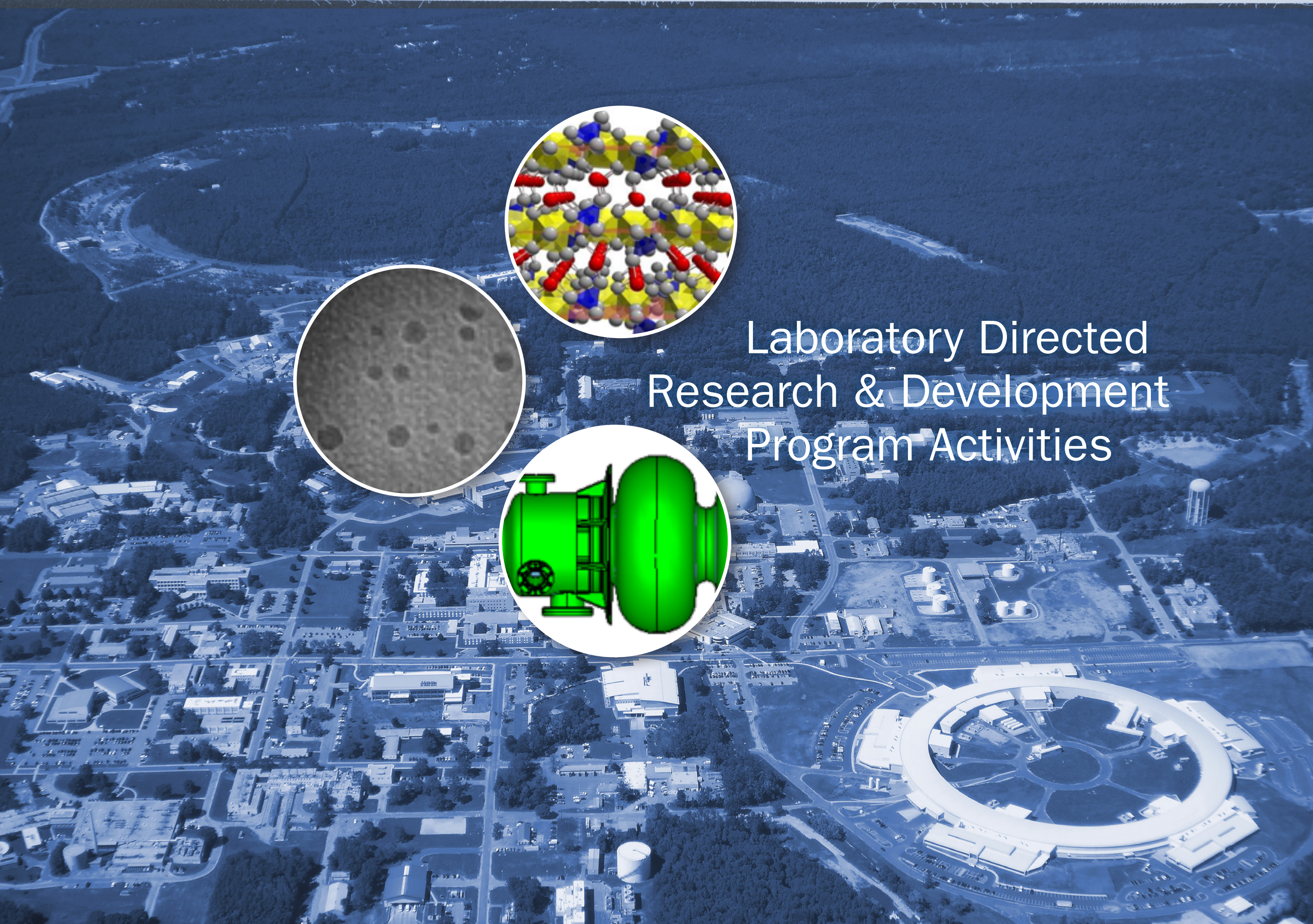
LDRD
2016 Annual Report

BROOKHAVEN NATIONAL LABORATORY

70 YEARS OF DISCOVERY
A CENTURY OF SERVICE



Laboratory Directed Research & Development Program Activities

BNL-52351-2016

BROOKHAVEN NATIONAL LABORATORY
BROOKHAVEN SCIENCE ASSOCIATES
UPTON, NEW YORK 11973-5000
UNDER CONTRACT NO. DE-SC0012704
UNITED STATES DEPARTMENT OF ENERGY

March 2017

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 2016 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.

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Introduction

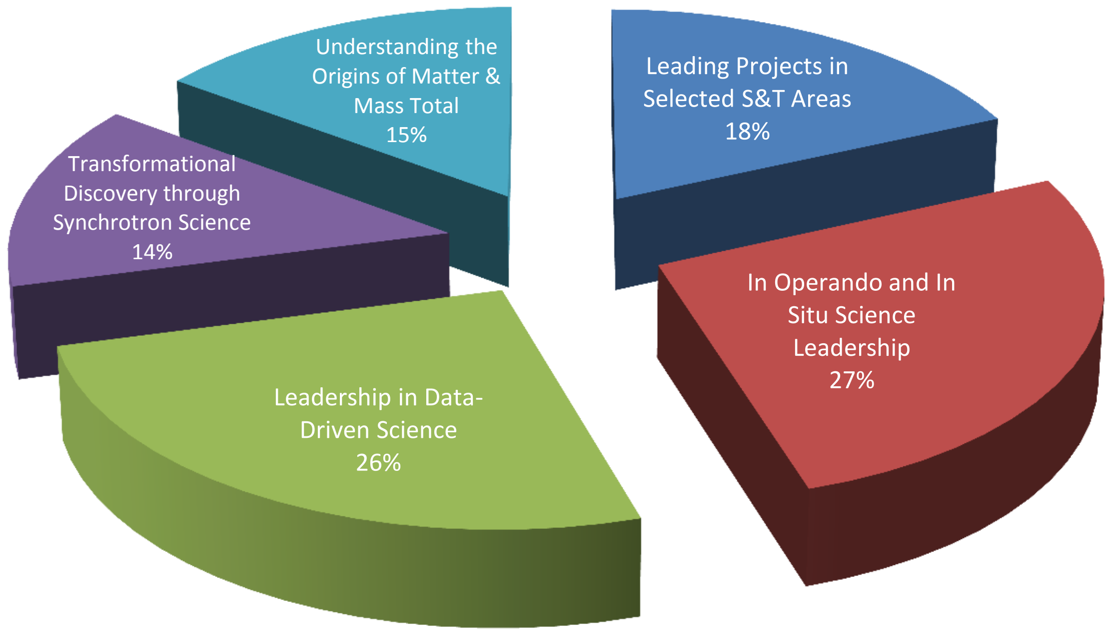
Each year, Brookhaven National Laboratory (BNL) is required to provide a program description and overview of its Laboratory Directed Research and Development Program (LDRD) to the Department of Energy (DOE) in accordance with DOE Order 413.2C dated October 22, 2015. This report provides a detailed look at the scientific and technical activities for each of the LDRD projects funded by BNL in FY 2016, as required. In FY 2016, the BNL LDRD Program funded 48 projects, 21 of which were new starts, at a total cost of $11.5M.

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. Of the funded LDRD projects, 82% 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 Outcomes



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.

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

2016 PROJECT SUMMARIES

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 Division. Time resolved X-ray registration is required in photon correlation spectroscopy (XPCS), which is an important tool in studies of nanoscale dynamics of materials, while the time-of-flight MS is an important analytical tool used widely in chemistry, biology, and medicine.

APPROACH:

We combine features of several established technologies in order to produce a novel device with as-yet unachieved capabilities. We have designed a new silicon pixel sensor, which in combination with the Timepix chip, 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 version of the readout chip, Timepix3, is fully compatible with the sensor and a Timepix3 based camera will be produced and tested as well.

TECHNICAL PROGRESS AND RESULTS:

We list below the main accomplishments in FY 2016:

- Characterized photodiodes produced in the same process as the sensor to determine the quantum efficiency, see Figure 1 below from a publication, which is being prepared.

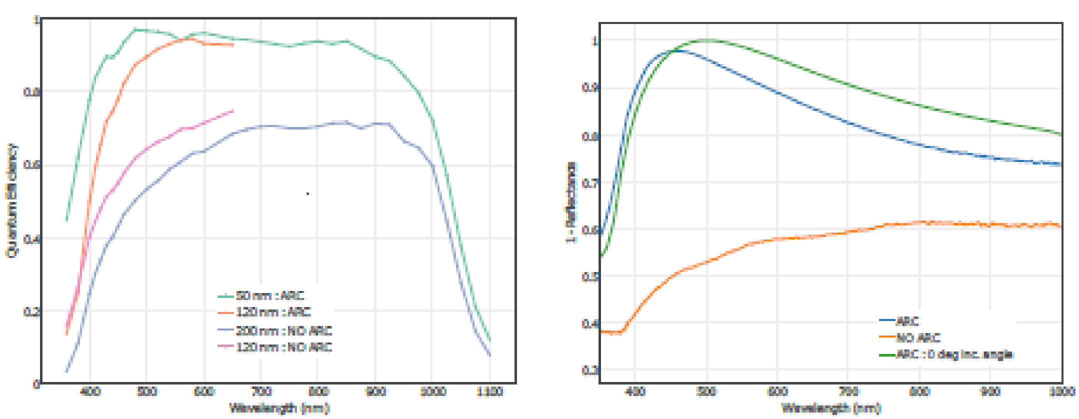


Figure 1. (Left) Measured quantum efficiency of the photodiodes as a function of wavelength, and (Right) the measured (1 - Reflectance) of the photodiodes as a function of wavelength with and without anti-reflective coating (ARC) at 45 degrees incidence angle; and a calculated (1 – Reflectance) at zero degrees.

- Characterized sensitivity and efficiency of the TimepixCam with different types of passivation of the sensor surface using LED, lasers and ions.
- Procured a fast image intensifier, which in combination with the TimepixCam, makes it sensitive to single photons. Characterized the camera in the single photon regime at BNL and performed experiments on single photon counting phosphorescent lifetime imaging with colleagues from the Kings College London. A publication is in preparation, see the results below (Figure 2).

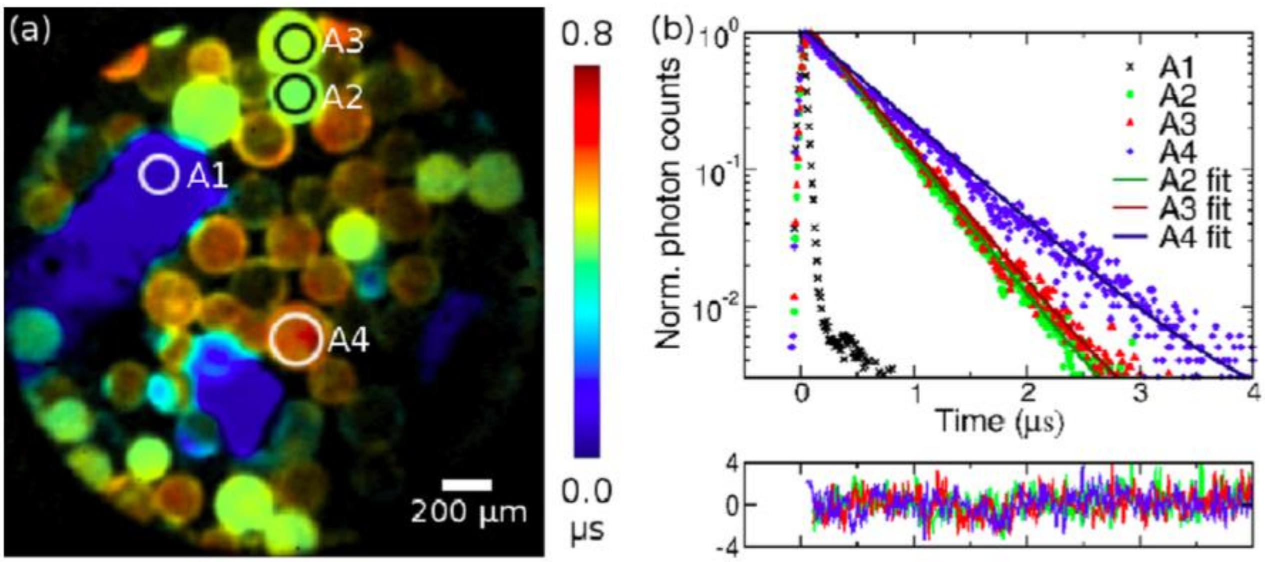


Figure 2. (a) Lifetime images of beads infused with different iridium (Ir) compounds and fluorescent plastic acquired with the TimepixCam. (b) Ir (phosphorescence decays) for areas A1-A4 indicated in (a), with monoexponential fits to the phosphorescence decays and residuals.

- Took fluorescent lifetime imaging data with the TimepixCam and intensifier with M. Cotlet's group in BNL's Center for Functional Nanomaterials; agreed on more measurements. The data analysis and preparation of corresponding publications are in progress.

In summary, we completed all planned milestones for FY 2016.

Milestone

The main milestone for FY 2017 is to complete the project by publishing the remaining papers and disseminating the results. The Timepix3 based camera will be tested, but this will be beyond the scope of this project.

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 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 (BER) when an expected Request for Proposals in Biosystems design is announced.

APPROACH:

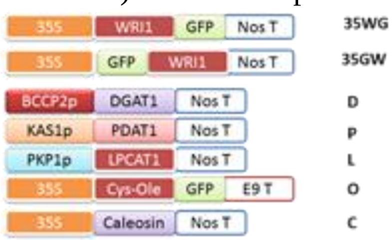
The project essentially involves two parts, 1) expanding the WRINKLED1 (WRI1) regulon, and 2) controlling the expression of the WRI1 transcription factor.

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 were previously 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.

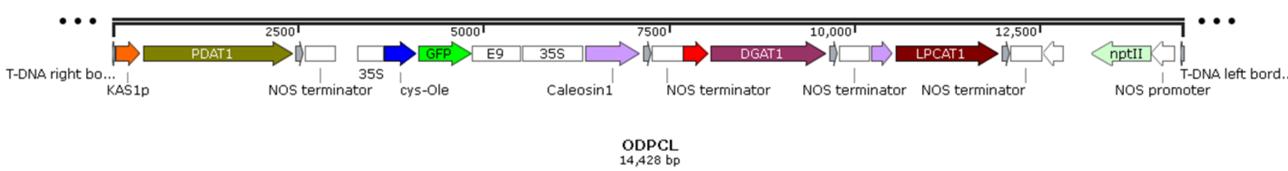
Examination of the *Arabidopsis* Information Resource expression database shows that WRI1 is not expressed to any significant level in vegetative tissues, and expression in leaves is specifically low. Thus, in order to turn on the expanded WRI1 regulon, we need to specifically express the WRI1 in leaf 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. 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 the 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 the last reporting period, 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 and transformed both *N. benthamiana* transiently and *Arabidopsis* stably. In 2016 we analyzed *Arabidopsis* lines expressing the AlcR/AlcA -inducible WRI1 construct using silica thin layer chromatography and gas chromatography coupled mass spectrometry. The growth rate and form of these plants is normal and we analyzed the TAG content of plants induced to express WRI1 at various stages of growth and compared TAG levels before induction, at 2 and 7 days after induction and at senescence. While we saw significantly higher levels of TAG in the 10% range, the levels fell short of those obtained with the use of high constitutive levels of expression obtained using the 35S promoter of 3.5%. We identified a mutant of WRI1 in which R2 and R3 were substituted for K at both positions. Expression of this version of WRI1 resulted in a doubling of TAG accumulation. We are following up on these experiments in a DOE BER proposal.

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 very 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 in the same electrodes under real working conditions. In this effort, a novel sealed electrochemical cell with the flexibility to use liquid electrolyte, along with a full suite of biasing systems, will be developed for both 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 (Figure 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.

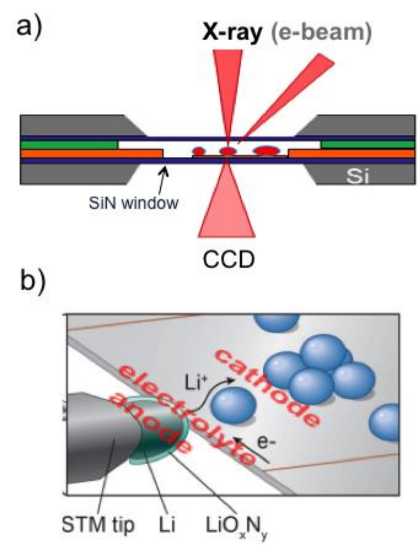


Figure 1. Schematic illustration of two types of *in situ* electrochemical cells, based on (a) liquid and (b) solid electrolyte, for measuring single-particle electrochemistry by TEM and synchrotron X-ray methods.

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 spectroscopy / diffraction, and Gerbrand Ceder (University of California, Berkeley) on modeling. In addition, a collaboration with Hummingbird Scientific was established to develop and refine the *in situ* liquid cells for electrochemical applications.

TECHNICAL PROGRESS AND RESULTS:

In the past year, we developed an electrochemical sample cell with a special design for correlative *in situ* TEM/synchrotron X-ray measurements of Li transport and reactions in batteries. This new development enables *real time* probing of structural/chemical evolution of electrode materials during electrochemical cycling under normal galvanostatic/potentiostatic conditions, from a single particle or multiple particles within the electrode.

The electrochemical functionality of the cell was tested through *in situ* electron energy-loss spectroscopy (EELS) studies of electrochemical reactions in the spinel $Li_4Ti_5O_{12}$ (LTO), a promising anode featuring "zero-strain" during (dis)charge. Here, Li EELS (more precisely, the near-edge fine structure in the spectra of the Li K-edge) was used as a unique probe to track the transport of Li through certain selected LTO nanoparticles. Results from this study not only validated the functionality of the cell (as demonstrated in Figure 2a-c), but also served as the first experimental evidence of co-existence of metastable phases ($Li_{4+x}Ti_5O_{12}$) with two stable phases (*i.e.*, $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$), which contradicts the traditional belief of a two-phase reaction in this material. A combination of this *in situ* observation with atomic imaging (Figure 2d, e) and *First Principles* calculations (G. Ceder's group), allowed us to identify all of the possible Li configurations and associated kinetic transport pathways in the metastable/stable phases (Figure 2f). The findings offer unprecedented insights into the structure-correlated electrochemical properties of LTO anodes.

