher was the main drawback that precluded our using the regular Poisson solver algorithms for evaluating the space-charge dynamics in beams. Hence, a traditional Poisson solver used in many codes to resolve electrostatic fields for nonrelativistic particle motion could not be applied.

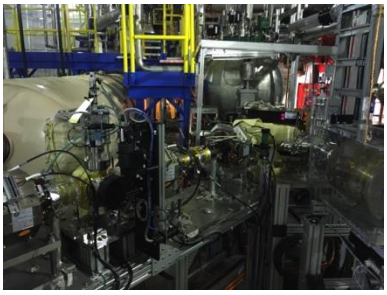
TECHNICAL PROGRESS AND RESULTS:

In addition to progress with the theoretical studies and simulations, which were published in three conference papers this year, we are designing, procuring and commissioning hardware for the ACeC experiment. Fig. 1 shows part of the beam diagnostics, which was purchased using the LDRD funds and is currently installed into the CeC proof-of-principle system at RHIC. We will be ready to use them for the ACeC experiment after the CeC accelerator is commissioned during RHIC Run16.

We determined parameters of the chicane system needed for the ACeC experiments and are in the process of designing and procuring it. It will be installed in the place of the fourth quadrupole magnet in the CeC modulator section (see Fig. 1 (d)) after the CeC proof-of-principle experiments are completed in FY17.

(a)

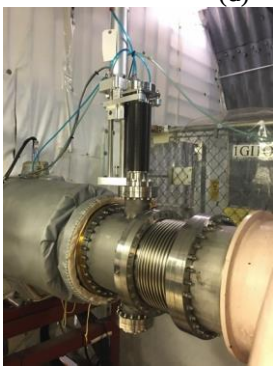
(b)



(c)

(d)

(e)



(f)

Figure 1. (a) The CeC proof-of-principle system installed into RHIC 2 o'clock Interaction Point ; (b) system for transporting and monitoring CsK_2Sb photocathode pucks; (c) Diagnostic system for measuring the energy spread of the electron beam for ACeC experiment; (d) Diagnostic station at the entrance of the wiggler system – the last quadrupole (black) will be replaced by a chicane for our experiments; (e) end of the beam-line diagnostic section; (f) Infrared optical system for diagnosing spontaneous radiation from ACeC electron beam – the diagnostic bread-board will be installed this Spring.

Milestones for FY16:

- Commissioning beam and IR optical diagnostics
- Procuring and magnetically measuring the chicane for the ACeC experiment
- Purchasing power supply for the chicane.

Design, Fabrication and Test of SRF Cavity Prototype for eRHIC ERL

LDRD Project # 15-006
W. Xu

PURPOSE:

The objective of this LDRD project is to design, prototype and test a high current superconducting RF (SRF) cavity for the eRHIC main linac, which requires 80 such cavities to provide 1.67 GeV energy gain for electron beams. eRHIC requires the cavity to operate at 18 MV/m with the cavity's quality factor of $2 \cdot x\ 10^{10}$. As the SRF linac is a major part of the eRHIC project, it is imperative that the technology and procedures for making such cavities be reliable and cost effective while not compromising the cavities' performance. This project will resolve all the potential issues for making eRHIC cavities and validate the Fixed-Field Alternating Gradient-based eRHIC design. A performance study and improvement of the niobium prototype cavity will be carried out with cavity processing and vertical tests. With these tests, the specifications for future eRHIC cavities' processing and test procedures will be developed.

APPROACH:

The cavity design involves the physics design, mechanical analysis and design, and multiphysics simulations. The cavity design includes optimization for both the cavity's good fundamental performance and good Higher Order Mode (HOM) damping capability. As the average HOM power is linear with the loss factor, the loss factor is also an important optimization factor during the cavity design. The mechanical design has to be carried out in various situations: vertical tests, cryomodule tests and tuning range, and so on. Multiphysics simulations are to analyze multipacting and the Lorentz detuning factor calculation.

After the cavity is designed, the cavity will be fabricated by industry. We will work/monitor closely every fabrication step from design of the dies to deep drawing or hydroforming, machining, chemistry and electron-beam welding and tuning. There will be a review of the cavity's conceptual design within one month after the contract is awarded.

Following the cavity's fabrication and room temperature measurement, it will be taken through the most advanced treatments of chemical polishing, vacuum furnace firing and high-pressure rinsing that are applied to SRF cavities. Then, vertical tests to study the performance of the cavity, including measurements of its quality factor as a function of the accelerating field, the residual resistance, helium bath pressure sensitivity and Lorentz detuning, will be performed.

TECHNICAL PROGRESS AND RESULTS:

In the past fiscal year, a 650 MHz 5-cell eRHIC cavity has been designed, including cavity geometry optimization, analysis of the HOM spectrum, analysis of multipacting in the cavity, and optimization of the Lorentz detuning factor. Also, the engineering design has been completed, which includes mechanical analysis of the cavity tuning plate design. This allows a helium vessel and cryomodule to be added onto this cavity for the eRHIC cryomodule test. The cryomodule-ready cavity has been sent out for bid and we expect to sign the contract for it in a few weeks. Figure 1 shows the completed 5-cell cavity design; its fundamental mode performance is listed in Table I. The cavity's HOM loss factor was optimized to be 2.55 V/pC for rms 3mm.

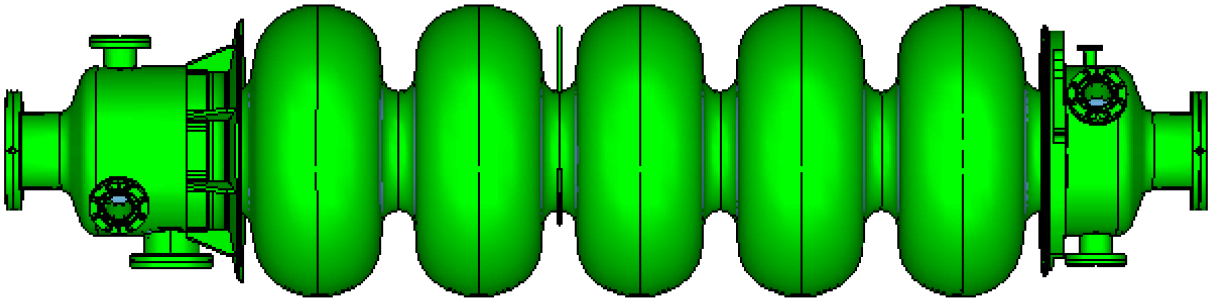


Figure 1. 5-cell 650 MHz eRHIC cavity.

Table I: RF parameters of the BNL5.

Parameters	**650 MHz 5-cell cavity**
Frequency [MHz]	650
Number of cells	5
Geometry factor [Ω]	273
(R/Q)/Cavity [Ω]	502
Epeak/Eacc	2.27
Bpeak/Eacc [mT/MV/m]	4.42
Coupling factor [%]	2.8
Cavity length [m]	1.72

As the cavity is going to be fabricated by a vendor, the main task for this year is to work closely with the vendor to make sure the cavity fabrication is progressing well. Exceptions to this are the RF couplers (input and pick up) and fixtures/tooling for the vertical tests that will be designed and fabricated. A 500 W CW 650 MHz RF amplifier, low-level radio frequency system will be purchased and built for vertical tests this fiscal year.

Nanoconfined Polymer Electrolytes for Rechargeable Lithium-Metal Batteries

LDRD Project # 15-009
C. Black

PURPOSE:
Although lithium (Li) metal has a storage capacity ten times higher than commercial battery anode materials, it is unusable for *rechargeable* batteries because growth of dendrites short-circuits the device after a small number of charge/discharge cycles. Solid polymer electrolytes with sufficient mechanical strength to suppress Li dendrite formation have not yet been realized. We are exploring a new battery design that confines polymer electrolytes within nanoscale structural templates, which we believe will frustrate crystallization and provide high ionic conductivity with sufficient rigidity to suppress dendrite formation/growth. "First light" at National Synchrotron Light Source II (NSLS-II) is essential for the project's success.