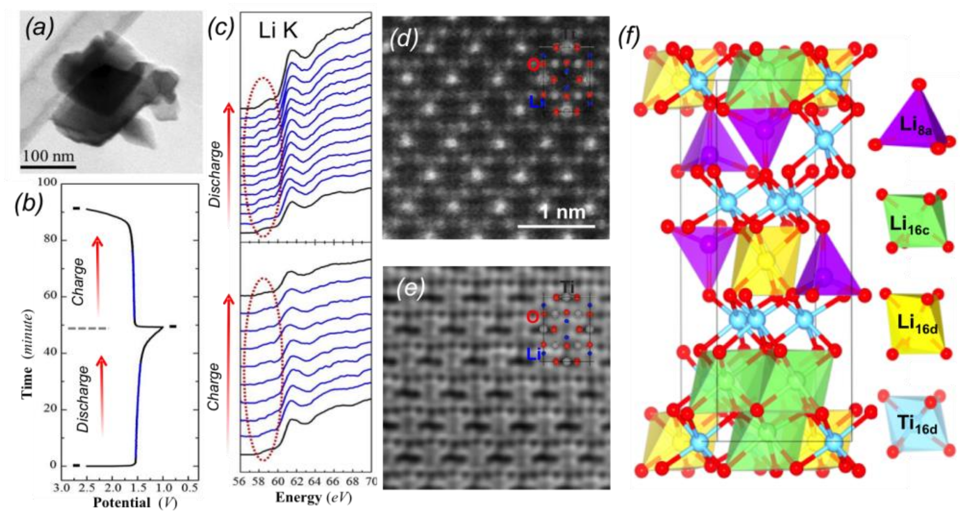


Figure 2. *In situ* TEM-EELS tracking kinetic transport of Li ions in LTO during electrochemical cycling. (a) Bright-field TEM image showing the LTO nanoparticles for the study. (b) Electrochemical cycling profiles. (c) Time-resolved EELS spectra of the Li K-edge, showing subtle but clear changes in the fine structure (as labeled) due to formation of metastable phases. (d, e) Atomic imaging *via* high-angle annular dark-field and annular bright-field techniques. (f) Illustration of one of the predicated low-energy structure configurations in metastable $Li_{4+x}Ti_5O_{12}$ (G. Ceder's group).

A Record of Invention and a manuscript are under preparation, detailing the cell design along with results from studying LTO systems. All goals/milestones for this project were completed. Through this project, tools and techniques were made available for correlative *in situ* TEM/synchrotron X-ray studies of ionic transport and reactions in batteries. Some of the developed capabilities were utilized for projects in the m2M Energy Frontier Research Center. Collaboration was recently initiated on further developing the cell design for studying new electrochemical systems (with scientists from the BNL Chemistry Division, the Center for Functional Nanomaterials, and NSLS-II).

Elucidating the Role of Nanostructured Domains in CIGS PV Device Performance

LDRD Project # 13-024

M. Eisaman

PURPOSE:

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

APPROACH:

As this project has evolved, we have developed an approach that addresses the project goals from two directions:

- **Correlation of single grain material properties with single grain electronic transport properties.** We have pioneered a new nanocontact method of single-grain measurement by depositing contacts onto single grains using lithography.

- **Novel device architectures for improved performance.** In addition to the above work to understand structure function relationships in the CIGS absorber, we are investigating novel CIGS device architectures that replace the CdS and ZnO layers (that are toxic and have parasitic optical absorption) with a graphene front contact.

TECHNICAL PROGRESS AND RESULTS:

- **Effect of single-grain composition on local recombination in $Cu(In_{1-x}Ga_x)Se_2$ Photovoltaics**

We found that there are significant variations in the composition and recombination dynamics at the length scale of a few grains. We used lithographically defined electrical contacts to measure the charge transport and current voltage (IV) behavior as a function of temperature over micron-scale (few-grain) areas within a CIGS device in order to understand the grain-to-grain variation of recombination. We correlated these electrical measurements with energy dispersive X-ray spectroscopy measurements of single-grain elemental composition, and transmission electron microscopy with selected-area electron diffraction to ascertain the single-grain material structure. We found that local regions with a higher fraction of copper-rich grains (and primarily chalcopyrite structure) show enhanced interfacial recombination, whereas regions with a higher fraction of copper-poor grains (and a stannite-type structure) show bulk recombination limited behavior. We believe these fundamental nanoscale electrical-compositional correlations of the recombination dynamics help point the way toward the fabrication of improved CIGS photovoltaic devices.

- **CIGS-graphene Schottky photovoltaic and discovery of low-cost graphene doping**

Scalable and low-cost doping of graphene could improve technologies in a wide range of fields, such as microelectronics, optoelectronics, and energy storage. While achieving strong p-doping is relatively straightforward, non-electrostatic approaches to n-doped graphene, such as chemical doping, have yielded electron densities of $9.5 \times 10^{12} e/\text{cm}^2$ or below. Furthermore, chemical doping is susceptible to degradation and can adversely affect intrinsic graphene's properties. We demonstrated strong ($1.33 \times 10^{13}\ e/\text{cm}^2$), robust, and spontaneous graphene n-doping on a soda-lime-glass substrate via surface-transfer doping from sodium without any external chemical, high-temperature, or vacuum processes. Remarkably, the n-doping reaches $2.11 \times 10^{13}\ e/\text{cm}^2$ when graphene is transferred onto a p-type CIGS semiconductor that itself has been deposited onto soda-lime-glass, via surface-transfer doping from sodium atoms that diffuse to the CIGS surface. Using this effect, we demonstrated an n-graphene/p-semiconductor Schottky junction with ideality factor of 1.21 and strong photo-response. The ability to achieve strong and persistent graphene n-doping on low-cost, industry-standard materials paves the way toward an entirely new class of graphene-based devices, such as photodetectors, photovoltaics, sensors, batteries, and supercapacitors.

[1] D. M. N. M. Dissanayake and M. D. Eisaman, Chemical-free n-type and p-type multilayer-graphene transistors, Appl. Phys. Lett. **109**, 053110 (2016).
[2] 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).

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

LDRD Project # 13-031

E. Dooryhee

PURPOSE:

In addition to understanding static or steady-state atomic structures of materials, it is important to understand how they evolve during operation under real working conditions, such as an electrode material in a charging and discharging battery or a catalyst material functioning during the abatement of exhaust gases in vehicles. The Modulation Enhanced Diffraction (MED) method has been implemented as a new characterization tool to recover information, which is otherwise buried in the larger signal emanating from the predominantly passive part of the structure. The aim of this project was to expand the *in situ* and *operando* time-dependent diffraction capabilities at the X-ray Powder Diffraction (XPD) beam line and other diffraction and scattering beam lines at the National Synchrotron Light Source II (NSLS-II).

APPROACH:

MED is a well-established technique in spectroscopy, but very new in powder diffraction. This project, which developed procedures and algorithms to implement MED, stems from a collaboration between two national laboratories (Brookhaven and Argonne) and Stony Brook University using NSLS-II at Brookhaven and the Advanced Photon Source at Argonne. Structural selectivity is enhanced in MED by cycling an external parameter, such as the reactant composition, temperature, pressure, or electrical field during the course of the diffraction measurement. For example, MED can be used to track the relative proportions of copper (Cu) and copper oxide (Cu_xO) supported on ceria (CeO_2) in several catalysts (see Figure 1). Procedures to implement MED were developed and benchmarked by studying the oxidation and reduction of a mixture of Cu and Cu_xO. The measurements were conducted by periodically pulsing H_2/CO gases over the catalyst. When the catalyst goes from inert to active, MED can detect the small structural changes that allow for the catalyst to selectively remove CO from a mixture of CO and H_2, prior to input to fuel cells. MED can uncover subtle changes normally undetected by conventional diffraction methods. Also importantly, MED can be executed over the timescale of interest for most functional materials, which ranges from seconds to minutes or even hours.

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 the NSLS-II XPD beamline. In previous experiments, we showcased the capabilities of MED. 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 otherwise used to enhance sensitivity and selectivity. This project was crucial to emphasize that MED has the potential to be applicable to industry-relevant processes, such as adsorption and desorption in membranes and filters, reversible ion intercalation in host matrices for batteries and fuel cells, polarization- or magnetization-induced structural shifts in piezoelectric actuators, and change of surface states in automotive catalysts under changing pressures of the reactants as well as for materials used in the nuclear industry.

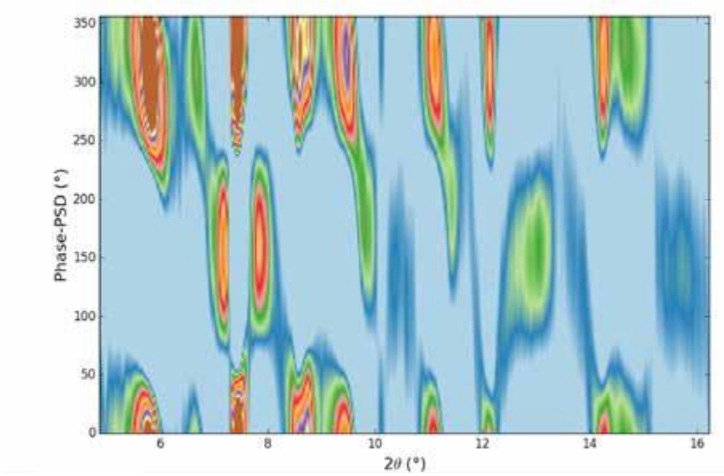


Figure 1. Oxidation-reduction of $Cu_{60}Ce_{40}$ in pulsing H_2/O_2 gases at 250°C in a constant stream of CO/O_2 mixture. The demodulated powder patterns as a function of phase angle are shown, where Cu, CuO, and Cu_2O phases can be distinctly identified.

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 future General User experiments at the NSLS-II XPD beamline.

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. Science commissioning at the NSLS-II XPD beamline performed.	Open MED to General Users
Experiment	MED benchmarked in real-case studies and test applicability. • *Operando* X-ray diffraction (aka XRD)+diffuse reflectance infrared fourier transform spectroscopy (aka DRIFTS) of Cu-CeO_x-TiO_2 for synthesis of alcohol from CO_2 hydrogenation. • *In situ* XPD Studies of High Pressure Gas Loading to Metal-Organic Frameworks.	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 readily be analyzed using this software. The software package is released to the community.	Publish. 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. This project was selected as a highlight for inclusion in the Office of Science 2016 LDRD Brochure for its relevance to the DOE Strategic Plan.

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. 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.

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 wavefront and use this as a feedback to perform the ultimate alignment. The second optical technology innovation of our LDRD proposal involves *wavefront 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.

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 (Figures 1 and 2) have been carried out to verify the algorithms are accurate enough for practical use.

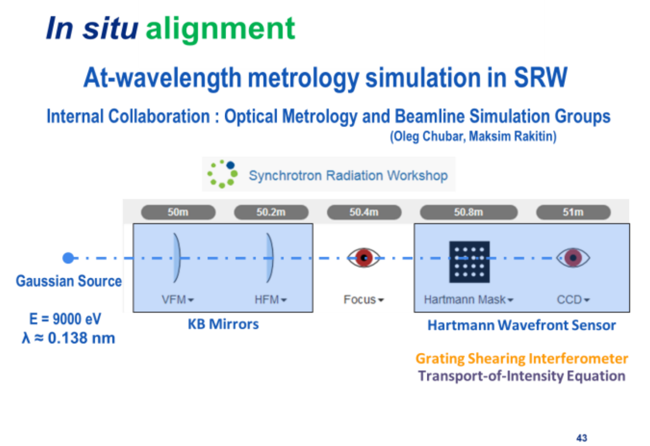


Figure 1. GUI interface of the software developed for Wavefront sensor simulation using the Open Source code SRW.

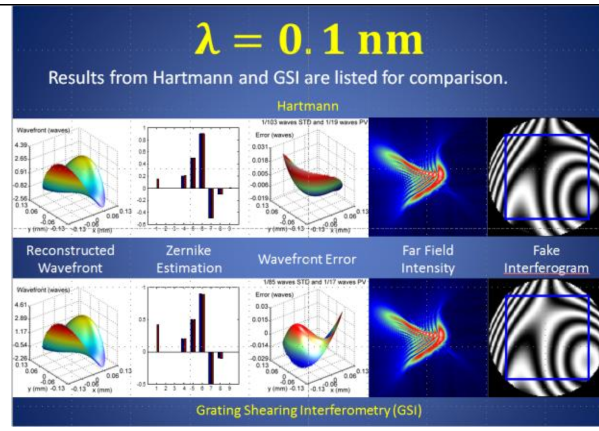


Figure 2. Hartmann and Grating Shearing Wavefront sensor simulation results.

The next step would be the real wavefront measurement test in beam lines. Some hardware has been purchased to start the construction of our high resolution detectors and a dedicated Hartmann sensor for At-Wavelength Metrology (Figure 3).

Figure 3. High resolution detectors and a dedicated Hartmann sensor for At-Wavelength Metrology.

The first test will be performed at one of the Advanced Beamlines for Biological Investigations with X-rays (aka ABBIX) of NSLS-II during the commissioning phase schedule before the end of June 2017.

This project targets the possibilities of measuring absolute diffraction limited wavefronts. The main issue in being able to develop such capabilities is the lack of absolute calibration in the hard X-ray domain. 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 scientists from 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 postdoctoral research associates, 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 acquisition, management and analysis infrastructure architecture was not yet defined and only basic EPICs control of hardware was implemented. The urgent need to define and deploy the underlying architecture and infrastructure to enable NSLS-II operations is the reason for the change in the goals of this LDRD. Over the last three years, the team has worked to define, develop and implement a data architecture and infrastructure for the NSLS-II.

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, does not need to 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 are 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 of 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.

In FY 2016, the group:

- Continued work on improving data acquisition software (bluesky)
- Overhauled the hardware abstraction layer (ophyd)
- Full integrated Area Detectors into ophyd/bluesky
- Organized the first DOE hackathon at BNL
- Continued to support JupyterHub for access to computational resources
- Deployed and supported software on the experimental floor.

This project was officially completed in May 2016.

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 currents and drastically improve spatial resolution. We will evaluate the performance of CNT-based tips using well defined samples and will conduct elemental mapping in $Cu_{0.05}ZrTe_3$. By locating the position of the substitutional copper (Cu), 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 Cu inclusions on the superconductivity.

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 utilized 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 evaluated 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, year one (FY 2014), pertains to nanofabrication, characterization, and initial evaluation of the CNT-based smart tips; the second step, year two (FY 2015-FY 2016 due to the delayed start of the project), involves further evaluation of CNT-based smart tips and nm-scale resolution elemental mapping of materials, such as Cu-doped ZrTe compounds.

One objective for FY 2015-FY 2016 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 grow 100 nm-3 um 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 the 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 the 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. 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.

The other objective in FY 2015-FY 2016 was to evaluate the performance of the developed smart tips in a lab-based/off-beamline environment and also to verify 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 the tips. We then utilized the Variable Temperature UHV 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. Results of the fabrication and characterization of the 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 Camino, Weihe Xu, Ming Lu, Xiao Tong, Nozomi Shirato, Daniel Rosenmann, Volker Rose, and E. Nazaretski, Journal of Nanomaterials, **2015**, 492657, (2015)).

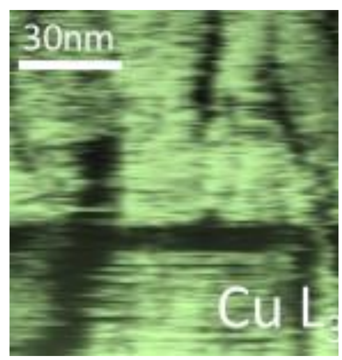


Figure 1. Elemental contrast at photon energy of 930 eV. The black areas show nanoscale Cu depletion.

In FY 2015-FY 2016, measurements on Cu-doped ZrTe samples were scheduled at the 26-ID beamline at the APS. A beamtime proposal was submitted and approved. Unfortunately, the SXSTM system was down during the scheduled beamtime. As a result, actual measurements were delayed until the last quarter of CY 2016. Figure 1 shows very preliminary data taken at the APS.

A manuscript on the ZrTe samples has been prepared and we expect to submit it after we acquire more X-ray SXSTM data.

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 and deriving higher resolution in shorter time. Transition metal containing 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 metal containing cathodes and of anode surfaces.

APPROACH:

Under this LDRD, samples will be fabricated which will be used to characterize active materials *ex situ*, *in situ* and *operando*. Extending the boundaries of current techniques at the National Synchrotron Light Source II (NSLS-II) will enable new information to be gathered with unprecedented speed and resolution. The techniques will provide fundamental information regarding the structures that is 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. During the previous phase of work, detailed studies using the *in situ* cell described in the previous report were completed and led to the submission of three publications with two more in preparation.

Over the course of discussions with staff scientists at the Sub-micron Resolution X-ray Spectroscopy (SRX) beamline at NSLS-II and expertise resident in our research group, an idea to extend the function of SRX into demonstration of μ-Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy was developed. This would provide a new method that SRX has not demonstrated and, in fact, has been only partially demonstrated elsewhere providing the opportunity for ground breaking research.

The initial experiment was planned to develop the μ-EXAFS capability at SRX beamline by collecting EXAFS spectra from sub-micron X-ray spot sizes. This would facilitate detailed structural modeling over specific 2D regions to accurately identify inhomogeneous local atomic structural changes within a large microstructure, opposed to an average structure obtained from bulk EXAFS. The μ-EXAFS would be a valuable extension of the current μ-X-ray Absorption Near Edge Structure (XANES) capability, which is limited in modeling and structural analysis.

The material system studied was magnetite (Fe_3O_4), a promising next generation battery material due to its low cost, low toxicity, and high gravimetric capacity (920 mAh/g). The first multi-scale mathematical model has been developed for predicting electrochemical performance of Fe_3O_4 electrodes, taking into account the mass transport limitations on both the crystal and agglomerate length scales. Using the mathematical model, simulations of the discharge and relaxation behavior of Fe_3O_4 agree well with experimentally observed electrochemical data, and indicate that lithium ion transport through the agglomerate significantly influences Fe_3O_4 electrochemistry. The novel µ-EXAFS technique developed would be used in combination with the existing X-ray Fluorescence mapping capability at the SRX beamline to provide direct experimental evidence of the mechanistic basis for the model.

Fe_3O_4 electrodes were prepared with the active material in the agglomerated state and discharged under various C-rates to determine the impact on lithium ion diffusion. A test sample using a mixture of Fe in various oxidation states was also prepared for the commissioning experiments. µ-EXAFS would enable sub-micron level spatial resolution of the discharged phases of Fe_3O_4. With the ability to spatially differentiate the local structure through µ-EXAFS measurements, a more detailed investigation of the structural changes associated with electrochemical ion insertion/removal would be possible. In particular, for systems in which kinetic limitations are under investigation, µ-EXAFS will provide the experimenter the opportunity to track structural changes within a larger microstructure, providing information on the kinetics of ion transport through a large crystallite/agglomeration that are difficult to obtain using bulk spectroscopic techniques, but are crucial to accurately modeling electrochemical processes.