APPROACH:
Li-ion batteries are currently the best vehicle for supplying mobile electrical power, storing electrochemical energy by reversibly shuttling Li ions between anode and cathode through an ion-conducting electrolyte. A long-proposed, but never-realized solution uses a solid polymer electrolyte with sufficient mechanical strength to suppress Li dendrite formation during battery cycling. Li metal batteries with polymer electrolytes such as polyethylene oxide (PEO) have shown promise. However, the crystallinity of PEO hinders Li ion conduction, requiring operation at high temperature in order to melt the PEO.

We have undertaken an ambitious project to understand the role of nanoconfinement on the structural, electrical, and mechanical properties of polymer battery electrolytes, with the goal of realizing a new, rechargeable Li-metal battery architecture with high-cyclability, -capacity, and -power delivery density. The project will explore all aspects by leveraging BNL facilities (NSLS-II and the Center for Functional Nanomaterials) and world-leading expertise in: nanofabrication/electrical characterization of solid-state electronic devices (Black); electrochemical properties of battery materials. (E. Takeuchi, K. Takeuchi, Marschilok); and sophisticated synchrotron X-ray methods for understanding both structural (Yager, Ocko) and mechanical properties (Fluerasu, Wiegart) of soft materials.

The project relies on unique BNL facilities and experimental techniques, foremost of which are X-ray scattering capabilities at the Coherent Hard X-ray (CHX) beamline at NSLS-II. We will measure the crystallinity and orientation of polymer electrolytes in different degrees of nanoconfinement and at different temperatures, Li-ion concentrations, and polymer electrolyte molecular weights using Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS). Simultaneously, we will measure the polymer viscoelastic moduli through X-ray Photon Correlation Spectroscopy (XPCS) by incorporating nanoparticle tracers into the material. We will fabricate confining templates at the CFN using state-of-the-art lithography and etching methods. In later project stages, we will design and fabricate functioning, nanoconfined batteries suitable for *operando* structural and dynamics measurements. Our ultimate experiments will measure Li dendrite structure using grazing-transmission Small-angle X-ray scattering (SAXS)/ Wide-Angle X-ray Scattering (WAXS) and dendrite growth kinetics using simultaneous XPCS; correlating formation of these deleterious structures to battery performance, and polymer electrolyte mechanical and structural properties.

TECHNICAL PROGRESS AND RESULTS:

We began this project in FY2015 by recruiting and hiring postdoctoral researcher Dr. Zheng Zhang. Dr. Zhang's expertise in polymer science is crucial for understanding the PEO properties. The early months were devoted to developing experimental protocols for polymer electrolyte thin film processing and nanofabrication of silicon templates for confining the polymer within nanostructured grooves with ~100 nm widths (Figs. 1a, c) and cylindrical pores with ~100 nm diameters (Figs. 1b, d). We have carried out initial GIWAXS measurements of PEO both in thin films (Fig. 2a) and confined within nanoscale volumes (Fig. 2b) using the CFN's lab-based X-ray source. These measurements suggest that confining PEO greatly suppresses its crystallinity compared to thin films – a promising result we will pursue with detailed measurements at NSLS-II in 2016. In parallel we have begun carrying out electrochemical measurements of PEO thin film devices doped with Li salts (Fig. 3), using the dry-room in the Interdisciplinary Sciences Building for sample preparation. We have been carrying out these measurements using the CFN's Electrical Characterization facility, and working with Stony Brook University graduate student Rachel Demayo for data analysis and modeling.

In FY2016, we expect to complete these project milestones:

- Carry out X-ray scattering measurements of polymer electrolyte crystallinity (WAXS) and viscoelastic modulus (XPCS) in different degrees of nanoconfinement at the CHX beamline at NSLS-II. Analyze/understand results and prepare manuscript.
- Develop nanofabrication scheme for devices to measure nanoconfined electrolyte conductivity. Perform conductivity measurements, understand results, and correlate to structure.
- Acquire and install a metal evaporator for deposition of Li thin films.

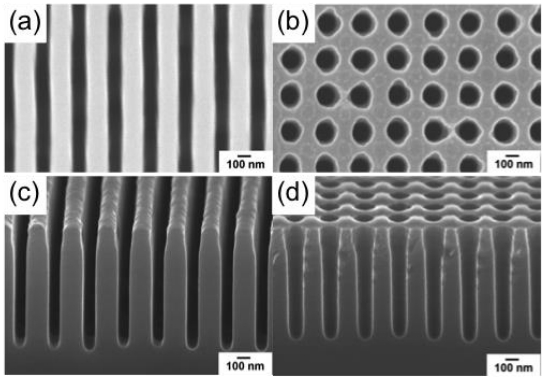


Figure 1. Topdown (a, b) and cross-sectional (c, d) Scanning Electron Microscope images of silicon templates with grating (a, c) and pore (b, d) geometries.

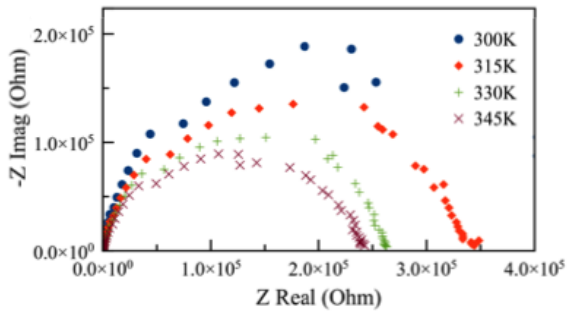


Figure 3. Electrical impedance spectra for PEO thin film devices at different temperatures.

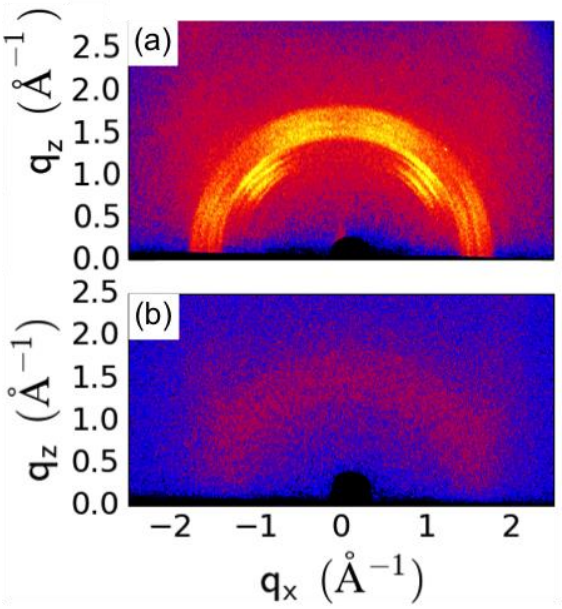


Figure 2. GIWAXS spectra of (a) highly crystalline PEO film, and (b) PEO film confined within nanoscale pores.

Hydrocarbon Chemistry on Zeolite Model Systems: Towards a Detailed Understanding of Energy-Relevant Chemical Transformations Using In-situ Techniques at NSLS-II, CFN and Chemistry Department

LDRD Project # 15-010
J. Boscoboinik

PURPOSE:

The purpose of this work is to elucidate fundamental aspects of energy-related hydrocarbon transformations using zeolite model systems taking advantage of advanced surface science tools available at BNL (National Synchrotron Light Source II (NSLS-II), Center for Functional Nanomaterials (CFN) and Chemistry Dept.) and tools to be developed as part of this project. While zeolites themselves are the most used catalysts in industry, in processes such as the cracking of crude oil and methanol to gasoline conversion, the mechanisms by which these processes occur are still far from well-understood. Detailed knowledge on other catalysts has been obtained using surface science methods, and we will use a related strategy to study zeolite chemistry, using a 2D-zeolite model system recently developed by the Principal Investigator (PI). Given the complexity of hydrocarbon chemistry in zeolites, it is necessary to take full advantage of the *in situ* methods available at BNL to develop new experimental capabilities.