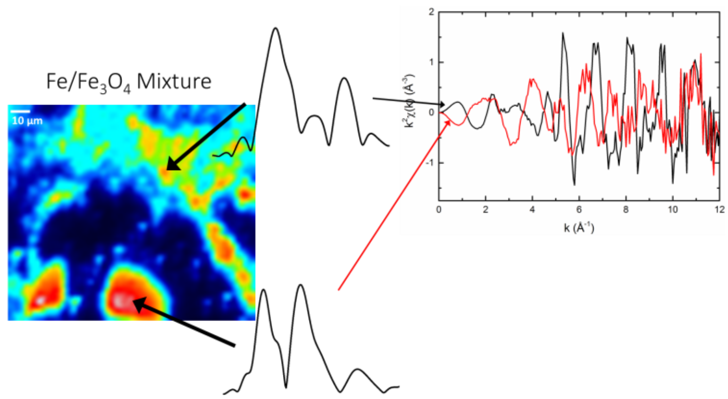


Figure 1. Fe/Fe_3O_4 materials. We are clearly able to spatially distinguish between Fe and Fe_3O_4 with the full EXAFS spectra. The signal to noise ratio is good enough to model EXAFS spectra (single scan).

The commissioning experiments were conducted and demonstrated feasibility, Figure 1. Remarkably, with a single scan, the quality of the data was sufficient for modeling. Several experimental improvements are planned for next year, including stabilizing the mounting of the sample so less movement within the beam is noted.

Milestones

- For FY 2017, measure battery samples using µ-EXAFS
- Correlate the data with modeling and other bulk characterization and electrochemical data.

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 the 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. The goal of the project is to develop a quantitative method for strain measurement in 3D and on the nanoscale, using inverse phase retrieval algorithms.

APPROACH:

We propose to use the nano-diffraction 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 the conventional method, the resolution is limited to the focused beam size and the measured strain is an "average" over the illumination volume, which is not sufficient to address our scientific question. Therefore, new techniques have to be developed. We pursue Bragg ptychography for 3D strain imaging. It is done by analyzing the Bragg diffraction intensity change on a flat 2D detector from pixel to pixel using an iterative phase-retrieval algorithm. Previous work has shown that 2D strain distributions with a resolution better than the focus size could be obtained. In this work, we will extend this technique to a 3D case to obtain a resolution substantially below 10 nm, and then apply it to study the strain in the Si fin of a FinFET *in operando*. So far we have achieved the following milestones in the past two years.

1. In FY 2015, we developed a forward diffraction modeling tool to generate synthetic diffraction data and then applied the inverse technique to obtain the strain field in the crystal. By comparing the input and output strain fields, we explored the limitation and accuracy of existing inverse algorithms, and obtained the optimum experimental condition for the best result.
2. In FY 2015, we investigated the impacts of dynamical diffraction effects on Bragg Coherenet Diffraction Imaging (CDI) and explored the limit of this technique, both in theory and experiment.
3. In FY 2016, we conducted the first Bragg ptychography experiment at HXN and succeeded in reconstructing the strain field of a thin film system at a resolution of ~10 nm. The computer code was debugged and the inverse phase retrieval algorithm was optimized.

TECHNICAL PROGRESS AND RESULTS:

Our efforts in the earlier fiscal years mostly focused on investigating the limitation of the inverse phase retrieval techniques in the Bragg case and debugging the computer code. In particular, we studied the impact of dynamical diffraction effects on Bragg CDI reconstruction, both in theory and in experiment. The observed experimental results were explained well by our theoretical modeling. In FY 2016, the effort was focused on the Bragg ptychography experiment at the HXN beamline using the nanobeam. We succeeded in reconstructing the strain field of a thin film system at a resolution of ~ 10 nm. We evaluated and compared different reconstruction algorithms, and proposed a new one based on the maximum likelihood principle, which seems to have worked best in our case. With the knowledge gained, Bragg ptychography for strain measurement has become more mature at the HXN beamline.

The term of the postdoctoral research associate working on this project ended on June 1st, 2016. Because the postdoc was away from the Lab on leave last year, there is a significant delay in publishing these results. Measurement on a real FinFET device at the HXN beamline also lags behind our original schedule, since we are waiting for our collaborator to provide it. Even though the project is officially completed, we hope to accomplish our initial goal this year.

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.

TECHNICAL PROGRESS AND RESULTS:

In year three, the LDRD had two different strands extending existing analytical tools, such as the Complex Modeling Infrastructure (CMI), and also looking at some promising new technologies for accelerated data analysis and visualization.

Complex Modeling Infrastructure: 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. We seek to overcome these difficulties, by combining multiple experimental and theoretical inputs in a single structure determination and/or structure refinement computational procedure. To overcome the increased complexity in the nanoscale structure, we combine multiple experimental inputs such as pair distribution function (PDF), small angle scattering (SAS), local chemical constraints (neighbor co-ordinations, allowed bond angle ranges) and theoretical energy calculations in a combined optimization procedure. The extra inputs that the solved structure needs to satisfy allow us to compensate for its more degrees of freedom and for insufficient signal in the experimental data. In FY 2016, we have released an updated version 2.0 of DiffPy-CMI. As a part of the new release, the source repositories at GitHub were set up for automated testing and test coverage analysis for the supported operating systems and Python versions. This setup allows us to promptly detect platform-dependent bugs or broken dependencies, which would be otherwise much harder to identify and fix. The new version 2.0 of DiffPy-CMI has been downloaded over 350 times since its release in March 2016.

A major highlight for the science impact of the DiffPy-CMI framework has been publication of our paper in Nature Communications, which revealed an unexpected alternate structure in ultra-stable gold nanoclusters $Au_{144}(SH)_{60}$. The study discovered existence of polymorphism in the well-studied nanoparticles of gold $Au_{144}(SH)_{60}$, which may assume either the formerly known icosahedral structure or a structure based on Marks Decahedron. The DiffPy-CMI software has been instrumental for fitting the experimental X-ray data and for automated generation and scanning of candidate structures.

NSLS-II Coherent Hard X-ray Scattering (CHX) and Coherent Soft X-ray Scattering (CSX-1) Beamlines Analysis Software: We developed improved versions of the one-time and two-time correlation software, adding capabilities to eliminate bad frames automatically from the analyzed data for improved accuracy. In addition, the software was adapted to handle streaming data, allowing users to analyze the data as it is created, allowing them to determine data quality on the fly.

Combining Visual Analytics and Deep Learning: This was a new FY 2016 effort. Deep learning is a very powerful technology for classification and recognition problems. Due to its complexity, it is also difficult to understand the intrinsic learning process and intermediate results and thus quite challenging to debug. An interactive framework was built on modern visual analytics technology that helps designers of deep neural networks to better understand, diagnose, and refine these massive structures. It consists of a set of interlinked, complementary high-dimensional information displays as well as mechanisms that map the information items back into their native network representation. This year, we successfully completed survey work of up-to-date visualization techniques for deep neural networks and devised a prototype system to visualize functional maps of the Convolutional Neural Network with different levels of details. In addition, we extended the concept of our existing context map work to facilitate the network display by replacing attribute-data pair with the class-neuron pair.

Analysis on the Wire (AoW) – This was a new effort in FY 2016. On-the-wire processing can provide real or near-real time information to speed up decision making processes, *e.g.*, in computational steering, in order to optimize and prioritize information routing and correlation, and to offer additional processing cycles to free data center resources. It is anticipated that AoW will be beneficial to NSLS-II experiments by facilitating decision making through the early processing of acquired data. Our approach is to connect one or more (federated) network devices that need to be programmed (and/or coordinated as a distributed computer) to recognize specific data flows and transparently apply certain types of computations, using suitably designed algorithms, on the data of network flows before forwarding them to their destination. In FY 2016 (the last 7 months), we evaluated the advertised characteristics and available information of candidate networking hardware to determine its suitability for use in the project and identified potential solutions for further evaluation in a testbed environment. We further experimented with available Software Defined Networking (SDN) software components in a worst-case scenario to determine their suitability for the development of the AoW framework and testing on the planned testbed. Our investigation indicated that even in a worst case scenario, the minimum overhead imposed by the on the wire processing is reasonably low, which makes the approach feasible. Furthermore, the developed algorithm establishes a basis for future comparison to forecasts based on streaming data from Smart Meters.

Tissue-specific Metabolic Models in Plants

LDRD Project # 14-028
J. Schwender

PURPOSE:

With the number of sequenced genomes and the amount of –omics data increasing exponentially, predictive models converting these massive data into biological knowledge become progressively more important. Genome-scale models of metabolism have emerged as a preeminent tool of predictive modeling in systems biology. Organism specific metabolic models are being constructed based on the information on all metabolic enzymes encoded in their genomes. Based on such genome scale metabolic networks, Flux Balance Analysis became the workhorse of predictive biology.

Compared to the advanced state of genome-scale metabolic modeling of microbial metabolism, the methodology and application of such modeling techniques in plants is lagging behind. One main reason is that plants are more complex organisms of multicellular organization. To be realistic, tissue-specific metabolic models need to consider the different pattern of gene expression activity in different tissues. The objective of this project is to derive high-quality genome-scale metabolic networks in plants, to differentiate these into tissue-specific networks based on gene expression data and to functionally connect the cellular models to simulate organism-scale metabolic activity. For this purpose, genomic data and literature were mined, existing computational simulation tools were used and adapted, and new code was developed. This project is synergistic for future efforts in the Biology Department to create an integrated program in quantitative plant sciences. It will enable us to answer DOE Office of Biological and Environmental Research (BER) proposal calls for metabolic modeling of plant species relevant to DOE and its biofuel 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 DOE BER.

APPROACH:

Genome scale metabolic models can be considered to contain a superset of the metabolic reactions ("master metabolic network") present in a given organism. Not every reaction encoded by the genome can be considered to be active at any time and under any environmental condition. Moreover, plants are multicellular organisms with different tissues like leafs, flowers or roots, each having specialized cells. Specialized cells tend to use only a sub-set of the genome encoded enzyme repertoire. Thus, modeling and simulation of cellular metabolism in a plant requires deriving tissue / celling type specific sub-networks. This can be done based on cell specific gene expression data. Microarray and next generation sequencing technology (RNAseq) allows gene expression to be determined comprehensively and in a quantitative way.

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). A method to integrate tissue specific gene expression data with the model to derive functional sub-networks was to be derived (Aim 2).

TECHNICAL PROGRESS AND RESULTS:

Aim 1, Genome scale metabolic network reconstruction: A genome scale metabolic network was developed for *Arabidopsis thaliana*, the preeminent model organism in plant science. The model features 11 compartments, 3889 metabolites, 5772 reactions and 1479 genes. The model was encoded and tested in the COBRA toolbox environment. Since the Schwender Lab has expertise in plant lipid metabolism, particular emphasis was put into defining the sub-network of glycerolipid metabolism in the most possible/realistic detail. In conventional plant metabolic models, lipid compounds that are represented as single metabolite species are actually complex and diverse classes of molecular structures. For example, phosphatidylcholine is a glycerolipid with two fatty acids attached to its glycerol backbone-structure. We consider 14 major fatty acid species to be present in *Arabidopsis* leafs. Allowing for all possible permutations, there are 196 molecular species of phosphatidylcholine. To generate the fully detailed glycerolipid subnetwork, we programmed a Visual Basic Applications Excel Macro that can automatically expand 14 different fatty acid species to each of the 196 phosphatidylcholine, phosphatidic acid, phosphatidylethanolamine, phosphatidylglycerol, phosphatidylinositol, phosphatidylserine, 1,2-diacyl-sn-glycerol, CDP-diacylglycerol, monogalactosyl-diacylglycerol, digalactosyl-diacylglycerol, sulfoquinovosyl-diacylglycerol species and 483 triacylglycerol species. About 4000 reactions connecting these species were automatically derived.

Aim 2, Construction of tissue-specific metabolic models: Four tissue specific models were derived representing leaf, stem and root cells. To simulate whole plant growth, we connect leaf, stem and root tissue-specific models by nutrition transport reactions (sucrose, glutamine). Briefly, there are separate day- and night- time simulations. For the day simulation, photosynthesis is active. The leaf model will absorb light and fix CO_2 to meet the exact requirements of the plant growth during the day as well as store starch for night usage. The night simulation has no photosynthesis activity. The leaf will break down the starch stored for its own consumption and for stem and root growth. All sub models for the three tissues in day or night were constrained by particular data derived by mining the plant physiology literature.

In addition, data for gene expression in different tissue and cell types of *Arabidopsis* were applied to the set of models, with the goal of making predictions of pathway flux more precise and realistic. This part turned out to be more challenging than expected. While exploring existing algorithms to integrate transcriptome data into flux prediction, we realized that the prevalent method of flux prediction itself might be too unrealistic. Linear programming is the widely used method for prediction of individual flux states of cellular networks. While computationally convenient, the problem with Linear Programming is that it gives access to only one specific numeric solution (state of cellular flux), while there is a large space of alternative solutions. In a way Linear Programming picks rather arbitrarily one solution that yields too little information about the entire solution space. Therefore, we adopted the idea of random sampling of the solution space, which turned out to require re-programming of existing code. We first developed code to obtain loop-less solutions (adapted from Sybil toolbox). We then revised the random sampling code in the COBRA toolbox to suit the size and complexity of our genome scale network.

Next we worked on the integration of gene expression data based on the iMAT algorithm, which requires transforming continuous numerical data into discretized information on gene activity. We decided to base our methods development on a published gene expression dataset which features expression profiles for multiple tissues and developmental stages of *Arabidopsis thaliana*. This allows us to discretize gene expression into on/off calls based on the range of expression a gene has across different tissues. The iMAT algorithm code in the COBRA toolbox was then adapted to work properly with our input model and the expression data.

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 yielded fundamental insights into catalysis, gained from the ability to perform spectroscopic studies at unprecedented gas pressures using the Coherent Soft X-ray Scattering-2 (CSX-2) beamline, a world-class soft X-ray beamline at the National Synchrotron Light Source II (NSLS-II). The planned experiments demonstrated 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, which were both carried out on reducible oxides (*e.g.*, ceria and titania), such a mechanistic understanding led to valuable concepts 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, the synthesis of methanol from CO_2 hydrogenation 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.

Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and X-ray absorption spectroscopy (AP-XAS) give us the ability to probe catalysts dynamically at pressures that are typically in the Torr regime, revealing the chemical state of the active phase from catalysts in the presence of weakly adsorbed or unstable critical intermediates. The new CSX-2 beamline at NSLS-II combines these two techniques successfully.

TECHNICAL PROGRESS AND RESULTS:

The project finished, accomplishing most of the initial objectives.

We were extremely active in setting up and commissioning the end stations for AP-XPS and AP-XAS at NSLS-II. The AP-XPS end-station achieved full operation, while operations at the AP-XAS station have reached the science commissioning stage. Beam will be offered to general users by the summer of 2017.

Using the already available end-station for AP-XPS, we studied the transformation of CO_2 into methanol on a series of $Pt/CeO_2/TiO_2$ catalysts (Figure 1) with and without doping with cesium. A manuscript is almost finished and will be submitted to a high impact journal soon. Our results show that the active phase of the catalysts contains metallic Pt in contact with reduced ceria. The

Pt-ceria interface is essential for the conversion of CO_2. Cesium promotes the bonding of the CO_2 reactant.

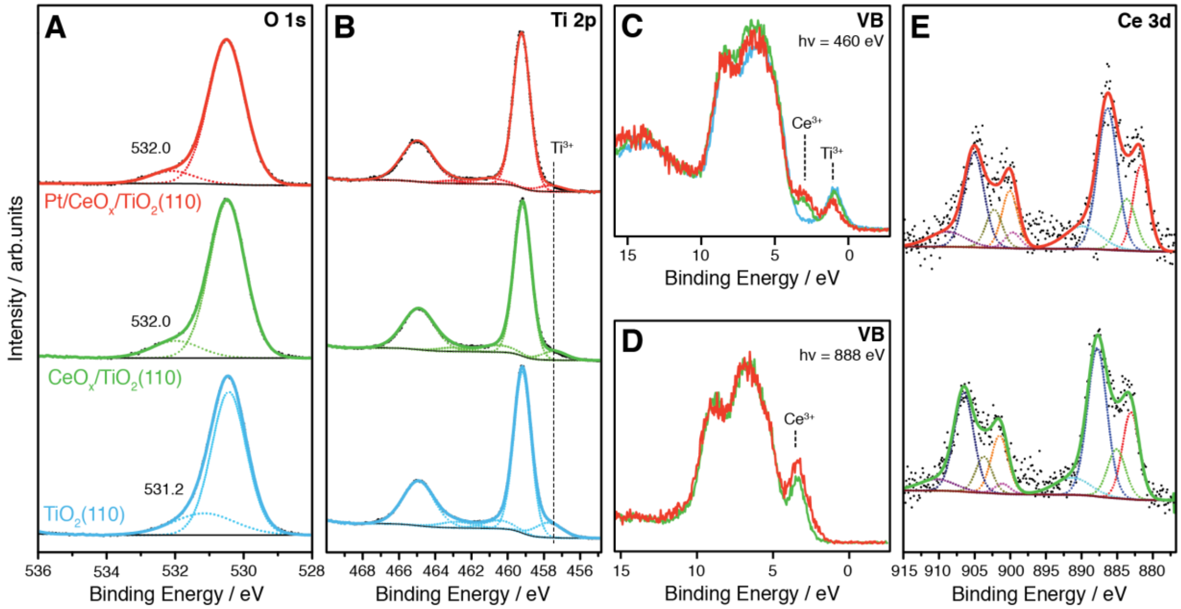


Figure 1. Comparison of the catalyst systems under 100 mTorr CO_2 + 900 mTorr H_2 at 473 K. **(A)** O 1s, **(B)** Ti 2p, **(C)** Valence Band (VB) on-resonance for Ti, **(D)** VB on-resonance for Ce, **(E)** Ce 3d. Blue: TiO_2(110), Green: 0.1 Monolayer Equivalent (MLE) CeO_x/TiO_2(110), Red: 0.2 MLE $Pt/CeO_x/TiO_2$(110).

The main objective for the rest of this year will be to make the AP-XPS end station at the CSX-2 beamline fully operational for general users.

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 first develop and then 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 both 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 period 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 actively working to catalyze the chemical reaction. By obtaining the data in an *operando* condition, it becomes possible to directly correlate the information about the system obtained from the measurements using each technique. The capabilities being developed through this effort are intimately linked to the proposed efforts of the Integrated Center for Energy Sciences for Catalysis Science, the core research programs at the CFN and Chemistry Department, as well as the Synchrotron Catalysis Consortium: in short, the methods being developed within this LDRD are well-aligned with the overall Laboratory strategy.

APPROACH:

Supported metal nanoparticles are commonly used in heterogeneous catalysis, and as such 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 either 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 through the use of microfabricated catalytic reactors that are compatible with a broad range of photon and electron based characterization methods based on imaging, spectroscopy and diffraction. These reactors allow provision of reactant streams at temperatures of up to 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. This allows us to make direct comparison between the measurements in an unprecedented fashion.

TECHNICAL PROGRESS AND RESULTS:
During the past year, we completed a study on ethylene hydrogenation by Pd/SiO_2 heterogeneous catalysts. In this work, we described a multi-modal exploration of the atomic structure and chemical state of silica-supported palladium (Pd) nanocluster catalysts during the hydrogenation of ethylene in *operando* conditions that variously transform the metallic phases between hydride and carbide speciations. The work exploits a micro-reactor that allows combined multi-probe investigations by high resolution transmission electron microscopy (HR-TEM), X-ray absorption fine structure (XAFS), and microbeam Infrared (μ-IR) analyses on the catalyst under *operando* conditions. The work specifically explores the reaction processes that mediate the interconversion of hydride and carbide phases of the Pd clusters in consequence to changes made in the composition of the gas-phase reactant feeds, their stability against coarsening, the reversibility of structural/compositional transformations, and the role that oligomeric/waxy byproducts (here forming under hydrogen-limited reactant compositions) might play in modifying activity. The results provide new insights into structural features of the chemistry/mechanisms of Pd catalysis during the selective hydrogenation of acetylene in ethylene—a process simplified here in the use of binary ethylene/hydrogen mixtures. These explorations, performed in *operando* conditions, provide new understandings of structure-activity relationships for Pd catalysis in regimes that actively transmute important attributes of electronic and atomic structures. This work has been recently submitted for publication to the Journal of the American Chemical Society.

In addition, we have continued the studies that we initiated last year associated with the atomic segregation that occurs in a model bimetallic catalyst composed of NiPt. In these studies, we utilized the microfocused beamline at the Swiss Light Source, as no beamline at NSLS-II is presently capable of providing the beam parameters necessary for these studies. In fact, this is one of the primary pieces of information we have gleaned from the past year's studies: proper *operando* studies can only be successful acquired from synchrotron beamlines that provide a spot of 20 to 50 µm. We discovered this through experiments conducted at the Submicron Resolution X-ray Spectroscopy (SRX) beamline, as well as the X-ray Powder Diffraction (XPD) beamline. In the case of SRX, the probe has extreme flux in a 100 nm spot. However, there is very little catalyst that is illuminated by this flux, leading to insufficient signal to noise. In the case of XPD, because of the lack of focusing optics, the only way to confine the probe to the active area is using slits to eliminate the beam from the reactor bulk: this leads to too small of a flux to obtain the required signal. Thus, one of the primary outcomes from this LDRD is the realization that a particular set of parameters is needed for the micro-reactor approach. This information has been communicated to specific Beamline Scientists at NSLS-II, so that it can be considered a part of the NSLS-II capability portfolio (*e.g.* Ryan Tappero, Juergen Thieme – X-ray Fluorescence Microscopy [XFM], Milinda Abeykoon, Eric Dooryhee, X-Ray Atomic Pair Distribution Function [PDF]).

Imaging Electronic Texture in High-Temperature Superconductors

LDRD Project # 14-037

S. Wilkins

PURPOSE:

The goal is to develop the use of coherent scattering techniques at the Coherent Soft X-ray (CSX)-1 beamline of the National Synchrotron Light Source II (NSLS-II). We will examine strategic samples of cuprate high-temperature superconductors (HTSC).

APPROACH:

This project will help the CSX-1 beamline team to produce data collection software and data analysis software for coherent diffraction applications.

TECHNICAL PROGRESS AND RESULTS:

This LDRD in the X-ray Scattering Group of the Condensed Matter Physics and Materials Science Department was to apply the new soft X-ray coherent capabilities of NSLS-II to the important question of the "stripes" found in the cuprate HTSC materials. The promise of 1000 times more coherent flux at the CSX beamline was indeed realized as soon as the NSLS-II facility opened for business in 2015 and this was applied to the better-ordered "stripe" material $La_{1.825}Ba_{0.125}CuO_4$ (LBCO) in one of the first experiments at CSX. LBCO's relatively long correlation length of 26 nm, compared with only 5.5 nm for the parent superconductor YBCO, meant that the resonant coherent diffraction signal level was sufficient. This successful experiment was published in Physical Review Letters in October 2016, the first such paper to appear from the NSLS-II.

It was known experimentally that charge-density-wave (CDW) "stripe" order coexists with superconductivity in essentially all cuprates. Since one expects that the CDW order would compete with superconductivity for electronic density of states near the Fermi level, the exact nature of the CDW and its relationship with superconductivity has come under intense scrutiny. A common theoretical scenario in trying to rationalize the cuprates is that quantum fluctuations near a quantum critical point might drive electron pairing and hence superconductivity. Theoretical proposals include bold ideas, such as that pairing may be driven by CDW fluctuations or that static CDWs may intertwine with a spatially-modulated superconducting wave function.

The result tested the dynamics of CDW order in $La_{1.825}Ba_{0.125}CuO_4$ by using X-ray photon correlation spectroscopy at the CDW wave vector (0.24,0,1.5), resonantly at the Cu L_3-edge using the new CSX-1 beamline. The main result was that the CDW domains were surprisingly static, with no evidence of significant fluctuations up to the 2.75 hour duration of the measurements, shown as a "waterfall" plot in Figure 1. It was also impressive that the beamline was sufficiently stable on this time scale, given that the samples were cooled as low as 10K. The visibility of the coherent diffraction "speckles" was found to be close to the estimated value, indicating that fluctuations faster than the exposure time were also excluded from the interpretation.

The optimized samples of this initial measurement were actually not superconducting, because of the well-known anomaly in the T_C *vs* doping curve at x=0.125 in $La_{2-x}Ba_xCuO_4$. This observation of non-fluctuation of the CDW was therefore repeated at x=0.11 and 10K where the sample was superconducting. The same static result was found, clearly ruling out the connection between CDW fluctuation and superconductivity, at least in this cuprate system. The result also opens up a new direction in these investigations, to explore the physics of the pinning, which must be responsible for the static CDW domain pattern responsible for the speckled coherent diffraction pattern. We showed that CDWs in LBCO are well-matched to the capabilities of the CSX beamline of NSLS-II. The resonance at the Cu L_3-edge is near the optimum performance of CSX where the high coherent flux is estimated to reach 10^{13} photons per second at the sample. Statistically significant speckle patterns can be obtained in less than a second and reasonable exposures will achieve Bragg Coherent Diffractive Imaging (BCDI)-quality data. These results led to the next step: experiments to continue exploring this "pinning" theme.

In order to avoid beamline drift problems between the illuminating beam and the sample, fabricated pinholes in thin sheets of gold, were laid directly on the face of the LBCO samples, cleaved to their c-axis, as shown in Figure 2. Since the (0.24,0,1.5) peak on resonance appears at near normal incidence, the shadowing effect of such a sample-pinhole is minimized. The first experiments have shown this method to work, but have not led to any image reconstructions. It is expected that we will be able to image the individual CDW domains contributing to the speckle pattern. We can see directly from the data of Figure 1 that there are about 50 speckles in a linear scan. Since the speckle size is the reciprocal of the beam size and the peak envelope is the reciprocal of the domain size, we can say already that the image will contain about 50 domains across its width, as set by the 10 micron pinhole used in that experiment.

Using the on-sample pinhole to prevent beam-sample drifts, we then looked for ways to "depin" the CDW domains, to investigate the physics of pinning to relate to the body of theoretical work on this subject. The simplest experiments were to look whether small temperature changes can excite rearrangements of the CDWs. The first results here suggest that the observed pattern of pinning is extremely robust and survives temperature excursions as high as 200K, well above the melting temperature of the CDW and close to the High Temperature Tetragonal-Low Temperature Orthorhombic (HTT-LTO) structural phase transition. This "return point memory" effect has been seen before in magnetic systems, but never for CDWs. The next step will be to look for the pattern on pinning sites in the LTO structure by BCDI.

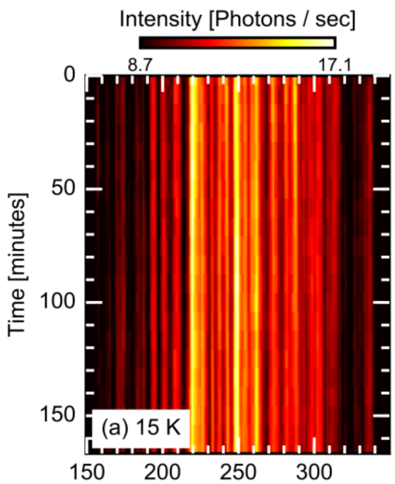


Figure 1. Time dependence of the coherent diffraction pattern observed for LBCO at x=0.125 and 15K. A single line through the speckle pattern, recorded on a CCD detector at the CSX beamline of NSLS-II, is shown in the horizontal as a function of time in the vertical.

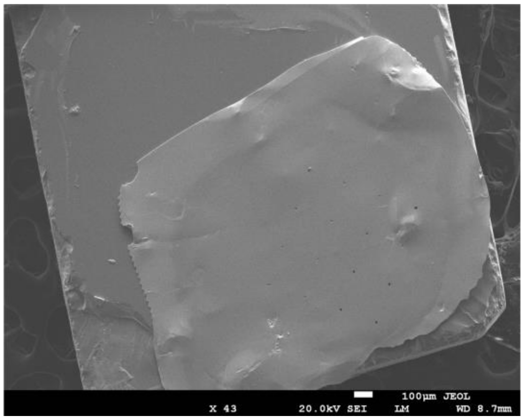


Figure 2. Scanning electron microscope image of an LBCO crystal covered with a fabricated array of pinholes, 10 microns in diameter. This will be used to confine the coherent illumination of the X-ray beam to study a particular region over a wide temperature range.

Bunch-by-Bunch Beam Position Monitor for eRHIC

LDRD Project # 15-003

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

PURPOSE:

The objective is to develop a beam position monitor (BPM) capable of resolving closely spaced bunches comprising the particle beam as motivated by the BNL-based initiative for a future electron-ion collider, eRHIC. The eRHIC design includes a novel cost-effective approach that transports multiple bunches of different energies in a common vacuum chamber. This project aims to develop a method to accurately measure the beam trajectories to ensure optimal collider performance. If successful, this development will reduce risk and cost in the eRHIC project.

APPROACH:

While a conventional BPM design 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. The adopted approach is well-suited for measuring the large range (30-50 mm) of transversely displaced beam trajectories. The BPM pickup consists of narrow gaps in the upper and lower walls of the vacuum chamber, which will be bridged by low-impedance resistors and coupled out using fast pulse transformers or transistors.

TECHNICAL PROGRESS AND RESULTS:

In FY 2015, simulations were completed to optimize the geometry, while minimizing the beam impedance, to estimate the signal strength generated by the beam's image currents and to analyze the signal transport through the resistor/transformer network. The assembly drawing for this design is shown in Figure 1. An engineering design, with dimensions adapted to the geometry of the vacuum chambers of the BNL Accelerator Test Facility (ATF), was produced and submitted for fabrication to BNL Central Shops in December 2015.

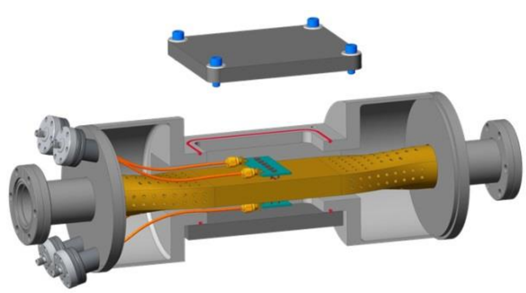


Figure 1. Assembly drawing of the proposed eRHIC time and space resolving BPM as adapted to the geometry of the ATF.

The detector (mechanical portion only), fabricated by Applied Vacuum Technology, was received in March 2016 (Figure 2, left). A method was developed, using a small oven and special soldiering material, for mounting and securing up to 35, 2 mm-by-0.4 mm, ~ 2 Ω resistors (model SMD0805 by Vishay) across each of the two narrow gaps of the detector. The transformers (model JA4220-AL by SMT) were procured and mounted on a printed circuit board prototype, which was then mounted onto the detector (Figure 2, right).

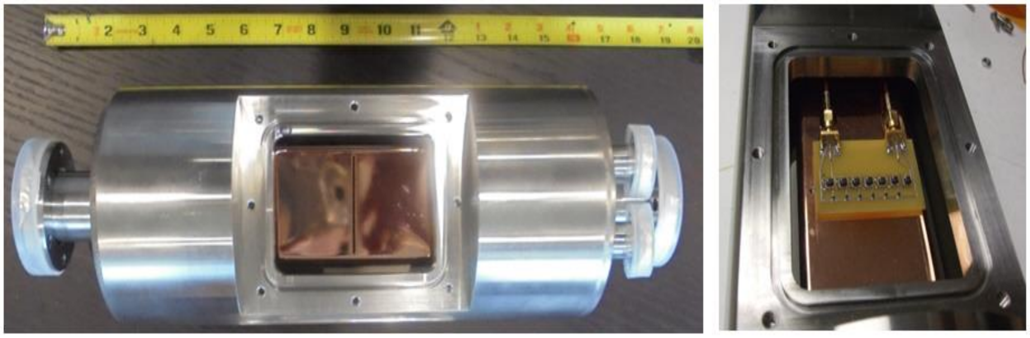


Figure 2: Beam position monitor (left) mounted in a cylindrical vacuum enclosure with tapered inserts (inside enclosure) to match the geometry of the detector to the ATF beamline. The signals are read out through SubMiniature version A connectors connected to each end of the series of transformers (right).

The detector was installed (Figure 3) and operated with electron beams at the ATF in July 2016. Adequate signal amplitudes and position sensitivity were observed; however the output signals were longer than expected. This discrepancy from simulations was determined to be due to an inadequate model of the transformers. Two alternate signal read-out approaches are presently under development: (1) a transformer-based readout, model A9900A by SMTWideband Tranformer Coilcraft, which is of the right type and should provide much improved results – however, the lack of a realistic model still poses some risk and (2) a transistor-based readout, model AT-32033 by Avago, which would be an option if the performance proves inadequate – the transistor offers a more predictable alternative since good models exist making simulations more reliable. The printed circuit boards for both designs and the corresponding components have been procured and are ready for assembly.

Figure 3: Beam position monitor mounted in the BNL ATF beamline.

Finally, development started on using narrow ceramic breaks coated with resistive films (to replace the resistors) to allow removal of the external vacuum chamber, as this is needed to make this BPM design approach practical for eRHIC.

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 will readily 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.

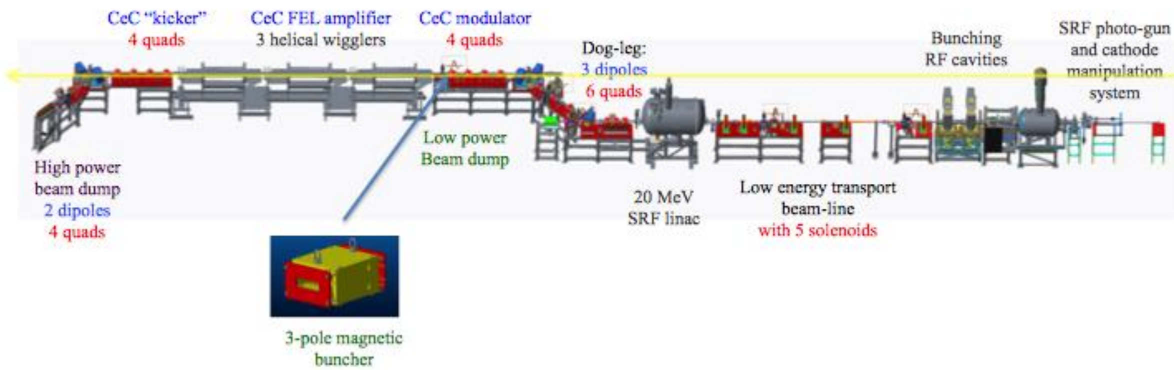


Figure 1. Layout of the experiment: 22 MeV electron beam from the superconducting radio frequency (SRF) linac will interact with ions circulating in RHIC's yellow ring in the CeC modulator section. Amplification of the signal from the CeC Free Electron Laser (FEL) system achieved by a 3-pole wiggler would be studied using dedicated Infrared (IR) diagnostics (not shown).

APPROACH:

This technique is undergoing 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, published in four conference papers and submitted to a refereed journal, we are designing, procuring and commissioning hardware for the ACeC experiment (Figure 1). Part of the beam diagnostics, purchased using the LDRD funds, is currently installed in the CeC proof-of-principle system at RHIC. We would be ready to use them for the ACeC experiment after the CeC accelerator is commissioned during RHIC Run 17. We determined parameters of the chicane system needed for the ACeC experiments and started the selection process for the vendors. We have developed a RHIC ramp suitable for the ACeC studies.

Milestones achieved for FY 2016:

- High fidelity simulation of ion's interaction with realistic electron beam in quadrupole channel (Figure 2)
- Procuring and installing of the optical diagnostics
- Commissioning beam and installing IR optical diagnostics
- Design of the chicane for the ACeC experiment (Figure 3).

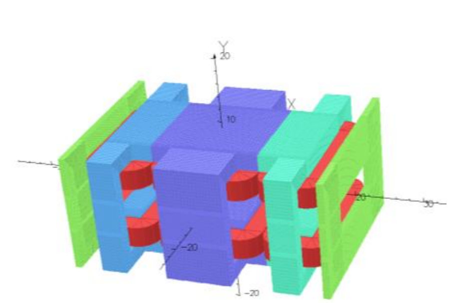


Figure 3. 3D rendering of the 3-pole magnetic chicane/buncher.