APPROACH:

Zeolites are the most important industrial catalysts. They are used for a number of energy related chemical transformations, including cracking of hydrocarbons and conversion of methanol to hydrocarbons. The active site for these processes is an extremely acidic bridging hydroxyl group within the crystalline porous framework of the zeolite. Despite extensive research carried out around the globe, we are still far from understanding the mechanistic aspects of these processes. On the other hand, the surface science community has successfully used simplified versions of industrial catalysts to provide insights on structure–reactivity relationships. By using so called "model" catalysts, the complexity of the catalyst can be reduced in order to disentangle structural, chemical and electronic effects in the reactions and elucidate reaction mechanisms. In particular, zeolites have remained a challenge to the surface science community due to the lack of a suitable zeolite model system. It was only recently that the PI developed the first successful zeolite model system (Figure 1). In parallel, the PI is participating in developing surface science instrumentation for studies at elevated pressures, closer to realistic conditions. Instrumentation at the CFN and NSLS-II that the PI is in charge of includes ambient pressure photoelectron spectroscopy (AP-PES), polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) and reactor scanning tunneling microscopy (r-STM). The combination of having a surface science model system for zeolites and state-of-the-art instrumentation to study these processes at realistic conditions puts BNL at the forefront in research that will allow the elucidation of reaction mechanisms for some of the most important energy-related industrial chemical processes.

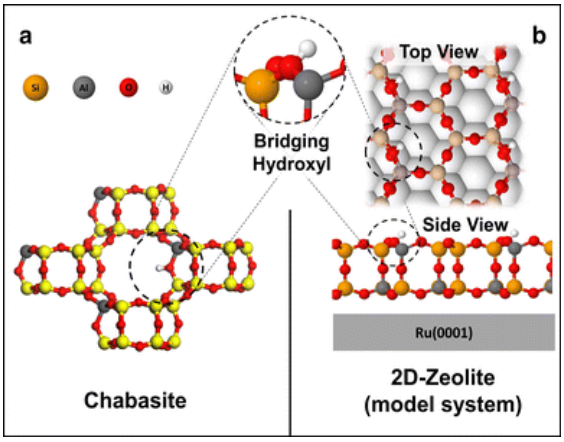


Figure 1. **a**. Zeolite chabasite in its protonated form. **b.** Protonated form of the 2-dimensional zeolite model system showing the bridging hydroxyl group. The top and side views of the structure of the model system are shown.

The AP-PES endstation and the CFN PM-IRRAS system count with mass spectrometers fed by capillary tubes adjacent to the sample surface to follow the conversion from reactants to products in the vicinity of the catalysts surface. Some experiments will be also carried out with the IRRAS instrument in the Chemistry Department in collaboration with Dario Stacchiola. The reaction pathways that are hypothesized based on this data will be studied using Density Functional Theory (DFT), in collaboration with Deyu Lu at the CFN.

TECHNICAL PROGRESS AND RESULTS:

This LDRD started in the second half FY15 with the hiring of postdoctoral researcher JianQiang Zhong to carry out the experimental work. In June, Stony Brook University student Mengen Wang joined the project to carry out DFT calculations to complement the experimental work. Dr. Zhong prepared zeolite model system samples at the r-STM at the CFN. These samples were transferred to the AP-PES endstation at the Coherent Soft X-ray Scattering and Spectroscopy (CSX-2) beamline of NSLS-II where they were used for technical commissioning of the endstation and beamline. These tests with LDRD-related samples were the first experiments carried out at the beamline and a manuscript based on this is ready to be submitted. Dr. Zhong won the best poster award at the BNL Young Researcher Symposium for this work. This is a groundwork study where the zeolite model systems (2D silicates and aluminosilicates), prepared on a Ru(0001) support are exposed to O_2 and H_2 molecules at elevated pressures and temperatures. Mengen Wang carried out DFT calculations to understand core level shifts observed in framework elements of the zeolite model. This work is important as the basis for future mechanistic studies since the catalytic activity is expected to be affected by the electronic structure of the system. Additional work was carried out using AP-PES on trapping small inert molecules in the pores of the zeolite model. DFT calculations related to these experiments are underway and another manuscript will be prepared based on this shortly. Understanding the relation between pore and molecule size for weakly interacting molecules is fundamental work that needed to be done to later be able to understand size-related effects when studying reactivity of industrially relevant molecules. Carrying out these test experiments at the AP-PES endstation helped in the commissioning activities to setup and test the endstation and its performance and that of the beamline, which started user operations in FY16.

In order to prepare for later implementation of the PM-IRRAS at the AP-PES endstation, a PM-IRRAS system was built at the CFN by a postdoc (John Kestell) supervised by the PI.

Milestones

Date	Objectives
FY15 (Half)	Started experiments at AP-PES at CSX-2, PM-IRRAS and STM at CFN and Chemistry: Groundwork for interaction of small molecules with zeolite model and support. Started complementary DFT work.
FY16	Publish first results. Start experiments with hydrocarbons: cracking experiments. Design PM-IRRAS implementation at AP-PES endstation.
FY17	Purchase parts for PM-IRRAS implementation at AP-PES endstation and construct. Develop hypothesis on cracking mechanism and coking. DFT calculations to back this.
FY18 (Half)	Analyze and publish results. Obtain further funding to continue after LDRD. Start C-C bond formation experiments using alcohols at the combined AP-PES/PM-IRRAS system. Carry out calculations to support these experiments. Summarize results of LDRD and plan future directions.

Revealing the Structure and Dynamics of Discrete Meso-Architectures

LDRD Project # 15-011

O. Gang, K. Yager, K. Kaznatcheev, A. Fluerasu, L. Wiegart, D. Yu

PURPOSE:

The major objective of our studies is to develop methods for assembly of non-periodic mesoscale structures and to develop coherent scattering and photon-correlation methods as new tools for probing finite-size mesoscale objects. A key component of this LDRD is the development of experimental and data analysis methods for resolving the structures of meso-assemblies using *in situ* X-ray methods

APPROACH:

Assembly: We are developing an approach for assembly of complex mesoclusters using nanoparticles (NPs) embedded in DNA frames to direct their interactions in a programmable manner. Our approach will permit formation of 2D NP clusters of arbitrary shapes.

Scattering methods: We will exploit correlation analysis of Coherent Scattering (CS). A rapid succession of coherent X-ray scattering images, obtained for a construct tumbling in solution, encodes meso-scale order. The correlations (e.g., angular) in a CS image can be accumulated to uncover local order (e.g., coordination number).

TECHNICAL PROGRESS AND RESULTS:

In our approach, DNA origami frames are used to anchor and organize gold NPs into planar architectures (Figure 1). We are developing methods for creating a matrix for positioning particles in a designed manner for the formation of targeted 2D clusters. Moreover, these NP planar patterns can be reconfigured, so the clusters can be altered on demand.

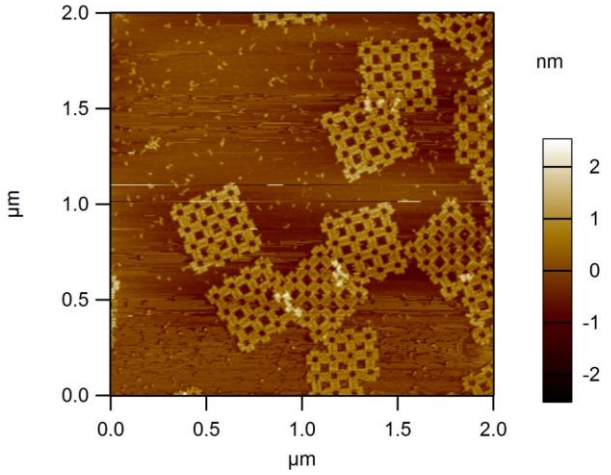


Figure 1. Self-assembled DNA scaffolds for the precise positioning of nanoparticles into designed meso-clusters.