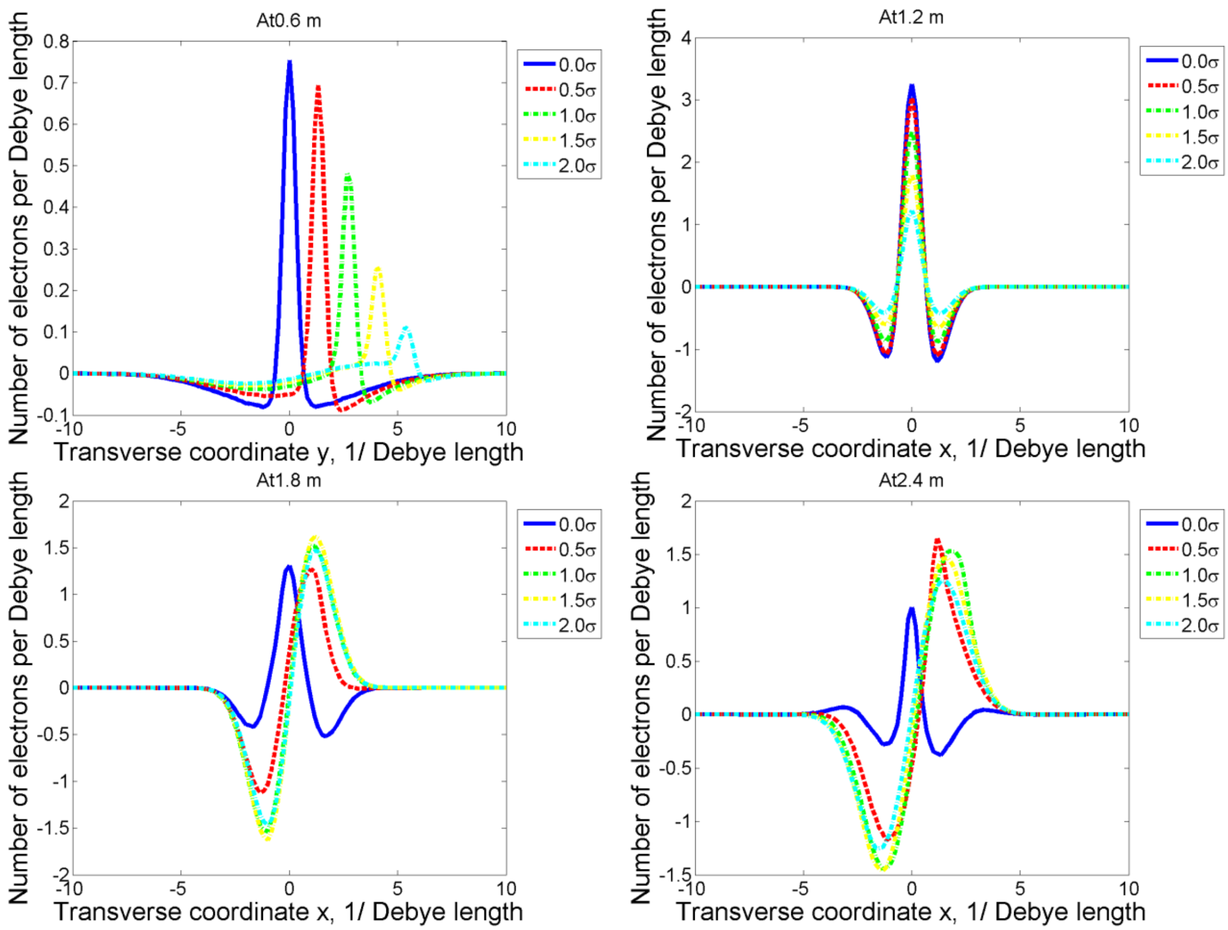


Figure 2. Evolution of the transverse response in realistic (finite) electron beam on the ion propagating with displacement from the beam axis. Interaction occurs in the CeC modulator containing four quadrupole magnets..

Five graduate students from Stony Brook University took part in this research project. Overall, we published twelve conference proceedings related to this research project and prepared one publication for a refereed journal. Our research was presented in two oral talks as well as in three invited talks.

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

LDRD Project # 15-006

W. Xu

PURPOSE:

The original objective of this LDRD project was to design, prototype and test a high current superconducting radio frequency (SRF) cavity for the eRHIC SRF linac for the Linac-Ring design, which requires the cavity to operate at 16 MV/m with a quality factor of $2{\cdot}10^{10}$ in continuous wave (CW) mode. To meet the requirements of the Ring-Ring eRHIC design, an additional R&D effort will be added in order to study the cavity's performance above 25 MV/m, which is the SRF linac gradient for the Ring-Ring eRHIC design. The SRF cavity required for proton bunching and the storage ring for the Ring-Ring eRHIC design is 16 MV/m in CW and 9 MV/m, respectively. So, all the SRF requirements or performance for both eRHIC designs will be studied with this cavity, by different post-processing procedures and vertical tests. With these tests, the specifications for the future eRHIC cavity's processing and test procedure 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. The multiphysics simulations are to analyze multipacting and the Lorentz detuning factor calculation.

The cavity has been undergoing fabrication at RI Research Instruments GmbH Germany since April 2016. Through weekly telephone conferences and visits for critical inspections and tests, we are working/monitoring closely every fabrication step from design of the dies to deep drawing or hydroforming, machining, chemistry and electron-beam welding and tuning.

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:

The physics and engineering design of the cavity was completed in February 2016. A 650 MHz 5-cell eRHIC cavity was 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 was completed, which includes mechanical analysis of the cavity's tuning plate design. This enables a helium vessel and cryomodule to be added onto this cavity for an eRHIC cryomodule test. Figure 1 shows the completed 5-cell cavity design.

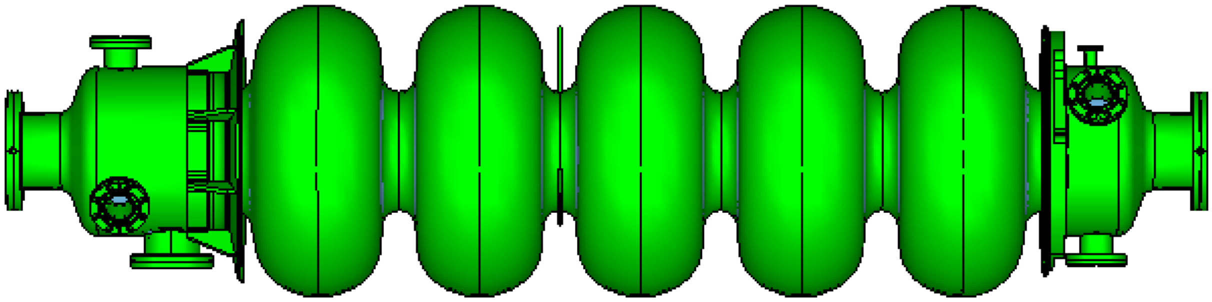


Figure 1. 5-cell 650 MHz eRHIC cavity.

Milestones

Cavity fabrication:

- The Nb cavity is undergoing fabrication at RI and it is expected to be completed in early April.

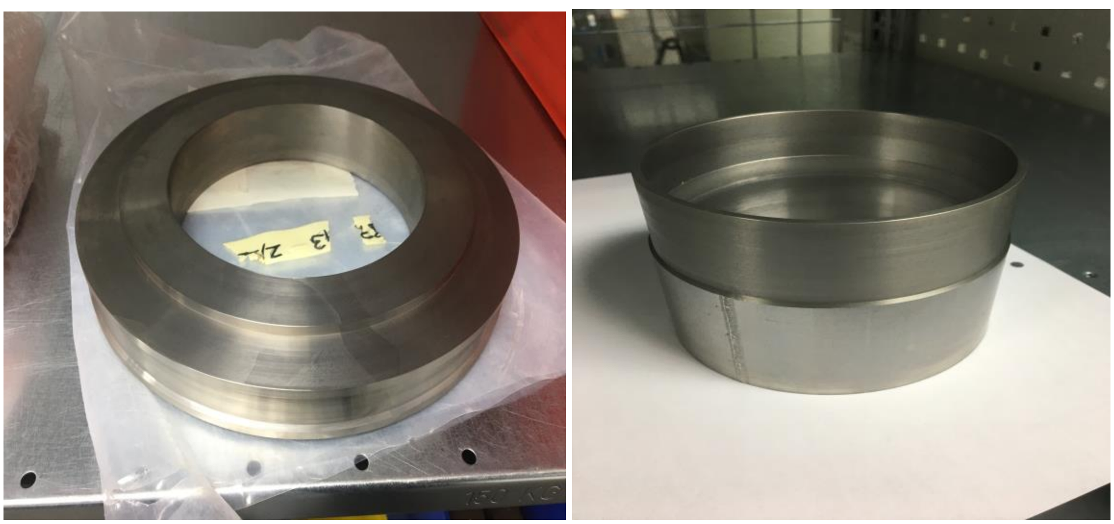


Figure 2. Beam-tube parts of the 5-cell cavity.

Preparation for the vertical test:

- The first cavity post-processing will be done at RI. The Statement Of Work will be ready to send to RI in early February.
- The vertical test will be carried out at BNL's Large Vertical Test Facility in building 912. A 500 W RF amplifier for the vertical test was ordered, received and tested. An adjustable fundamental power coupler and pick-up has also been designed and fabricated. The mechanical preparation (design, parts' fabrication) will be finished in late February 2017 and will be shipped to RI.
- The first vertical test is expected to occur in July 2017. After that, we will do more post-processing and vertical tests to study the cavity's performance.

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. These nanostructured battery architectures thus incorporate an idealized electrolyte, giving rise to improved performance. The goal of this project is to develop the fundamental understanding necessary to realize this concept.

APPROACH:

Lithium-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. This technology cannot be used to generate *rechargeable* batteries owing to the forming of dendrites during recharging, which short-circuit the device. A long-proposed, but never-realized solution uses a solid polymer electrolyte with sufficient mechanical strength to suppress Li dendrite formation during battery cycling. Lithium 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 is exploring fundamental aspects by leveraging the National Synchrotron Light Source II (NSLS-II) and the Center for Functional Nanomaterials (CFN)) and world-leading expertise in: nanofabrication/electrical characterization of solid-state electronic devices (C. Black); electrochemical properties of battery materials (E. Takeuchi, K. Takeuchi, A. Marschilok); and sophisticated synchrotron X-ray methods for understanding both structural (K. Yager, B. Ocko) and mechanical properties (A. Fluerasu, L. 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 Scattering (CHX) beamline at NSLS-II. We are measuring 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 Scattering. Simultaneously, we are measuring the polymer viscoelastic moduli through X-ray Photon Correlation Spectroscopy by incorporating nanoparticle tracers into the material. We have fabricated confining templates at the CFN using state-of-the-art lithography and etching methods. Looking forward, we will design and fabricate functioning, nanoconfined batteries suitable for *operando* structural and dynamics measurements.

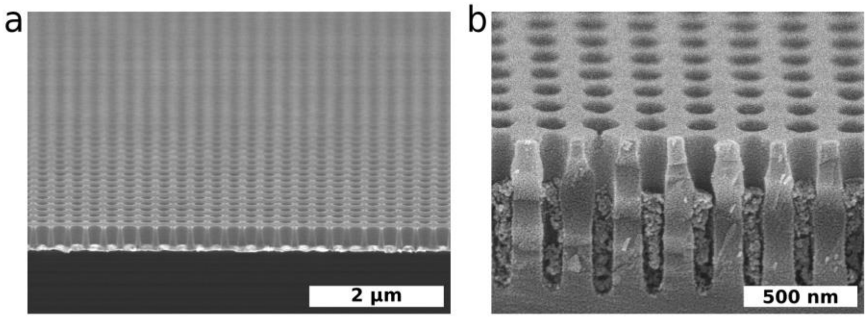


Figure 1: (a) Example of wide-area nanopatterned battery architecture, including a metal bottom-contact for electrochemical cycling. (b) Example of nano-architecture filled with ion-conducting polymer, thereby acting as a high-stiffness, nanostructured battery electrolyte.

TECHNICAL PROGRESS AND RESULTS:

During FY 2016, enormous progress (Figure 1) was made in studying new nano-architectures for battery electrolytes, paving the way towards potentially record-setting battery devices.

Nanofabrication: We developed methods to efficiently fabricate nanoconfined polyelectrolyte membranes. We developed a protocol based on optical interference lithography to enable rapid wide-area patterning, and exploiting subsequent atomic layer deposition to precisely control nanoconfinement size-scale. We moreover developed optimized protocols for infiltrating polymer materials into these nano-volumes. Our nano-architecture design allows for inclusion of electrically-isolated top and bottom electrodes; that is, this nanoconfined electrolyte sits within an electrochemical cell that can be used to test ion conductivity and battery cycling.

Structural characterization: We completed an exhaustive series of experiments to understand how the crystallinity of PEO is influenced by nanoconfinement and additives. We demonstrated that salt additives strongly influence crystallinity; thus additives can be used to tune electrolyte properties. We also showed that while PEO crystallinity is only weakly affected by nanoconfinement, the melting and crystallization behavior (*e.g.* melt temperature or crystallization rate) can be strongly influenced. This supports our hypothesis that nano-architectures can be used to modulate functionality.

Mechanical characterization: We exploited the unique capabilities of the CHX beamline, to enable new 'tracer-based' measurements of the nano-mechanical properties of constrained polymers. We mapped the dynamics (and thus mechanical properties) of nanoconfined PEO materials. Preliminary analysis indicates that we succeeded in greatly increasing the viscosity and modulus of the nanoconfined polymer electrolyte by using nanoconfinement architectures.

Electrical characterization: In order to test our new architectures as functional batteries, we devised a device setup including top and bottom electrodes for electrochemical cycling. Over the last fiscal year, we performed necessary control experiments on simpler electrolytes (including unconfined PEO).

Milestones

Forthcoming experiments will measure the electrical properties of nanoconfined polymer electrolytes (ionic conductivity) and battery architectures incorporating them (capacity, cyclability). By cross-correlating the structural and mechanical measurements, with these new electrochemical measurements, we will be able to probe the fundamental nature of nanoconfined electrolytes, and to ultimately design an optimized nano-architecture battery. Over the next year, we will complete the foundational characterization studies. Following that, we will generate an optimized nano-architecture battery, and report on the capacity and cyclability improvements that can be obtained thereby.

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.A. 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 Department) and tools to be developed as part of this project. While zeolites themselves are the most widely 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 and to develop new experimental capabilities.

APPROACH:

Zeolites are the most important industrial catalysts. They are used for many 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 (models) of industrial catalysts to provide insights on structure–reactivity relationships. Using "model" catalysts, the complexity can be reduced in order to disentangle structural, chemical and electronic effects in the reactions. Zeolites remained a challenge to the surface science community due to the lack of a suitable zeolite model system. It was only recently that the first successful zeolite model was developed by the PI (Figure 1). In parallel, the PI is participating in developing surface science instrumentation for studies at elevated pressures, as opposed to traditional ultra-high vacuum studies. This includes instrumentation at the CFN and NSLS-II: ambient pressure photoelectron spectroscopy (AP-PES), polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) and reactor scanning tunneling microscopy (r-STM). The combination of 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 of research that will allow the elucidation of reaction mechanisms for some of the most important energy-related industrial chemical processes.

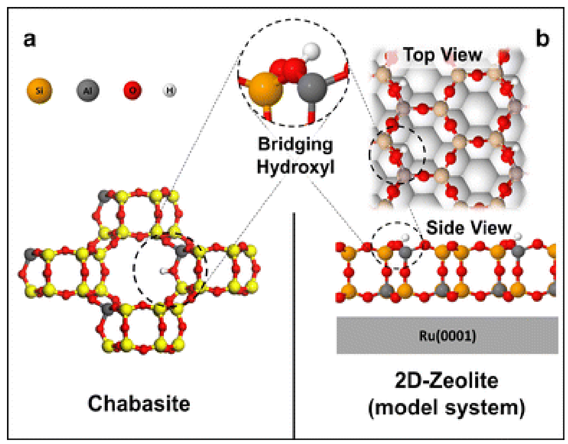


Figure 1. **a**. Zeolite chabasite in its protonated form. **b** Protonated form of the 2-dimensional zeolite model system showing the bridging hydroxyl group. The top and side views of the structure of the model system are shown.

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 were carried out with the IRRAS instrument in the Chemistry Department in collaboration with Dario Stacchiola, a group leader at the CFN since FY 2016. The reaction pathways 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 research started in the second half of FY 2015 when postdoctoral researcher JianQiang Zhong was hired to carry out the experimental work. 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. In order to understand PM-IRRAS to be later implemented at the AP-PES endstation, John Kestell, a postdoc supervised by the PI, built a PM-IRRAS system at the CFN.

In FY 2016, these LDRD-related first experiments at CSX-2 resulted in the first publication from the CSX-2 beamline, including authors from NSLS-II and the CFN (J. Phys. Chem. C 2016, DOI: 10.1021/acs.jpcc.6b02851.). JianQiang 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 mechanistic studies, since the catalytic activity is expected to be affected by the electronic structure of the system. This resulted in a second publication including theory and experiments (Top. Catal., 2016, DOI: 10.1007/s11244-016-0704-x). 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 were carried out and another manuscript was prepared and is ready for submission. We also started exploring methanol adsorption within zeolite nanosheets using AP-PES at CSX-2 and the newly built PM-IRRAS system at the CFN, which resulted in a third publication (Catal. Today, 2016, DOI: 10.1016/j.cattod.2016.07.015). We started experiments to study cracking of small hydrocarbons on the zeolite model; this data is still under analysis and interpretation. We also started the design of the AP-PES+PM-IRRAS endstation.

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. PM-IRRAS standalone implementation, design AP-PES + PM-IRRAS system.
FY17	Develop hypothesis on cracking mechanism and coking. DFT calculations to back this. Move forward with design and implementation of AP-PES+PM-IRRAS implementation.
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.

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 research 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 imbedded in DNA frames to direct their interactions in a programmable manner. Our approach will permit formation of 2D nanoparticle clusters of arbitrary shapes.

Scattering methods: We propose to 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:

The *in situ* measurement of individual meso-structures is an enormous challenge, owing to weak scattering power and large background inherent to such experiments. We have made considerable progress in the development of methods to address this measurement challenge. By combining simulations and experiments, we have devised a robust analysis pipeline that exploits correlation analysis to yield improved signal-to-noise. We have further developed a novel measurement strategy for weakly-scattering samples, which consists of exploiting coherent interference between the sample and a specially-designed "amplifier" nanostructure Figure 1. By combining this amplification method with our angular correlation pipeline (Figure 2), we have demonstrated the ability to measure ultra-small meso-structures (*e.g.* only 8 nanoparticles) in a high-background environment (Figure 3).

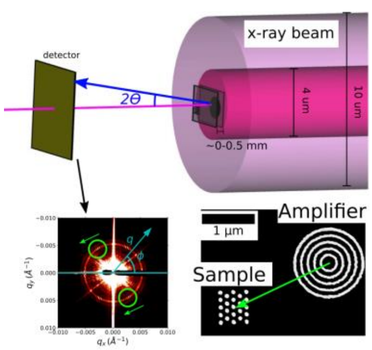


Figure 1. Experimental setup. The amplifier (ring structure) is placed upstream of the sample of interest. The X-ray beam is denoted by the large purple cylinder; the inner cylinder denotes the approximate transverse coherence length (the longitudinal coherence length is large). When the sample and amplifier are within the same coherence volume, the scattering pattern (lower left) exhibits fringes (circled in green) whose spacing and direction are related to the transverse separation between the two scattering entities (green arrow). The lower right shows a Scanning Electron Microscope (SEM) image of a validation structure, where the sample and amplifier were patterned on a single substrate.

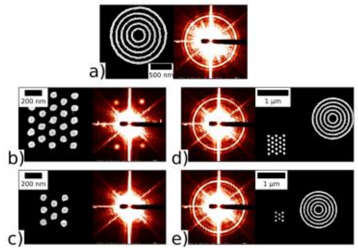


Figure 2. SEM images and Small Angle X-ray Scattering data for some meso-structures. (a) A pattern of concentric rings generates a strong isotropic ring of scattering: this structure is used as an amplifier. (b) A 5x5 array of dots, fabricated as a test sample. (c) A 3x3 array, which acts as a very weakly scattering sample. (d) When a sample is coherently interfered with the amplifier (by patterning them side-by-side on a single substrate, fringes appear in the scattering pattern wherever both sample and amplifier scatter strongly. (e) For a weakly scattering sample (which cannot be discerned above the experimental background) coherent interference with the amplifier generates a visible fringe pattern, *i.e*., the sample alone cannot be resolved; coherent amplification can be used to infer the sample's scattering pattern..