We have studied, through analytic methods and numerical simulations, the intrinsic and pragmatic limitations of "correlation methods", from which local symmetry can be determined. These results have guided our ongoing synchrotron experiments (at the Coherent Hard X-ray

Scattering beamline at the National Synchrotron Light Source II), where we have validated our results, and identified the primary bottlenecks to resolving the structure of individual meso-objects.

Future work will involve synchrotron experiments tailored to these conditions, to provide a proof-of-principle for the measurement of individual meso-objects.

Milestones
FY 16

- Conduct the initial feasibility experiments using lithographically fabricated samples in order to verify the range of parameters for the design of self-assembly systems
- Develop the analysis scattering formalism for probing finite-size planar clusters
- Explore methods for enhancing the signal using interference effects
- Establish an assembly approach for creating designed NP clusters
- Establish an experimental platform for full scale studies, including scattering measurements, sample preparation and scattering analysis.

FY 17

- Optimize assembly methods for creating structures which are directly relevant for scattering experiments
- Achieve high yield and high fidelity of the designed assembled structures
- Demonstrate single cluster sensitivity in scattering experiments
- Develop the methodology for reconstruction of planar cluster architecture from scattering experiments
- Demonstrate assembly of reconfigurable NP clusters and conduct the first experiments for revealing structural changes in liquid conditions.

A New Frontier for Improving Processes for Regional and Global Climate Modeling

LDRD Project # 15-020
W. Lin, S. Endo, Y. Liu, A. Vogelmann, M. Jensen

PURPOSE:

This project aims to develop a novel modeling system to advance regional and global climate simulations, particularly climate change projections of extreme weather events. Deficiencies in physical process representation are long known to be responsible for uncertainty in climate change projection, more so for the projection of extreme precipitation. The new development has the potential to provide a platform to study and improve process representation in climate models and a modeling framework for regional climate simulations. The unique combined capability aligns well with the Environmental and Climate Sciences Department's long term strategic vision to be a leader in regional and local climate modeling for the Northeastern U.S. This project also addresses the DOE Climate and Environmental Sciences Division strategic goals to "develop, test, and simulate process-level understanding of atmospheric systems" and to "develop core capability to target the research on key earth system processes that represent significant uncertainty and currently limit the predictive understanding of climate."

APPROACH:

The fidelity of climate projections depends on the representations of a wide range of cloud and turbulence processes. These processes operate at scales that are smaller than climate models and can explicitly resolve and, thus, have to rely on overly simplified representations, or so-called physical parameterizations to realize their collective influences in the climate system. Deficiencies in such parameterizations are known to be responsible for large uncertainties in climate projections that heavily rely on global climate models.

Even more challenging is the simulation of extreme weather events under climate change scenarios. This is because key physical processes such as clouds, turbulence and convection not only influence the mean state and variability of the large-scale atmospheric environment that spawn the extremes, but also dictate the extent of individual weather extremes when they occur. One example is how the intensity of extreme precipitation scales with global warming due to anthropogenic greenhouse gas emissions. The percentage increase in extreme precipitation intensity per degree of warming differs by several fold among climate model projections, which is largely due to diversified but inadequate representations of clouds and convection.

Extreme precipitation can have disruptive consequences on society. Accurately modeling extreme precipitation is becoming more urgent as studies have indicated that extreme precipitation will likely be more common and more extreme in a warmer climate. In the U.S., a nationwide uptick in the frequency and intensity of extreme precipitation events has been observed in the past century. Among all states, the economy in New York State has been found to be most vulnerable to the negative impact of weather variability.

This project is motivated by these challenges to develop an integrated capability to deconstruct the parameterizations of entangled atmospheric physical processes with an aim to improve their representations in climate models, while providing a venue to more accurately simulate weather extremes at local and regional scales in the context of global climate projections. This is achievable with the system being developed by integrating the regional Weather Research and Forecasting (WRF) model into the framework of the Community Earth System Model (CESM) to enable the inline coupling of a high-resolution process model (WRF) with a global climate

model CAM (Community Atmosphere Model, which is the atmospheric model component of the CESM).

TECHNICAL PROGRESS AND RESULTS:

Progress was made on developing the building blocks for integration of the WRF and CAM models, and companion development of utilities to facilitate the modeling and validation of extreme weather events.

A diagnostic study of simulations from the global model CAM and the cloud-resolving WRF was performed (Fig. 1) to establish physical connections between the parameterized representations and the explicitly resolved same underlying processes. It shows characteristics of cloud and convection associated with tropical precipitation and the underlying physical processes the CAM model struggles to represent. The study serves as the stepping stone for the coupled WRF-CAM system that is being developed.

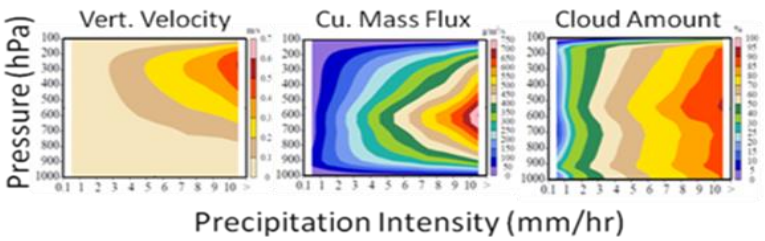


Figure 1. Vertical velocity, cumulus mass flux and cloud amount from WRF simulation as a function precipitation intensity. Companion CAM simulation has weaker vertical velocity and weaker cumulus activities peaked at much higher altitudes, suggesting weaker entertainment and lack of anvil representation.

A new moisture treatment in the dynamical core of the WRF model was introduced to improve modeling capability at large-eddy resolving scale, which is critical for the integrated WRF-CAM to be effective.

The one-way coupled WRF-CAM system was updated to incorporate recent community developments for the CAM; a new entrainment-mixing parameterization was implemented for improved representation of cloud microphysics in the process model. Both are being testing.

A generalized extreme value modeling framework is being established based on R-statistics packages. It is being applied to climate model simulations to analyze the projection of extreme precipitation over the Northeastern U.S. under climate change scenarios. This serves to identify the uncertainties in the current climate model projection and develop cases for using a high-resolution model to investigate the role of process representation in modeling the extremes and pathway for improvement.

To enhance our extreme modeling capability, a multi-scale data assimilation system is being ported to improve the initialization of convection-permitting process modeling with strict observational constraints.

Milestones for FY2016:

- Complete the creation of a generalized extreme value modeling framework based on R-statistics
- Complete the testing of one-way integrated WRF-CAM for the projection of extreme precipitation over the Northeastern U. S. using metrics based on generalized extreme value modeling
- Establish a convective-scale data assimilation system to facilitate extreme precipitation modeling
- Deliver a conceptual two-way integrated WRF-CAM modeling system.

Milestones for FY2017:

- Complete the design of a coupling strategy for two-way integration of WRF and CAM
- Deliver an enhanced and scientifically validated two-way integrated WRF-CAM system
- Investigate the role of cloud/convection process representation in modeling extreme precipitation.

Growth of Self-Activated Scintillators for Dual Gamma- and Neutron-Detection

LDRD Project # 15-025

U. Roy, G. Camarda

PURPOSE:

The main goal of the project is to establish BNL as a major R&D contributor in the field of scintillators for national security applications. There is an urgent need for large-volume, inexpensive, uniform scintillators for detecting and imaging gamma-rays and neutrons for several nonproliferation applications, such as emergency response, counter-terrorism, treaty verification, and nuclear safeguards, and for medical imaging. Our objective is to develop self-activated scintillating compounds for simultaneously detecting gamma-rays and neutrons, which will resolve the problems of doped scintillators, such as Ce-doped Cs_2LiYCl_6 (CLYC). The results and outcomes of the project are expected to lead to substantial new funding from agencies, such as the National Nuclear Security Administration, the Department of Homeland Security, and the Defense Threat Reduction Agency.

APPROACH:

Cs_2LiYCl_6:Ce (CLYC) perhaps is the most efficient scintillator for a dual gamma- and neutron-detector. Doped scintillators undergo significant degradation with an increase in the detector's volume due to the segregation of the dopant (i.e., the activator) along the growth direction, thus lowering the yield of large detectors and increasing their cost. In contrast, self-activated compounds will ensure the homogeneity of the material throughout the grown ingot, and thus, assure a uniform response from the detector, independent of its volume.

We are developing $Cs_2LiCeCl_6$- and $Cs_2LiCeBr_6$-scintillators for the dual detection of gamma-rays and neutrons, which are self-activated (Ce in this case). $Cs_2LiCeCl_6$ has a cubic structure, and crystals were grown by the vertical Bridgman growth technique. The crystals were characterized for different properties associated with scintillators. Emission- and excitation-spectra were studied, and the decay time was estimated for light output, using near-ultraviolet (UV) excitation and 662-keV gammas. The crystals were evaluated for their detection of gamma rays and neutrons. Collaborators are Y. Cui, G. Yang, A. Hossain, and R. James.

TECHNICAL PROGRESS AND RESULTS:

$Cs_2LiCeCl_6$ was synthesized in a sealed quartz ampule via the reaction, $2CsCl+CeCl_3+LiCl = Cs_2LiCeCl_6$ and left to grow in this same ampoule. Growth was accomplished by the vertical Bridgman growth technique in a three-zone vertical furnace. Figure 1a shows the resulting 12-mm-diameter ingot. The material may react with the quartz tube, and hence, has a severe sticking concern. Fig. 1b shows the luminescence from the ingot excited with UV light. The luminescence is fairly uniform over the whole ingot, indicating the homogeneity of the compound over its entire length. To avoid sticking, the crystals were grown with a semi-transparent carbon coated quartz ampoule (Fig.1c). The ingot grown from such an ampoule did not show any sticking problems and slid easily out of it. Fig. 1d shows the grown ingot. The lower part of it is opaque, which might be due to our lack of knowledge on the compound's melting point. We plan to determine the melting point by differential scanning calorimetric measurements and will grow the next ingot accordingly.

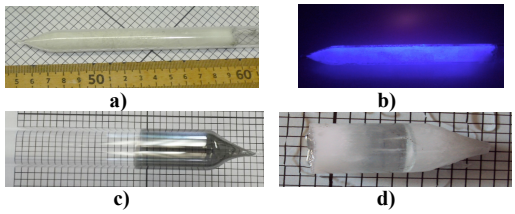


Figure 1. a) As-grown ingot (12-mm diameter), b) UV-light excited ingot, c) semi-transparent carbon coated ampoule, and, d) as-grown ingot (22-mm diameter).

Figure 2 shows the emission- and excitation-spectra for the sample taken from the first ingot. The double peak observed at ~384 and 402 nm is typical for the Ce^{3+} state. The emission spectrum for both ingots matches exactly; this is the signature of the formation of a homogeneous compound. The optical decay time estimated for the sample was ~55 nsec, measured at the Center for Functional Nanomaterials. The decay time for 662-keV excitation comprises three components that were estimated to be ~ 140 nsec (82% decay), 617 nsec (15% decay), and 4.8 nsec for 2.8% decay, all are faster than that of CLYC. The gamma response for the scintillator was evaluated. Figure 3 shows the response for a ^{137}Cs source; the energy resolution is 6.1% at 662 keV, and the corresponding value for the 1st ingot was ~7%. Further improvement is expected by purifying the material by zone refining. The light output estimated by comparing to Bismuth Germanate was ~20,000 ph/MeV. The response to neutrons was evaluated by measuring the pulse-height spectra using an Am-Be

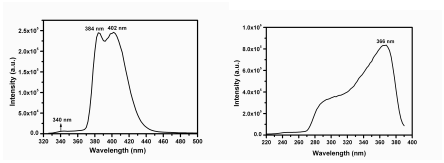


Figure 2. Left: Emission and Right: excitation spectrum.

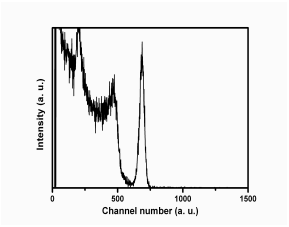


Figure 3. Pulse height spectra of $Cs_2LiCeCl_6$ crystal ^{137}Cs source.

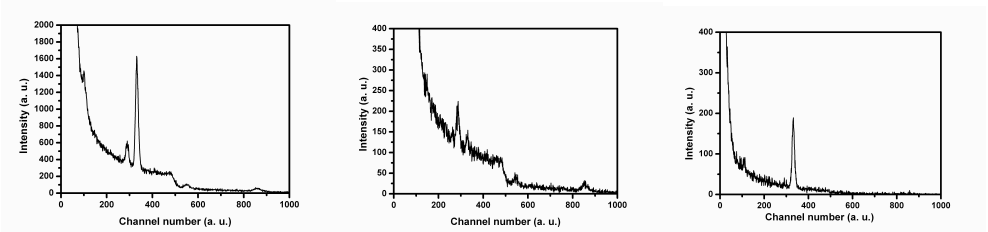


Figure 4. Pulse-height spectra for an Am-Be source; a) open source, b) window blocked with cadmium sheet and c) the window blocked with a 2-inch-thick lead shield.

source. Figure 4 show the neutron pulse height spectra for the $Cs_2LiCeCl_6$ sample. Since the neutron source also generates gamma lines, to confirm the neutron findings, experiments were performed with the neutron source open, and after shielding with cadmium and lead. Fig. 4a shows the spectrum with the neutron source window open. The sharp peak at channel #319 is likely associated with the neutron signal. To confirm this, the window was blocked with cadmium, which attenuates thermal neutrons, and, as shown in Fig. 4b, the neutron peak at channel #329 diminished drastically, while a two-inch lead window blocked most of the gamma lines, but allowed neutrons to be transmitted. Fig. 4c shows the appearance of the peak at channel #329, confirming our detection of neutrons. Calibrating the peak with 662-keV gamma-rays, the gamma-equivalent peak position of the neutron line was estimated to be at 1.48 MeV with a resolution of ~4%.

Summary: We successfully grew self-activated $Cs_2LiCeCl_6$ for dual gamma-ray and neutron detection.

Milestones FY16:

- Grow $Cs_2LiCeCl_6$ and $Cs_2LiCeBr_6$ crystals with enriched ^6Li to enhance the neutron signal
- Purify the compound by zone refining and subsequently grow crystals with improved energy resolution. Characterize the grown materials and fabricated detectors.

Milestones FY17:

- Grow and characterize larger diameter $Cs_2LiCeCl_6$ and $Cs_2LiCeBr_6$ ingots
- Synthesize and grow novel scintillators with good detector performance.

Inelastic X-ray Scattering Determination of the Inter- and Intra-Particle Dynamics of Nanoparticle Superlattices: Key to the Development of THz Phononic Crystals

LDRD Project # 15-031
A. Cunsolo, Y. Cai, S. Bhatia, O. Gang

PURPOSE:
The project aims to study phonon propagation in programmable assemblies of nanoparticles. It addresses the BNL strategic vision on complex nanostructured materials from both an applied and fundamental point of view. The main purposes are: 1) exploration of a new science frontier - characterization of the inter- and intra-particle high frequency elastic (acoustic) properties of nanoparticle superlattice assemblies synthesized at the Center for Functional Nanomaterials (CFN); 2) development of terahertz (THz) phononic structures; 3) conducting high-impact first experiments using the unique capabilities of the National Synchrotron Light Source II (NSLS-II) Inelastic X-ray Scattering (IXS) beamline.

APPROACH:
The goal of THz acoustic manipulation is aggressively pursued through the synthesis of nanoparticles of various shapes, sizes and materials, arranged in nanometer-spaced superlattices and linked by ligands with tunable strength. The aim is to form new structures functioning as THz phononic crystals, i.e., enabling manipulation/programming of phonon transport and, consequently, of heat management based upon structure engineering. The use of the new high-resolution/high-contrast IXS spectrometer at NSLS-II is combined with the most advanced nanostructure engineering developed at the CFN at BNL.