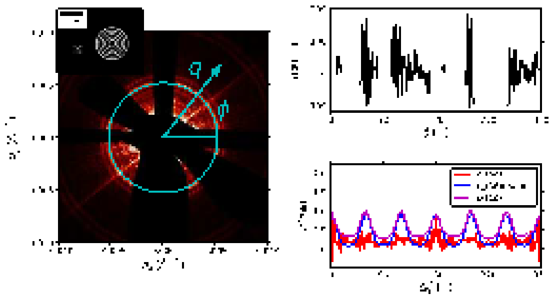


Figure 3. Diffraction pattern measured for a sample (3x3 hexagonal array) interfered with an amplifier (concentric ring structure). The corresponding SEM (upper left). The ring along the blue contour is remapped to a (average-subtracted) 1D curve vs. φ (top right). The first- and second-order angular correlations are plotted (lower right). The first order correlation (red) is flat and noisy. The second-order correlation function (magenta) closely matches the idealized expectation for the known sample symmetry (blue). The interference fringes oscillate as the inverse sample amplifier distances $\approx \frac{2\pi}{1\ \mu m} \approx 6 \times 10^{-4}$ Å^{-1}.

In assembly, we advanced fabrication of chain-like one-dimensional (1D) clusters using the DNA-based self-assembly method. The nanoparticle chain-like structures can facilitate control over optical responses and energy transfer, and they are considered for building magnetic and electrical materials. These functions highly depend on the structure, dimension and fidelity of the assembled chain organization. One of the challenges in building such 1D structures is devising methods for creating hetero-structures and error-forgiving assembly schemes. To address this challenge, we developed a general method of assembling diverse nanoparticle linear architectures (Figure 4) with internal organizations based on a simple DNA origami template. By rationally controlling the number, position, size, and composition of nanoparticles in each layer, a variety of nanoparticle linear structures can be assembled. The relative orientation of adjacent layers can be controlled by the position and sequence of anchoring strands. We have applied scattering and electron microcopy to characterize the structure of these clusters.

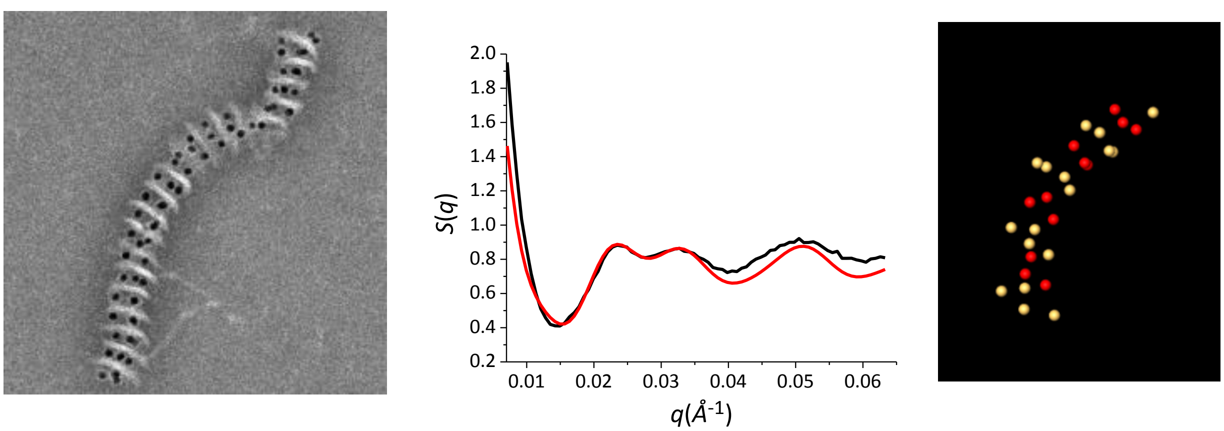


Figure 4. Assembly of the linear cluster (left); the corresponding structure factor, model (red) and data (black) for such clusters (center); and 3D electron microscopy tomography reconstruction of the cluster (right).

Milestones

- Completing the study on the signal amplification based on the coherent scattering
- Conducting plasmonic and electrical study on linear clusters, and applying the developed approach for assembly of heteromaterial clusters
- Submitting two papers on this work for publication.

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. 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 cloud and convection.

Extreme precipitation can have disruptive consequences on society. Accurately modeling of 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 the states, the economy in the 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 achieved 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, the atmospheric model component of the CESM). The detection and analysis of regional climate extremes will be augmented with the establishment of a generalized extreme value modeling framework.

TECHNICAL PROGRESS AND RESULTS:
The project focused on utilizing the strength of high-resolution atmospheric modeling to identify the deficiency and improve the representation of cloud processes in global climate models. In previous years, we contributed to the improvement of the WRF model's capability for modeling at large-eddy scale with the incorporation of a new moisture treatment in the dynamical core; developed building blocks for the one-way integrated WRF-CAM system through establishing physical connections between the explicitly resolved and parameterized representation of common cloud processes. During FY 2016, continued progress was made on 1) testing the existing one-way integrated WRF-CAM in a realistic setting for modeling regional weather extremes; 2) testing a preliminary two-way coupling strategy for WRF-CAM; 3) establishing a generalized extreme value (GEV) modeling framework to enhance the analysis of regional climate modeling; 4) diagnostic study of improved simulations of climatically important low-level clouds by the DOE's Accelerated Climate Modeling for Energy (ACME) model with unified representation of boundary layer turbulence and shallow cumulus convection.

GEV analysis of projected simulations by the National Centre for Atmospheric Research and the Geophysical Fluid Dynamics Laboratory (GFDL) climate models under more extreme global warming scenarios (Figure 1) showed a dramatic increase in the rainfall amount of 100-year events in year 2100 over the Northeastern U.S., but the increase is more than twice as much in the GFDL model. Improvement in cloud process simulations is expected to be able to narrow such uncertainties.

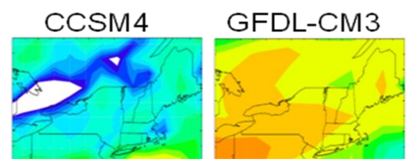


Figure 1. Increase in 100-year rainfall amount projected by NCAR Community Climate System Model Version 4 (CCSM4) and GFDL Coupled Climate Model (CM3) under a high greenhouse gas emission scenario.

Uncertainty in climate change projection at the global scale is largely attributable to difficulty in simulating low-level clouds over the vast marine environment. Our analysis showed that the adoption of the unified schemes (CLUBB and SILHS) in the ACME model dramatically improved the simulated clouds along the cross section that embodies typical oceanic cloud regimes from the coast of California through near Hawaii to the equator (Figure 2). Compared to the control simulation (CNTL), the simulated cloud structures are much more consistent with the observation (C3M). Improvement in the global model is expected to have a cascading effect on improving regional climate simulations, particularly in the framework of integrated WRF-CAM system.

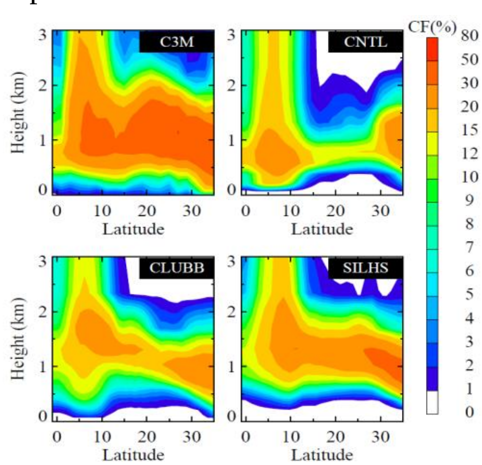


Figure 2. Observed and simulated cloud amount along the transect from the stratocumulus regime off the California coast to the convective regime near the equator.

Milestones

- In FY 2017, Complete the design of the 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 the 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 and G. Camarda

PURPOSE:

The main purpose of this project is to establish BNL as a major R&D contributor in the field of scintillator detectors for national security applications. There is an urgent need for large-volume, economical, uniform scintillators for detecting and imaging gamma-rays and neutrons for nonproliferation applications, such as emergency response, counter-terrorism, treaty verification, and nuclear safeguards, and for medical imaging. Our objective is to develop intrinsic scintillating compounds for simultaneously detecting gamma-rays and neutrons, which will resolve the problems in 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 various agencies, such as the National Nuclear Security Administration, the Domestic Nuclear Detection Office, and the Defense Threat Reduction Agency.

APPROACH:

Cs_2LiYCl_6 doped with Ce is perhaps the most efficient scintillator for a dual gamma- and neutron-detector. Detectors fabricated using doped scintillators undergo significant degradation with increasing volume, due to the segregation/striations of the dopant (i.e., the activator). The resulting non-uniformity of response reduces the yield of large detectors and increases their cost. In contrast, intrinsic compounds will ensure the homogeneity of the material throughout the grown ingot volume, and thus, assure a uniform response from the detector regardless of its volume.

We are developing $Cs_2LiCeCl_6$ (CLCC), an intrinsic scintillator for the dual detection of gamma-rays and neutrons. CLCC crystals have a cubic structure, and were grown by the vertical Bridgman growth technique. The crystals were characterized for different scintillator properties and device performances for both gammas and neutrons. Collaborators are Y. Cui, G. Yang, A. Hossain, P. Vanier and R. James. We have also established a collaboration with Steve Payne's group at Lawrence Livermore National Laboratory (LLNL).

TECHNICAL PROGRESS AND RESULTS:

CLCC crystals of different diameters, up to 22 mm, were grown by the vertical Bridgman growth technique. Figure 1shows the emission of CLCC. A double peak was observed at ~384 and 402 nm. The appearance of a double peak is typical for the Ce^{3+} state. The decay time, which is one of the most important parameters for scintillators, was estimated using 662 keV gamma excitation. Figure 2 shows the decay time of CLCC, which comprises three components. The fastest decay time constant for ~80% of the total light yield is ~90 ns, which is much faster than the CLYC. Figure 3 shows the gamma response from a ^{137}Cs source; the energy resolution, measured at LLNL, is 5.1% at 662 keV. It is worth noting that, our first crystal showed 7% resolution at 662 keV. The resolution can be further

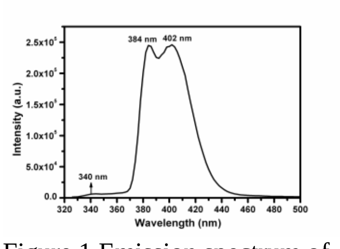


Figure 1.Emission spectrum of CLCC.

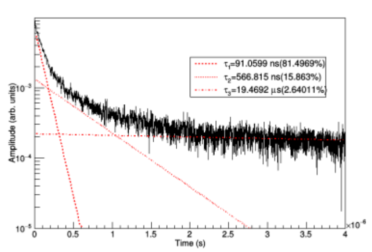


Figure 2. Fluorescence decay obtained from CLCC using 662-keV excitation from a ^{137}Cs source.

improved by purifying the starting material by zone refining. The light output estimated by comparing to Bismuth Germanate (BGO) was ~20,000 ph/MeV, while 34,000 ph/MeV light output was obtained at LLNL comparing to NaI. The reason for the lower light yield obtained at BNL might be: i) the samples are highly hygroscopic; we performed the sample preparation and measurements under ambient conditions, immersed in oil/optical grease; the surface degradation might have caused lower light yield and ii) the BGO we used might have a different light yield than claimed. At LLNL, all the processes were done in a controlled atmosphere. The results show that the light output is higher than CLYC. The non-proportionality for CLCC was estimated using the Scintillator Light-Yield Non-proportionality Characterization Instrument (SLYNCI); the results of experiments carried out by Steve Payne's group are shown in Figure 4. It was observed that carrier trapping in CLCC is much smaller than CLYC or CLLB ($Cs_2LiLaBr_6$):Ce.

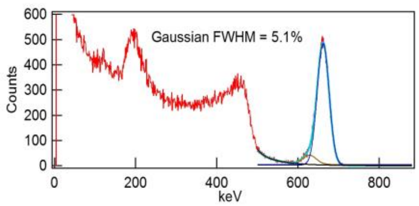


Figure 3. Pulse height spectra of CLCC crystal for ^{137}Cs gamma source.

The response to dual gammas and neutrons was evaluated by measuring the pulse-height spectra using Am-Be and ^{137}Cs sources together. Figure 5 shows the dual gamma and thermal neutron spectrum for the device using CLCC. The measurement was carried out at BNL. The well resolved 662 keV gamma line and the thermal neutron line are marked with arrows in Figure 5. The inset shows the emission from the CLCC sample under ultraviolet (UV) excitation. The gamma-equivalent peak position of the neutron line was estimated to be at 1.46 MeVee with a resolution of ~4%; the resolution obtained at LLNL was ~3% and the gamma-equivalent peak position of the neutron was at 1.4 MeVee.

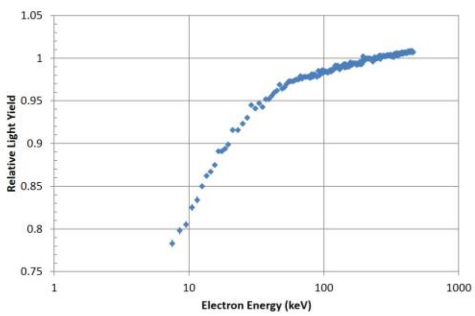


Figure 4. Non-proportionality plot for CLCC, measured at SLYNCI by the LLNL group.

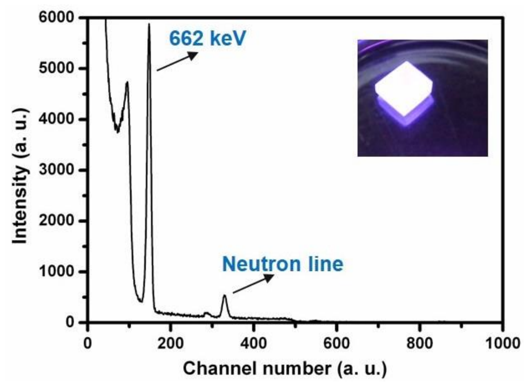


Figure 5. Pulse height spectra of a $Cs_2LiCeCl_6$ crystal from Am-Be thermal-neutron and ^{137}Cs gamma source. Inset shows the sample excited by UV light.

Summary: We have successfully grown intrinsic $Cs_2LiCeCl_6$ for dual gamma-ray and neutron detection. CLCC showed several advantages compared to the well-known crystal CLYC for dual gamma-neutron radiation detectors. CLCC is faster and brighter than CLYC. However, the gamma equivalent peak position of the thermal neutron line is lower than for CLYC. Pulse shape discrimination experiments will be carried out to determine if the lower value affects the pulse shape discrimination.

Milestones

We recently procured enriched ^6LiCl. CLCC crystals will be grown with enriched ^6Li to enhance the thermal neutron capture. Growth of another intrinsic scintillator doped with 10 mol% enriched ^6LiBr is being carried out in order to explore a new dual gamma-neutron detector material.

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

PURPOSE:

This project aims to explore a new science frontier - characterization of the inter- and intra-particle high frequency elastic (acoustic) properties of soft matter materials, such as superlattices of nanoparticle assemblies, simple liquids, liquid crystals, block copolymers, and phononic crystals. The development of well-defined approaches was among the first priorities of the project: to address frontier challenges and to elucidate fundamental aspects of sound propagation, which is essentially responsible for heat propagation at the molecular level. Therefore, this project is important for the development of future applications for energy and heat management at nanoscales.

APPROACH:

In this project, the Inelastic X-ray Scattering (IXS) technique combined with Molecular Dynamics computer simulations were used. The IXS is the experimental technique best suited to probe the Terahertz (THz) collective dynamics in soft matter materials, materials with tunable and programmable structures.

TECHNICAL PROGRESS AND RESULTS:

Ideal candidates to implement heat flow control based on structural engineering are phononic crystals. These are composite materials whose structural arrangement deeply interferes with acoustic waves of certain frequencies, reflecting, trapping, slowing down or even stopping them. It was demonstrated [1] that these devices are useful in a variety of applications, such as optical cooling, energy harvesting and management of thermal conductivity. Although the search for new classes of phononic crystals is rapidly maturing, the development of devices operating at extremely high (terahertz) frequencies still remains essentially unexplored. This is a particularly penalizing limitation, since the heat transport utilizes terahertz phonons as carriers. In order to produce phononic crystals efficient in the terahertz frequency window, nanoparticle assemblies must be arranged in superlattices with inter-particle distances comparable with the wavelengths of terahertz phonons.

One of the milestones of our LDRD project is an investigation of the high frequency excitations in two-dimensional gold nanoparticle arrays in a water matrix (see Figure 1) through a series of large-scale molecular dynamics simulations [1]. The results obtained were explained in the framework of a unified phonon-based approach [2], which we developed earlier as an important theoretical foundation for the LDRD project; therefore, the latter can also be considered as a milestone. We showed that phononic excitations of two-dimensional gold nanoparticle arrays and the water matrix have reciprocal impact, which can be tuned via a manipulation of the structural arrangement. It is well-known that sound waves, both compression and shear, can propagate over long distances in structurally ordered bulk solids. However, there was limited knowledge about their propagation in nanoparticle assemblies merged in liquid media, which is a crucial topic of our LDRD project. To shed insight on this topic, we conducted inelastic X-ray experiments combined with molecular dynamics simulations on argon gas, which is an ideally suited prototypical system to study high frequency sound waves and heat propagation.

The spectra determined by computer simulations were found consistent with experimental data. Furthermore, we observed that, upon a temperature increase, a low-frequency transverse phononic gap [3] emerges while high-frequency propagating modes become evanescent. Furthermore, we observed for the first time a strong localization of the longitudinal acoustic mode in the supercritical phase. We also independently discovered the presence of a similar high-frequency propagation gap of transverse sound waves in lipid membranes [4]. This effect is brought about by the transition from an oscillatory to a ballistic dynamic regime, which we demonstrated with the support of molecular dynamics computer simulations [5]. This transition takes place across the Frenkel line [6] thermodynamic curve, which demarcates the boundary between a liquid-like and a solid-like domain in the phase diagram. These results are crucial to advance the development of novel terahertz thermal devices, phononic lenses, mirrors, and other THz metamaterials.

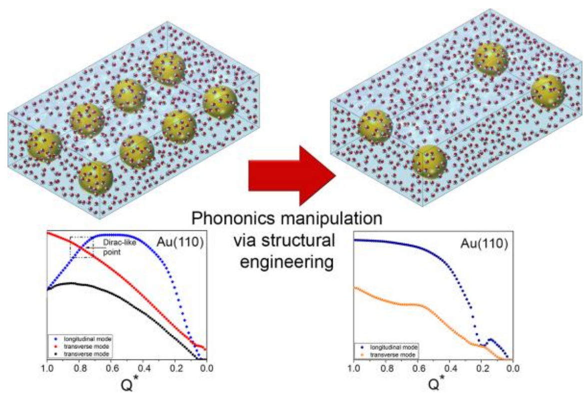


Figure 1. Schematic of the two-dimensional gold nanoparticle array in a water matrix.

References:
1. D. Bolmatov *et al.*Terasonic excitations in 2D gold nanoparticle arrays in water matrix as revealed by atomistic simulations. Journal of Physical Chemistry C 120(35), 19896-19903 (2016).
2. D. Bolmatov *et al.* Unified phonon-based approach to the thermodynamics of solid, liquid and gas states. Annals of Physics 363, 221-242 (2015).
3. D. Bolmatov *et al.* Thermally triggered phononic gaps in liquids at THz scale, Scientific Reports 6, 19469 (2016).
4. M. Zhernenkov, D. Bolmatov *et al.* Revealing the mechanism of passive transport in lipid bilayers via phonon-mediated nanometre-scale density fluctuations, Nature Communications 7, 11575 (2016).
5. D. Bolmatov *et al.* Revealing the mechanism of the viscous-to-elastic crossover in liquids, Journal of Physical Chemistry Letters 6(15), 3048-3053 (2015).
6. D. Bolmatov *et al.* The Frenkel line: a direct experimental evidence for the new thermodynamic boundary, Scientific Reports 5, 15850 (2015).

Milestones

- In 2017, we submitted a paper to Nature Materials based on the first scientific results obtained at the new IXS beamline
- We plan to perform the first IXS measurements on phononic properties of liquid crystals, a way to new opportunities for investigation and a totally new line of research
- We proposed further IXS measurements on different prototypical Soft Matter systems. Two General User Proposals got a top rating and were approved for beamtime.

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). 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 (Figure 1a). More complex strategies are possible based upon the radiation robustness of the crystal (Figure 1b, c). However NSLS-II will bring scientists into completely new regimes where data sets will be generated from thousands of crystals (Figure 1d).

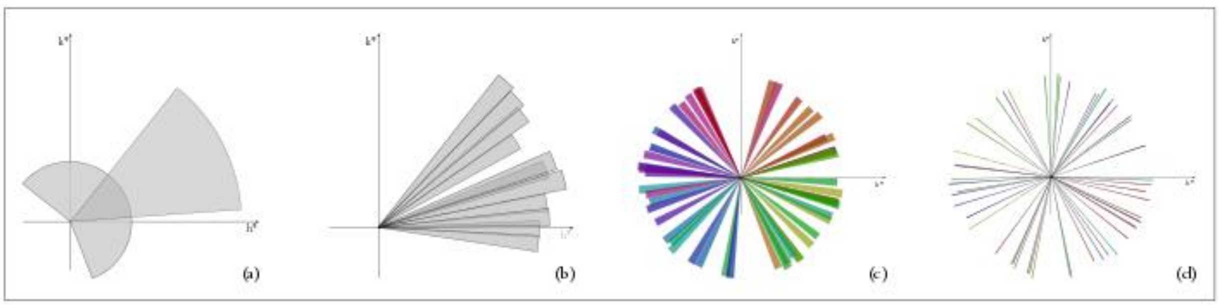


Figure 1. Data collection strategies for MX data; each wedge represents an experiment sweep revealing part of the data for a crystal structure. (a) Low and high resolution sweeps (b) "complicated" multi-orientation strategies (c) optimistic multi-crystal strategies where several degrees of data per sample 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 is first 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. Subsequently we have started the exploitation of the new structural biology beamlines to collect and examine initial data sets.

TECHNICAL PROGRESS AND RESULTS:

We have developed robust sample supports for handling and delivering micro crystals to the beam. We have been able to specify and create a data collection routine allowing for flexible definition of the areas to be investigated by raster based techniques on the beamlines (Figure 2). Our efforts have then continued to determine the most effective way to recognize promising diffraction patterns and subsequently to merge partial data so that complete data sets can be established from the rather fragmentary sampling from individual diffraction patterns. We are also exploring the data collection strategies of continuous-raster scan and step-raster scan and evaluating their effectiveness in data quality improvement.

Milestones

The next steps will be to refine the categorization of the samples and diffraction patterns further, to evaluate the accumulated diffraction signals in micro-crystallographic structure determination and phasing, and to apply the steps to more demanding samples, such as micro-sized needles and slurries, and ultimately to make the process available to all users of our structural biology facility.

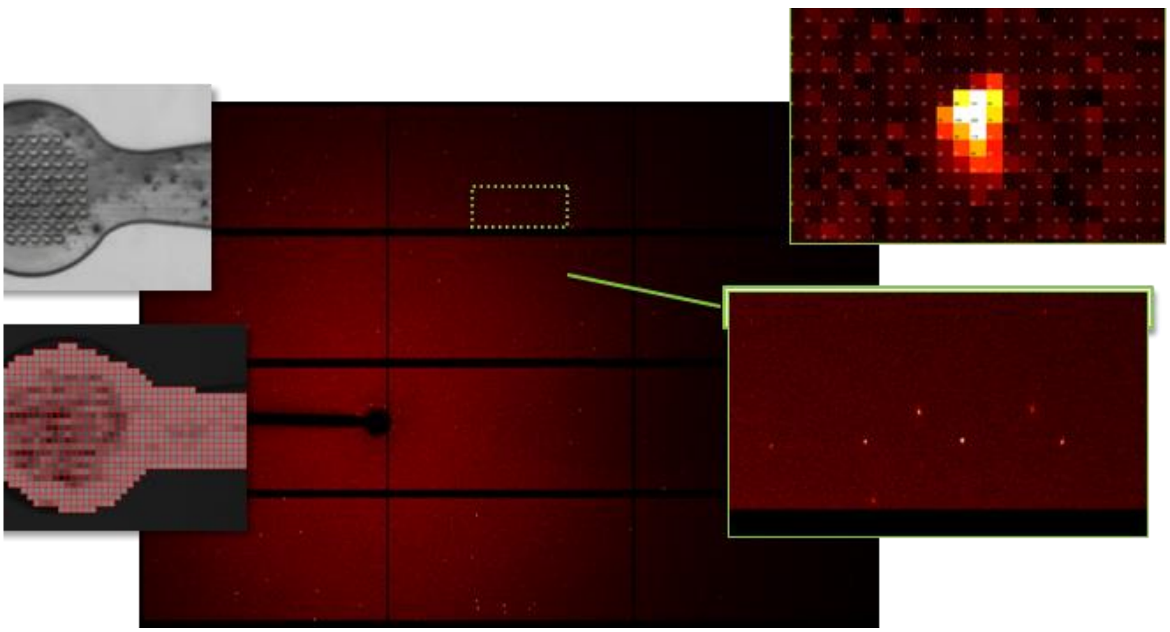


Figure 2**.** The flexible raster approach for data collection from micro crystals. Main picture - the diffraction pattern from one portion of the scan. Anticlockwise from top left: Optical image of a sample support ready for examination; the grid automatically defined based on the optical image; the diffraction orders visible in the zoomed area indicated on the main image; one diffraction order within this region.

In addition to the technical development, we published one review article on membrane protein structure.

TMBIM-mediated Ca^{2+} homeostasis and cell death *Biochim Biophys Acta*. 2017 doi: 10.1016/j.bbamcr.2016.12.023. [Epub ahead of print].

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 a 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 to 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. 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 developed three different *in situ* cells with different purposes. An *in situ* cell developed through a commercial vendor provides the capability to perform TEM and X-ray microscopy measurements. The second cell is an optimized X-ray cell, which allows both X-ray fluorescence and diffraction measurements. The third cell is a modified coin-cell that offers the highest familiarity to battery researchers. All the cells are used at the HXN beamline for this research, as well as for the general user science experiments at the HXN beamline. Our second aim is to use these cells to conduct *in situ* microscopy experiments in order to image how the nanostructure at the battery interface transforms under *in situ* controls. In the course of our research, we realized that we had to develop methods to analyze the collected image data. We began tackling a way to quantify the amount of different chemical species in a sample. We also began exploring a method to solve the self-absorption problem for fluorescence nanotomography. Initial attempts demonstrated highly encouraging results. We are now applying these methods to user experiments at the HXN beamline.

TECHNICAL PROGRESS AND RESULTS:

We fabricated two additional *in situ* cells. Figure 1a shows the schematics of our optimized X-ray *in situ* cell. This cell offers significantly greater flexibility and robustness. It has a dedicated sub-chamber for lithium (Li), so that Li does not get depleted during the *in situ* reaction. It allows different materials (Kapton, Mylar, or Carbon sheet) as the X-ray window, so that the type of window can be chosen optimally for each experiment. Figure 2b shows *in situ* discharging and charging of an iron oxide battery material. Figure 2c shows the oxidation state image of iron and iron oxide species when discharged (A) and charged (B). The image shows their relative concentrations during the *in situ* reaction. In order to expand *in situ* X-ray imaging applications, we also produced a modified coin-cell (1 inch in diameter). Both cells are fully tested and are being offered to the HXN beamline users. The TEM/X-ray *in situ* cell, developed in FY 2015, has been fully tested and used for *in situ* TEM and X-ray microscopy experiments. Using this cell, we conducted an *in situ* electrochemical silver (Ag) growth experiment. During this experiment, we observed an anomalously fast growth rate, which we attributed to the interaction of the electron beam with the solution and the catalytic behavior of metallic platinum. A manuscript summarizing the result of this study, "Anomalous Growth Rate of Ag Nanocrystals Revealed by *in situ* TEM", was submitted to Scientific Reports. In addition, our TEM/X-ray *in situ* cell was loaned to the Submicron Resolution X-ray Spectroscopy beamline of the NSLS-II in 2016 for a general user experiment. This cell will be also used by an HXN beamline user for performing an *in situ* corrosion experiment ("In situ XRF and DPC studies of inter-granular corrosion (ICG) in stainless steel using hard x-ray nanoprobe").

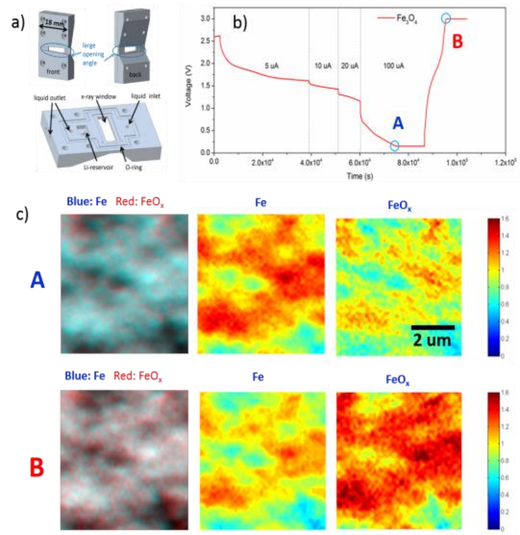


Figure 1 (a) Optimized X-ray *in situ* cell (b) *In situ* electrochemical control of a Fe_3O_4 battery material (c) Fully discharged chemical map of the sample (A) and fully charged (B). The image in the first column show the relative fractions of Fe (blue) and FeOx (red).

While performing this research, we had to spend a considerable amount of time in developing imaging analysis methods. One area is for analyzing a spectromicroscopy data set, similar to that shown in Figure 1c. In order to perform quantitative analysis of the electrode transformation under *in situ* controls, we needed to quantify the concentration of different chemical species co-existing in the sample. This development is in progress. Another important imaging analysis method is solving the self-absorption of the fluorescence X-rays, in order to achieve a fully quantitative 3D fluorescence tomography analysis. Figure 2a shows a side view of reconstructed fluorescence tomography data. Due to significant absorption, the reconstructed cross sectional view (Figure 2b) shows an uneven elemental distribution. We use an iterative solution with corrected detection geometry, in order to solve the self-absorption problem. This is the first demonstration of a self-absorption correction for nanoscale 3D X-ray imaging. A manuscript summarizing this work is in preparation.

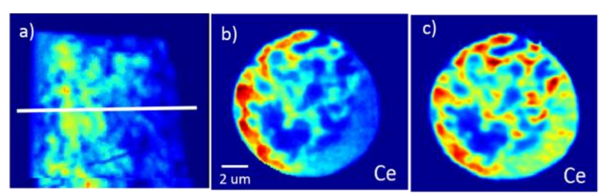


Figure 2: a) Side view of a reconstructed sample. Cross sectional view along the line shown in (a) without correction (b) and with correction (c).

Milestones

- In FY 2017, perform a TEM imaging experiment using the developed in-situ cell
- Perform a X-ray Nanoprobe imaging experiment using the developed in-situ cell
- Refine 3D fluorescence tomography data collection and analysis method including absorption correction
- Present the results at conferences.

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 performance. Novel mechanical design of magnet systems and new advanced shimming methods that are developed in this project will also be applicable to conventional hybrid in-vacuum undulators and will improve their performance.

APPROACH:

The project includes calculations of 3D magnetostatics, synchrotron radiation, heat conductivity, and mechanical stress analysis, most of which are already completed. Based on the results of these calculations, prototypes of two key SAGIVU sub-systems – magnet girders and liner foil – are designed and almost fully manufactured, and their assembly, magnetic and mechanical tests have been started. To reduce costs, several existing mechanical and magnetic parts will be used, in particular three old mini-gap undulators of the decommissioned NSLS ring. In addition, the magnetic and mechanical tests are being performed using a small magnetic measurements bench available at the NSLS-II ID lab. This final stage of the project can be realized only with participation of NSLS-II engineers and technicians. Besides C. Eng, the engineer hired for this project, members of the ID group (D. Harder, M. Musardo, J. Rank, T. Corwin, G. Aparicio) are making contributions to the project at this stage.

TECHNICAL PROGRESS AND RESULTS:

The main accomplishments during FY 2016, targeting the construction and tests of the SAGIVU prototype, are listed below.

- The designs of all components of the SAGIVU magnet system, planned in the scope of this project, were fully accomplished. This includes 7 inner girders (6 for the 3-segment SAGIVU prototype for low-beta straight section and 1 test girder for high-beta straight section), magnet and pole support system (keepers and clamps), poles and magnets for central parts and terminations of all girders, and directly-cooled copper liner foil system with its fixation and stretching mechanism. Final manufacturing drawings of all components were produced and for the most part released by NSLS-II (more than 100 drawings in total).
- All the mechanical and magnet parts listed above were ordered, manufactured (mainly “built to print”) and delivered to NSLS-II (Figures 1, 2).
- Assembly of the main modules comprising the SAGIVU magnet system has started (Figure1).
- Magnetic characterization of individual modules using the flip-coil and Hall probe has started (Figures 3, 4). These data will be used for the assembly of the magnet system on the inner girders.
- Mechanical carriages of 3 old mini-gap undulators of NSLS were partially disassembled; new parts required for tests of the SAGIVU prototype (for mounting new inner girders and

attaching spring system for compensating magnetic forces) were manufactured and/or purchased.

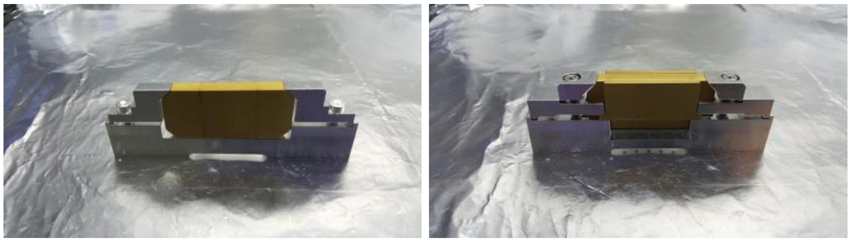


Figure 1. Two main types of assembled modules for an intermediate segment of SAGIVU prototype: (left) "M" (single magnet) and (right) "PMP" (pole-magnet-pole).

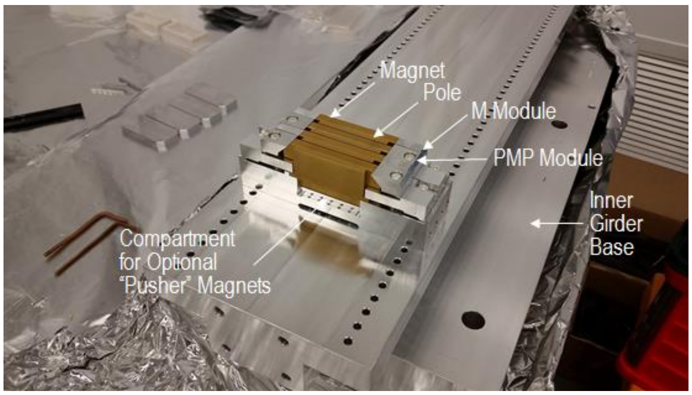


Figure 2. Test assembly of two PMP and two M modules making two periods of undulator magnet structure (one half, lower or upper). The inner girder base and all modules are ultra high vacuum-compatible.

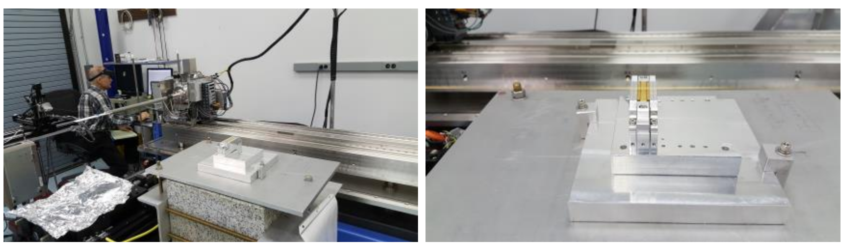


Figure 3. A PMP module mounted on a special support structure next to magnetic bench (left), and in the process of measurement of its field integrals by a flip-coil (right).

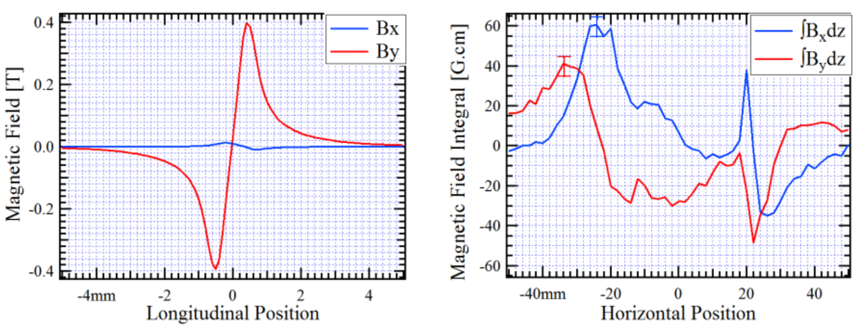


Figure 4. On-axis horizontal and vertical magnetic field components measured as functions of longitudinal position using Hall probe (left); and the horizontal and vertical field components integrated along the longitudinal position, measured as functions of horizontal transverse position using flip-coil (right), for one PMP module.