TECHNICAL PROGRESS AND RESULTS:
Dmitry Bolmatov, the postdoctoral research associate who was hired for this project, performed several computer calculations on model systems simulating phonon propagation in different nanoparticle suspensions. The results clearly indicated that high frequency acoustic modes in these systems become non-propagating at short distances, which likely hinders the transport of high frequency heat flow. A publication focused on this computational work is currently in preparation. Furthermore, a beamtime proposal for measurements of nanoparticles of different shapes in suspension was approved for beamtime at the IXS and Coherent Hard X-ray Scattering (CHX) beamlines of NSLS-II.

The general aim of the experiment was to characterize the whole dynamic transition from the ballistic to the Brownian motion in nanoparticle suspensions characterized by different nanoparticle size, shape and concentrations. In the period from February 3 – 5, 2016, a first run of X-ray Photon Correlation Spectroscopy (XPCS) measurements was successfully performed at the CHX beamline using the first slot of allocated beamtime. The results of such measurements are currently being analyzed. Furthermore, a first cycle of IXS measurements is scheduled at the IXS beamline of NSLS-II (starting from March 5). The optimal sample characteristics have been identified and the samples will soon be produced at the CFN.

In the near future, we plan to jointly analyze both the CHX and IXS measurements and publish the results in prestigious international journals. Furthermore, these results will be presented at international meetings, such as the 2016 International Soft Matter Conference to be held in Grenoble, France on September 12-16, 2016.

Milestones for FY16 and FY17:

Date	Milestones
March 2016	• Completion of data analysis of XPCS measurements on the transition between ballistic and Brownian motion in prototypical nanoparticles' suspensions (measurements already performed at the CHX beamline) • Use of beamtime allocated at NSLS II to perform IXS measurements on prototypical nanoparticles' suspensions
April 2016	• Preparation and submission of a manuscript on CHX-XPCS measurements on nanoparticles' suspensions • Completion of the analysis of IXS measurements in prototypical nanoparticles' suspensions • Use of allocated beamtime at the beamline IXS to measure the THz phonon propagation in liquid crystals
May 2016	• Submission of a manuscript on Molecular Dynamics simulation on nanoparticles (computer simulations already performed) • Analysis of IXS results on liquid crystals • Use of allocated beamtime to perform measurements on phonon propagation in lipids' membranes
June 2016	• Second run of XPCS measurements at the CHX beamline on nanoparticles' suspensions • Second run of IXS measurements on nanoparticle suspensions at the IXS beamline
July 2016	• Joint analysis of IXS and CHX results on nanoparticles' suspension • Submission of a manuscript focusing on phonon propagation in liquid crystals investigated at IXS
August 2016	• Preparation of a manuscript focusing on CHX and IXS results on nanoparticles' suspensions • Analysis of the IXS measurements on lipid membranes
September 2016	• Presentation of results at a Conference in Grenoble, France • Preparation and submission of a manuscript focusing on IXS measurements of the THz spectrum of lipid membranes • Submission of a manuscript focusing on CHX and IXS results on nanoparticles' suspensions
October 2016	• Second computer simulation run on the dynamics of prototypical nanoparticles' suspensions analogous to the ones used for CHX-IXS measurements
November 2016	• Combined analysis of computational and experimental results on the dynamics of prototypical nanoparticles' suspensions • Use of allocated beamtime at NSLS II to perform IXS measurements on phonon propagation in various arrays of nanoparticles having different shape, size and interaction strength
December 2016	• Data analysis of IXS results on nanoparticle arrays
January 2017	• Preparation of a manuscript on phonon propagation in programmable arrays of nanoparticles
February 2017	• Manuscript submission on phonon propagation in programmable arrays of nanoparticles.

Searching and Sorting Haystacks

LDRD Project # 15-034
S. McSweeney, Q. Liu, W. Hendrickson

PURPOSE:

The new National Synchrotron Light Source II (NSLS-II) beamlines will provide entirely new problems, and opportunities, for macromolecular crystallography (MX). The flux delivered to the sample by these instruments will allow for diffraction measurements to be made from samples previously unmeasurable at any other synchrotron light source. Such power is not without its problems. In particular, the lifetime of the typical protein crystals in these beams is estimated to be about 10 ms and thus the collection of data sets from a single protein crystal will be essentially impractical without X-ray attenuation factors of 99% or greater. Traditional MX experiments require one or at most two (a low and a high resolution) sweep data collection plans (Fig 1a). More complex strategies are possible based upon the radiation robustness of the crystal (Fig 1b, c). However NSLS-II will bring scientists into completely new regimes where data sets will be generated from thousands of crystals (Fig 1d).

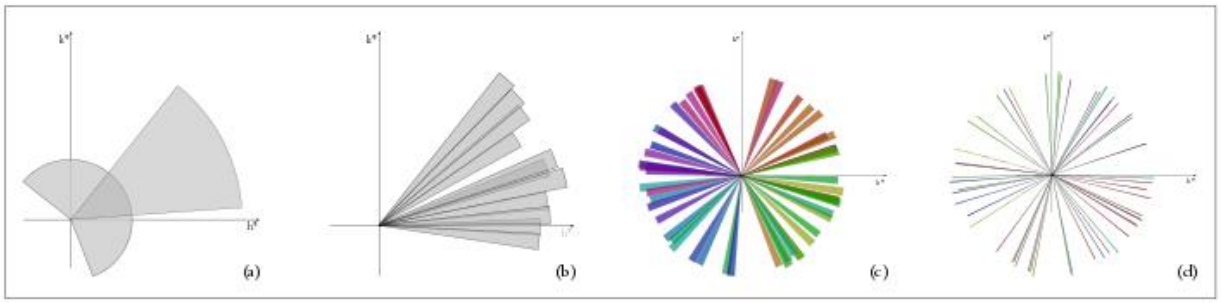


Figure 1. Data collection strategies for MX data; each wedge represents an experiment sweep revealing part of the data for a crystal structure. (a) Low and high resolution sweeps (b) "complicated" multi-orientation strategies (c) optimistic multi-crystal strategies where several degrees of data per sample are possible; many samples lead to a data set (d) at NSLS-II narrow fragments of data sets will be possible for each crystal 0.2 degrees per-sample; hundreds or thousands of crystals will be necessary for each data set. In (c) and (d) the color represents the order in which the samples contributed in the simulation; changes in length represent different diffraction limits for the samples.

APPROACH:

Our approach to this problem first is to develop the infrastructure and methods for simulating the diffraction experiments expected at our new beamlines. In parallel, optimized tools for examining these data will be created and benchmarked. Once the simulation methods are established, the focus will turn to the development of appropriate tools for recognizing similarity between partial data sets; various methods will be employed and tested for efficiency. In addition, to supplement these computational investigations, we will be developing crystal samples to provide experimental data for further refinement of the technique.

We expect to provide software capable of rapidly and reliably sorting partial MX data sets, such that an ensemble is achieved that creates a complete data set with accuracy appropriate to the question posed by the experiment. The target function for the sorting will be adapted to the type of MX experiment. To develop the software we will first create a simulation environment to explore the impact of different possible sources of experimental noises on the data. This software will be required to enable the full potential of the NSLS-II source to be exploited for MX.

TECHNICAL PROGRESS AND RESULTS:

In the first year of funding, computing nodes were purchased and installed at NSLS-II. These nodes form part of a prototype compute facility designed to provide infrastructure for the NSLS-II as a whole. Our intent was to facilitate the creation and analysis of simulated diffraction data. These data were then used to benchmark algorithms and stress test the network infrastructure under the conditions to be expected for NSLS-II experiments. Methods were developed by Drs. J. Jakoncic (BNL) & W. Shi (Case Western Reserve University), to allow for simulation of diffraction from crystals varying in linear dimension from 5 microns through 10 microns, with flux densities consistent with the expected performance at the new NSLS-II crystallography beamlines. Simulation of the diffraction utilized the code fastBragg developed by Dr. J. Holton.

Working independently Dr. H. Bernstein (Rochester Institute of Technology) developed methods to perform initial analysis of diffraction data at 1kHz frequency. We are working to draw this development into our analysis strategy. To enable closer integration with the data analysis at X-ray Free Electron Laser sources, a collaboration with Dr. N. Sauter (Lawrence Berkeley National Laboratory) was established by Dr. Jakoncic.

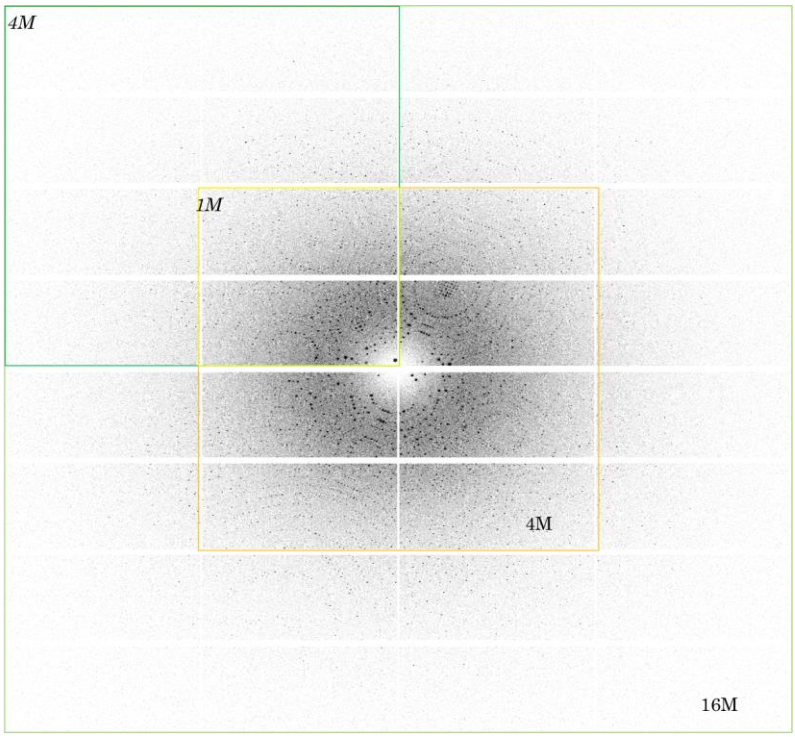


Figure 2. Example of simulated diffraction and various possible regions of interest.

In order to investigate the most efficient mechanism for accurate initial analysis of diffraction images, the use of regions-of-interest was explored. Initial results are promising, indicating speed ups of the initial evaluation are possible, when the full detector was evaluated (16 M pixels), compared to smaller areas within the detector (Figure 2).In the next year, we expect to establish efficient schemes for evaluation of the real diffraction images. We also expect to establish the initial steps toward characterizing the similarity and dissimilarity between subsets of the whole data set.

In-situ Microscopy Investigation of Complex Manganese Oxides for Energy Storage

LDRD Project # 15-037
Y. Chu

PURPOSE:

Advanced battery materials have complex hierarchical structures, ranging from the atomic to the millimeter scale. Development of more efficient and safe batteries requires comprehensive understanding of how these complex interfacial structures are transforming during the charge / discharge reactions. One of the major challenges is lack of suitable imaging methods that can provide comprehensive structural and chemical information with sufficient resolution and sensitivity. The scientific purpose of this research is develop multi-scale and multi-modality imaging methods under an *in situ* sample environment. A key fundamental scientific goal of the project is to understand the interplay between the nanoscale electrode structure and electrochemical reversibility, by leveraging the world-leading microscopy capabilities of the Hard X-ray Nanoprobe (HXN) beamline at National Synchrotron Light Source II (NSLS-II) and electron microscopes at the Center for Functional Nanomaterials (CFN). Successful implementation of the project will strengthen BNL's scientific leadership in energy research, and the developed capabilities will be offered to the general users of these facilities.

APPROACH:

In order to investigate battery materials from the mesoscale down to the atomic scale, we employ the HXN beamline and the transmission electron microscope (TEM). In addition, we collaborate with Esther Takeuchi of BNL/Stony Brook University, who has world-leading materials' knowledge on a wide range of battery materials. There are two specific aims of this research. Our first aim is to develop liquid electrochemical cells that allow HXN and TEM investigation under *in situ* conditions. We work with a commercial vendor (Hummingbird Inc) to make important design modifications to achieve additional capabilities for performing X-ray microscopy experiments. One of the most critical requirements is to enable nanodiffraction and nanofluorescence measurements. The first aim was completed in FY15. Our second aim, to be completed in FY16 and FY17, is to employ the developed cell to perform HXN and TEM investigations, so that we can image how the complex electrode interfaces are transforming during battery operation. In order to make progress on this research, we plan to perform TEM experiments (*ex situ* and *in situ*) at the CFN and X-ray microscopy experiments (*ex situ* and *in situ*) at the Advanced Photon Source (APS) before the HXN beamline is ready for science experiments. We plan to perform *ex situ* experiments to screen samples and learn about the samples' structural and chemical modifications. Initial *in situ* experiments will focus on learning about the actual performance range of the cell and optimizing the *in situ* experiments. In the final phase, we will perform *in situ* TEM and HXN experiments on the same sample.

TECHNICAL PROGRESS AND RESULTS:

We developed an *in situ* TEM/HXN cell through a commercial vendor (Hummingbird Inc) by modifying the design of an existing TEM cell. The existing design is highly effective for *in situ* TEM investigations, but is incompatible with nanofluorescence and nanodiffraction measurements at the HXN beamline. We significantly increased the opening angle of the incidence and exit windows, so that the emitted fluorescence X-rays and diffracted X-rays can be detected without being blocked. Fig 1a shows a photograph of the cell and Fig 1b shows the arrangement of cell electrodes around the X-ray/electron window. Another important

modification was to reduce the overall form factor of the cell, so that the new cell (together with electrical

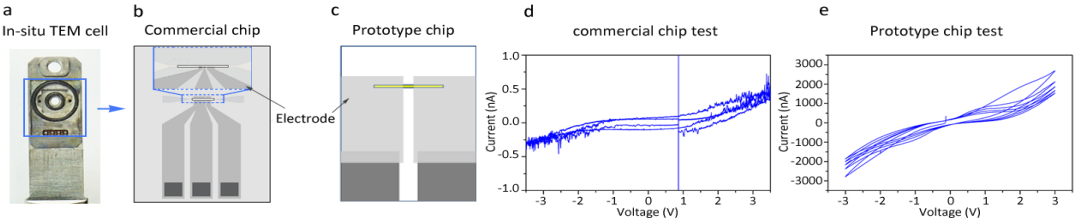


Figure 1. (a) Optical image of the *in situ* TEM cell. Electrode diagrams for (b) commercial chip and (c) prototype chip. Electrochemical measurements of water dissociation using (d) commercial chip and (e) prototype chip.

wires and liquid plumbing lines) fits into the HXN X-ray microscope (a one-of-a-kind X-ray microscope capable of 10 nm X-ray imaging which took 5 years to develop) which has an extremely small working space. One of the critical components of the cell, referred to as a chip, is a 50 nm-thick silicon nitride window (for passing the X-ray or electron beam) and the metal electrode providing the electrical contact for the sample. Due to the small surface area of the electrodes (Fig 1b), the commercial chip yields small current signals (Fig. 1d). By designing a prototype chip with a larger surface area (Fig. 1c), we achieve much more stable electrochemical control (Fig. 1e).

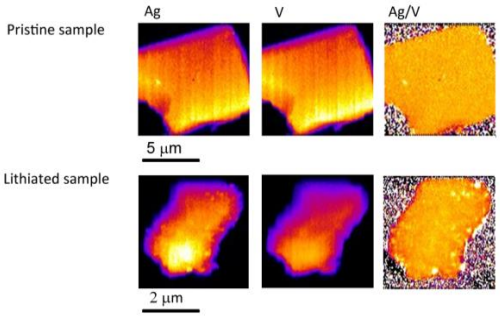


Figure 2. X-ray fluorescence images of Ag, V, and normalized Ag (i.e., Ag/V) from pristine and lithiated $Ag_2VO_2PO_4$ samples.

We performed comprehensive *ex situ* TEM and X-ray microscopy experiments on the $Ag_2VO_2PO_4$ system. The X-ray microscopy experiments include: white-beam X-ray diffraction and transmission X-ray microscopy at APS and fluorescence microscopy at the HXN beamline. Fig. 2 shows the X-ray fluorescence images of the samples, obtained using a 15 x 15 nm beam at the HXN beamline. These are the first X-ray images on this material, showing Ag nucleation from the crystalline lattice due to lithiation. Another exciting scientific discovery is that we can induce localized nucleation of Ag atoms by exposing the sample with the nanobeam, which we believe is due to electrochemical reduction of Ag ions by the beam-induced photoelectrons. The size of the Ag clusters depends on the dose of the X-ray beam. By comparing results from TEM and three types of X-ray microscopy experiments, we were able to provide a comprehensive model on beam induced Ag nucleation in the $Ag_2VO_2PO_4$ system. A manuscript summarizing the work is being drafted.

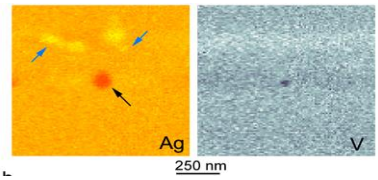


Figure 3. Ag clusters induced by X-ray beam.

Milestones for FY16, FY17, and FY18:

- FY16: Perform *in situ* TEM and HXN experiments. Considerable focus will be on succeeding strain imaging at the HXN beamline using diffraction/Bragg CDI.
- FY17: Perform *in situ* TEM and HXN experiments on the same sample and perform cross analysis between TEM and HXN. Expand the research on the Ag hollandite system.
- FY18 (request for extension): Perform TEM and HXN experiments on other material systems. Primary focus is to develop 3D imaging via nanotomography. Additional year (i.e., 3rd year LDRD funding) is needed for completing this task.

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 # 15-038
O. Chubar, C. Kitegi

PURPOSE:

The purpose of this project is to develop an innovative insertion device – a Segmented Adaptive-Gap Undulator (SAGU) – that will enable the most complete and efficient use of the low electron beam emittance and long straight sections available for insertion devices (ID) at the National Synchrotron Light Source II (NSLS-II). The main concepts of SAGU are applicable to all known undulator technologies; however, our project targets first the development and design of a room-temperature hybrid Segmented Adaptive-Gap In-Vacuum Undulator (SAGIVU) that can be used at many NSLS-II beamlines, resulting in improvement of their performance.

APPROACH:

The current project includes 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 girders and liner foil – are designed and partially realized, and a number of magnetic and mechanical tests are ready to be performed on them. To reduce the costs of the project, several existing mechanical and magnetic parts will be used, in particular three old mini-gap IVUs of the NSLS - X9, X13 and X29 - which became available after the end of its operation. The planned magnetic and mechanical tests will be performed using an auxiliary small magnetic measurements bench that is available in the ID lab of the NSLS-II.

TECHNICAL PROGRESS AND RESULTS:

The most important "steps" accomplished during FY15 by the LDRD team towards construction and tests of an SAGIVU prototype are listed below.

- Three mini-gap in-vacuum undulators were extracted from the NSLS X-ray ring after the end of its operation and relocated to the ID lab of the NSLS-II. The vacuum chambers of these undulators are being disassembled (Fig. 1). The "native" small magnet girders of these undulators will be shortly replaced by new girders of the SAGIVU prototype, on which the new magnet system will be installed and the planned tests will be accomplished.
- The new aluminum inner girders were designed in collaboration with ADC Inc. Seven such girders (six for the 3-segment SAGIVU prototype for the Low-Beta straight section and one for the High-Beta straight section of NSLS-II) were ordered and received at BNL (Fig. 2).
- Detailed design of the modular magnet support system has been accomplished (Fig. 3). This new design is optimized for use of a special liner foil, which is directly cooled over the entire SAGIVU length. Besides, this design allows for using "pusher" magnets that can be placed "underneath" the poles (PMP module, second from left in Fig. 3).
- Magnets and poles for the 3-segment 2-m long SAGIVU for the Low-Beta straight section were ordered from KYMA Srl and are ready for shipment to BNL. Representative magnetic measurement data (obtained using a Helmholtz coil) was supplied by KYMA and demonstrates good quality of the manufactured magnets (Fig. 4). Besides these new magnets, spare magnets of NSLS-II IVU22 will be used for the SAGIVU prototype tests.

- A high-precision computer-controlled diamond disc saw was purchased and customized for shimming the poles by micro-machining their faces that are close to the electron beam (Fig. 5, left).
- An auxiliary 1.5 m long magnetic bench of NSLS-II ID group was commissioned and is ready for measurements of SAGIVU segments during their magnetic assembly and shimming (Fig. 5, right).

Figure 1. Mechanical carriages of old mini-gap IVU in the ID lab of NSLS-II. Left: vacuum chamber is still present, middle and right: it is disassembled and the "native" inner girders can be seen.

Figure 2. New "inner girders" for the SAGIVU received from ADC. Left: unpacking in the ID lab of NSLS-II. Right: one girder is placed together with a prototype foil stretching mechanism part.

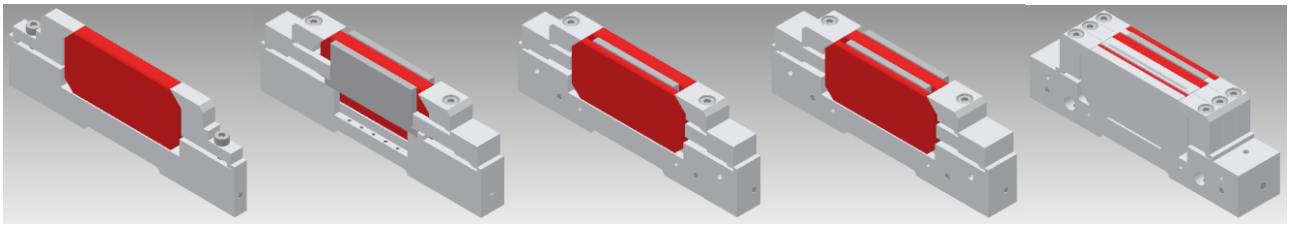


Figure 3. Computer Aided Design models of modules (left to right: M, PMP, MPN, PMPN, T) constituting the SAGIVU magnet system. Such models and fabrication drawings were produced for 3 SAGIVU segments for the Low-Beta straight section of NSLS-II and for 1 segment for the High-Beta straight section. This set includes 20 different modules and more than 100 individual fabrication drawings. All drawings and technical specifications are currently "released" and prepared for a "build-to-print" type procurement procedure.

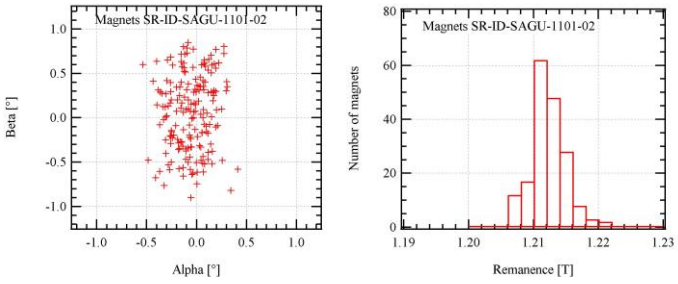


Figure 4. Measured errors in angles and amplitudes of magnetization vectors in NdFeB magnet blocks manufactured for one (of 3) SAGIVU segments for the Low-Beta straight section of NSLS-II. Both angular and amplitude errors are within specs.

Figure 5. Left: new high-precision computer-controlled diamond disc saw, purchased and customized for shimming of the poles, is ready for validation of its operation by the Safety Group. Right: 1.5 m long magnetic bench is prepared for measurements of SAGIVU magnet girders during their magnetic assembly and shimming.