The magnetic measurements illustrated in Figure 4, were taken at ~2 mm vertical offset from the magnet/pole faces, which is close to half of the minimum gap in the corresponding segment. The irregular field integral dependency on the horizontal position is mainly due to magnetization errors in the magnet of the PMP module. Such data will be obtained for ~400 modules constituting the 3-segment SAGIVU. After this, a special sorting procedure, complemented by additional measurements, will ensure maximal-possible compensation of the magnetic errors during the segment assembly. Later, special shimming methods will allow for correcting the remaining field imperfections and fine-tuning the entire SAGIVU magnet structure.

Chiral Magnetic Effect (CME): from Quark-Gluon Plasma at RHIC to Dirac Semimetals at NSLS-II

LDRD Project # 16-004

Q. Li, D. Kharzeev

PURPOSE:

This cross-disciplinary project aims at establishing the existence of quantum phenomena specific to relativistic quasi-particles in condensed matter experiments and exploring the potential applications. The project will combine experimental and theoretical studies to understand the nature of the chiral magnetic effect (CME) - generation of electric current induced by the chirality imbalance between left- and right-handed fermions in a magnetic field, a dramatic consequence of chiral anomaly in the theory of Dirac fermions.

APPROACH:

The relativistic theory of charged chiral fermions (massless spin 1/2 particles with a definite projection of spin on momentum) in three spatial dimensions possesses so-called chiral anomaly – non-conservation of chiral charge induced by the external gauge fields with non-trivial topology. One of the anomalies is the chiral magnetic effect. This phenomenon is currently under intense study in relativistic heavy ion collisions at the Relativistic Heavy Ion Collider (RHIC) at BNL and at the Large Hadron Collider at CERN.

Interactions of quasiparticles in Dirac and Weyl semimetals, having linear energy dispersions, have led to chiral fermions that opened unprecedented opportunities to study the quantum dynamics of relativistic field theory in condensed matter experiments, with the potential for important practical applications, such as non-dissipative charge transport (1, 2). Currently, topological physics in a 3D Dirac system is a very active field. Data are rapidly being produced on electronic structures and transport properties. However, the pieces of information are not well connected leaving important questions unanswered, for example, how does the chiral magnetic effect respond to the change of electronic structure and topology in Dirac/Weyl semimetals? A coordinated investigation that brings together theory, materials synthesis, and characterization of crystal structure, electronic structure, and transport properties is desirable. This coordinated investigation is the approach used in this LDRD.

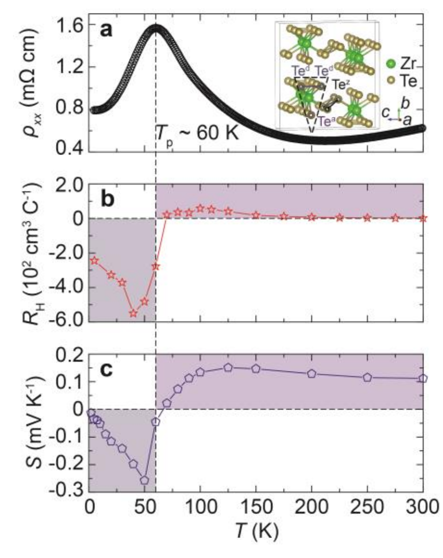


Figure 1. The temperature-dependent (a) electrical resistivity ρ_{xx}, (b) Hall coefficient R_H, and (c) Seebeck coefficient S. The dashed line, at the ρ_{xx} peak temperature T_p (approximately 60 K), indicates the resistivity "anomaly" occurs essentially at the temperature when both R_H and S change sign. The crystal structure of $ZrTe_5$ is illustrated in the inset of (a).

TECHNICAL PROGRESS AND RESULTS:

Zirconium pentatelluride $ZrTe_5$ hosting chiral fermions exhibits a strong chiral magnetic effect (1). However, the origin underlying its anomalous resistivity peak (Figure 1) has been under debate for decades. We provided transport evidence substantiating the anomaly to be a direct manifestation of a Lifshitz transition in the Dirac band with an ultrahigh carrier mobility. We demonstrated that the Lifshitz transition was readily controllable by means of carrier doping, which sets the anomaly peak temperature T_p. T_p is found to scale approximately as $n_H^{0.27}$, where the Hall carrier concentration n_H is linked with the Fermi level by $\varepsilon_F \propto n_H^{1/3}$ in a linearly dispersed Dirac band. This relation indicates T_p monotonically increases with ε_F, which serves as an effective knob for fine tuning transport properties in pentatelluride-based Dirac semimetals.

Dimensionality plays an important role in the chiral magnetic effect, which requires 3D chiral fermions with left handed and right handed chirality that exists in 3+1 space and time, but not in 2D systems. We took advantage of nano-fabrication facilities at the Center for Functional Nanomaterials in preparing electrical contacts on the exfoliated Dirac semimetal $ZrTe_5$ single crystals (Figure 2) for transport measurements in the Condensed Matter Physics and Materials Science Division. Figure 2 shows the thickness dependence of resistivity as a function of temperature in a bulk $ZrTe_5$ single crystal and exfoliated 10 nm thick samples. We found nearly two orders of magnitude increase in resistivity for a 10 nm thick sample at low temperature, suggesting the transport behavior changes from a semimetal to insulator-like. The strength of the chiral magnetic effect decreased as the thickness of the sample is reduced to the range of a few tens of nanometers. However, the same bulk temperature- and magnetic field-dependent resistivity was observed in samples thicker than 100 nm, indicating the Dirac semimetal nature. This observation is in fact consistent with an earlier prediction that monolayer $ZrTe_5$ behaves as a strong topological insulator with a large gap (3). In this study, we demonstrated dimensionality is another effective parameter that can be used to tune the band structure of Dirac semimetals, and hence control the strength of the chiral magnetic effect.

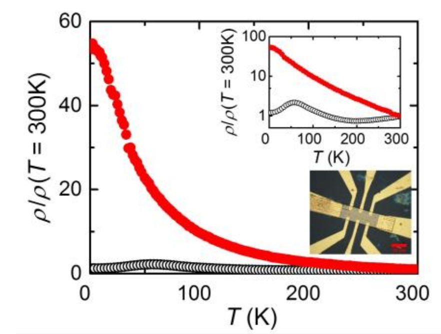


Figure 2 Normalized temperature dependent resistivity of $ZrTe_5$: bulk single crystal sample (black symbols, 0.2 mm thick) and 10nm thick nano-devices (red symbols, the red line in the inset photo represents a 20 μm scale bar), with room temperature resistivity of 0.8 mΩcm and 7 mΩcm, respectively. Inset figure: the same data in semi-log plot.

Milestone

In FY 2017, we plan to submit a paper to Nature Physics, tentatively titled "Chiral magnetic effect: towards an unconventional superconductivity."

REFERENCES:

[1] Q. Li, D. E. Kharzeev, C. Zhang, Y. Huang, I. Pletikosic1, A. V. Fedorov, R. D. Zhong, J. A. Schneeloch, G. D. Gu and T. Valla. "Chiral magnetic effect in $ZrTe_5$" arXive:1412.6542, *Nature Physics* **12** 550 (2016) doi:10.1038/nphys3648

[2] Q. Li and D. E. Kharzeev "Chiral magnetic effect in condensed matter systems" *Nuclear Physics* A **956** 107–111110 (2016)

[3] H. Weng, X. Dai, and Z. Fang. "Transition-Metal Pentatelluride $ZrTe_5$ and $HfTe_5$". Physical Review X, 4, 011002 (2014).

Serial Micro Crystallography at Full Flux

LDRD Project # 16-006

M. Fuchs, E. Nazaretski

PURPOSE:

Making use of the world leading emittance of the National Synchrotron Light Source II (NSLS-II) storage ring, the Frontier Macromolecular Crystallography beamline (FMX) at full target specifications will achieve unprecedented flux densities and therefore dose rates. These specifications will provide a great advantage for serial micro-crystallography – cutting measurement times from hours to minutes – and time-resolved serial crystallography measurements with ms resolution. In both cases, a complete crystallographic dataset for determining the structure of a biological molecule is being assembled from hundreds of sub-datasets obtained from micron-sized crystals. To provide the instrumentation basis for such measurements, we will design and construct an ultra-high-speed, high precision goniometer, including specialized sample supports. Successful implementation of the instrument will enable data collection from previously intractable small crystal sizes, often encountered in the case of challenging structural biology projects, *e.g.* membrane proteins.

APPROACH:

Serial micro-crystallography methods were originally developed for data collection from microcrystals at Free Electron Laser facilities. The method has since been re-appropriated by the synchrotron crystallographic community for its ability to yield useable data from ever smaller crystals. With the FMX beamline's maximum crystal half-life in the 10 ms range, to realize the speed advantage, a nanometer precision high-speed piezo scanner stage optimized for fast rotation will provide the required sample positioning performance. This will enable us to collect datasets within minutes rather than hours, and realize the full time resolution.

The project requires the integration of piezo positioners on an infinite rotation rotary spindle, which to our knowledge has not yet been done with the repeatability requirements needed for our application. To inform the design process and validate the goniometer performance, a mobile metrology setup will be implemented using capacitive and optical micrometer distance sensors. The instrument will be embedded in the beamlines controls and data processing environment. Successful structure solutions of challenging microcrystal samples will establish the method of rapid scanning serial micro crystallography as a unique tool for structure determination of previously intractable molecular targets.

Yuan Gao from Argonne National Laboratory was hired as a postdoctoral research associate and joined the team on May 16, 2016. Weihe Xu from the NSLS-II Experiment Group provided support for metrology measurements. Ming Lu from the Center for Functional Nanomaterials (CFN) supported sample support nanofabrication.

TECHNICAL PROGRESS AND RESULTS:

The core objective for FY 2016 was to design, procure and commission an ultra-high-speed high-accuracy scanning goniometer. We conducted extensive research for a coarse and fine piezo scanning stage with the companies nPoint, Piezojena and Physik Instrumente USA, including visiting the companies and hosting representatives of the companies at BNL. From these discussions, two critical complications in designing the stages were identified: To provide high-speed infinite rotation capability for the goniometer, a slip ring for the control and signal cables is required. In addition, spatial restrictions of the sample environment make integration of the stages challenging. To verify whether such piezo stages are viable for scanning in serial micro-crystallography, we conducted tests of a piezo stage's performance loaned from Physik Instrumente, with the stage connected through a slip ring. Our test demonstrated that the peak-to-peak noise of the piezo actuator increased from ~10 nm to ~25 nm when it was connected through the slip-ring. The extra noise was caused by the increased noise of the analog encoder of the piezo system, which affected the feedback control. This problem was addressed by replacing the analog encoder with a digital version. Based on these results, we procured a Physik Instrumente Nexline-Nanocube piezo-scanner, which was delivered on September 23, 2016. The Nexline piezo walk stages in this system provide a coarse travel range of ± 2 mm in X and Y, and the Nanocube a fine range of ± 100 µm. To match the tight envelope for the stages, the Nanocube block was integrated with the cube's body diagonal along the rotation axis, and the XYZ translations realized as combined motions of all three piezo positioners.

For the site acceptance testing of the piezo-scanner, we evaluated its performance utilizing a laser interferometer displacement sensor at BNL's nano-metrology laboratory. The piezo-scanner achieved >200 Hz scanning frequency, >15 mm/s scanning speed in all three dimensions, and < 50 nm bidirectional repeatability, matching all key performance parameters. Minor overshooting and ringing observed during the tests showed that the load-tuning of the piezo-scanner is critical for the application at our beamlines. For this final load tuning, the unit was sent to the manufacturer. During a visit on December 19, we verified the optimized ramp and raster trajectory performance. For final cable integration in the air bearing bore, a custom connector holder is currently implemented at the factory, and the anticipated return date to BNL is February 2nd.

To validate the performance of the goniometer, we developed a mobile metrology setup for testing the goniometer's sphere of confusion. The setup includes capacitive sensors, the corresponding manipulators, and a graphical user interface. The peak-to-peak sphere of confusion of the current devices is < 1 µm. By implementing an active correction function, the remaining irreproducible error suggests the possibility of reducing the sphere of confusion down to < 100 nm, ~10% of the smallest beam focus.

Another key objective in FY 2016 was to begin the development of optimized sample mounts. In collaboration with our colleagues in the Life Science and Biological Research group (Wuxian Shi, Jean Jakoncic and Alexei Soares) and the BNL Biology Department (Qun Liu), we chose to develop micro-patterned silicon chips as the sample holder. To determine the best patterns for our experiments, we have a user proposal approved at the CFN at BNL, for the usage of a number of fabrication and characterization techniques. The user proposal was activated for the January - April 2017 cycle.

In October 2016, we conducted the first serial micro-crystallography experiments with the current slow goniometer setup in collaboration with Qun Liu. The experiment was aimed to prove the concept, test the beamline properties, and conduct data acquisition and processing. In a 3 hour experiment, we observed useable diffraction patterns from 1 – 5 µm sized Thaumatin crystals loaded on a Kapton mesh. Even with a large horizontal beam focus of 20 µm due to the not yet installed focusing mirror, we achieved ~2Å resolution from the micro-crystals.

Milestones

For FY 2017, we plan the final integration of the new goniometer, first test experiments, and eventually scanning serial microcrystallography data collection with new molecule targets provided by collaborating users, *e.g.* RNA molecules by Anna Marie Pyle (Yale University) and membrane transporter proteins by Da-Neng Wang (New York University).

3D Ptychography Imaging without Rotation using Highly Convergent X-ray Beam

LDRD Project # 16-007

X. Huang

PURPOSE:

The objective of this project is to develop a novel microscopy method for obtaining high-resolution three-dimensional (3D) images without sample rotation. This technique will revolutionize the way of extracting 3D structural information, since the performance and resolving capability of existing microscopy tools are inherently limited by the detection geometry. The successful implementation of this method will find wide application in quantitative characterization of specimens in an *in situ* environment. Elimination of the rotation requirement removes the limitation imposed by the usually bulky sample cell and provides high quality 3D structure with ultimate spatial resolution.

APPROACH:

The limitation of existing X-ray microscopy systems arises from the narrow depth-of-focus and short working distance, and this limitation becomes more severe when pursuing higher spatial resolution. Our approach to solve the issue is to adapt the multi-slice concept with the ptychography method.

The multi-slice approach models the interaction between the incident X-ray and sample, frame by frame. The structural information on each slice is encoded into the propagating wavefront independently. Under this framework, a thick sample is no longer considered as a projected plane, but each individual plane will be precisely recovered. The performance limitation imposed by shallow depth-of-focus won't apply any more.

Ptychography is a scanning version of the coherent diffraction imaging method. As there is no objective lens in this imaging system, the achievable spatial resolution is determined by the scattering power of the sample itself, instead of the instrumentation. The scanning nature of ptychography also provides almost infinite field-of-view in the lateral plane. The redundancy from overlapped scanning trajectory makes it possible to recover 3D layers using 2D lateral scans alone.

The combination of the multi-slice concept with ptychography offers ultimate 3D imaging capability with no sample rotation. Thus, it removes the physical constraint for realistic sample environments, and is able to provide diffraction-limited resolution in the meantime.

TECHNICAL PROGRESS AND RESULTS:

The main challenge of this project is to improve the depth resolution to the sub-100 nm scale. We propose to use the wavefront diversity of the highly converging X-ray beam from a multilayer Laue lens (MLL) along the beam propagation direction to enhance the depth resolution.

In the first fiscal year of the project, progress was made in numerical simulation and experimental work.

The feasibility and potential of the proposed method was tested with numerical simulation. The results show that the achievable depth resolution scales with the width of the depth-of-focus. Compared with Kirkpatrick-Baez (KB) mirrors, MLL brings the depth-of-focus from several mm to several microns. This three-order improvement in depth resolution is thus expected in the multi-slice ptychography approach. Considering about 100 micron depth resolution was achieved with KB mirrors, we should be able to improve the number down to about 100 nm by using MLL.

We also developed a simulation framework that can model the diffraction process and numerically generate 3D diffraction data for coherent diffraction imaging measurements. Reconstruction of simulated data provides a way to characterize the performance of the phase-retrieval-based method. A manuscript has been prepared and will be submitted shortly.

Milestones

In FY 2017, we conducted experimental measurements at the Hard X-ray Nanoprobe (HXN) beamline in November. Two types of samples were measured for the proposed multi-slice ptychography method. One is a two-layer structure separated by various distances. This is considered as the simplified version of a true 3D structure, and it provides well-defined sliced features, which can be used to characterize the achievable resolution. The other sample is a porous core-shell tungsten oxide sample. This is a true 3D object with sharply defined boundaries. A tomography measurement was performed on this sample to provide 3D structural reconstruction as a reference. A multi-slice ptychograph is expected to give a similar structure using a single 2D scan.

The data analysis is still in progress. We observed that we can improve the experiment for better performance. The separation of the two-layer structures that we used in the previous measurement was too small, which makes the reconstruction extremely challenging. The porous sample for the 3D tomography measurement was a little too large, which makes it take a relatively long time to collect full tomography data and also makes it challenging to sufficiently sample the entire sample for multi-slice ptychography reconstruction. Based on these considerations, we prepared two-layer structures with proper separations and a smaller porous sample for the next scheduled HXN beamtime.

Toward 100fs Single-shot Electron Imaging Using Electron Beam Slicing Technology

LDRD # 16-010

L. Yu, Y. Zhu, T. Shaftan, L. Doom

PURPOSE:

The objective of the project is to realize the compression of electron bunches of 50 pC (~10^8 e^-/bunch) to 160 fs and the beam focus to 30 mu, and to test the principle of the method to remove time jitter between the laser and electron bunch. The immediate objective of this and next year is to achieve experimental confirmation of the focusing of electron bunches to 30 mu in size within the range of a few fC to 50 pC, with a divergence angle between 0.1 to a few mradian. This will better position us to respond to DOE funding opportunities for ultrafast electron scattering and provide technology breakthroughs in key development areas.

APPROACH:

We developed a novel unconventional scheme to combine the correlated energy spread with the energy dependent path length to compress the electron bunch. The main point is to use space charge to generate the time-energy correlation. The project includes the construction of a test beamline for electron bunch diagnostics and focusing, followed by the construction of a chicane for electron beam compression. However, due to budget constraints, our immediate goal is the construction of a beamline with experimental confirmation of the focusing of electron bunches to 30 mu size within the range of a few fC to 50 pC, with a divergence angle between 0.1 to a few mradian in 2017.

In addition to the principle investigators, our collaborators from the Condensed Matter Physics Division, the National Synchrotron Light Source II, and the Accelerator Test Facility (ATF) include J. Tao, J. Li, W. Cheng, A. Blednyk, V. Smalyuk, X. Yang, A. He, M. Fedurin, M. Babzian, and others on the ATF team.

TECHNICAL PROGRESS AND RESULTS:

The first year was dedicated to the following aspects of the project: the physics design, the specification and procurement of the magnets, beamline design, including the vacuum chamber design and power supply test, the design of the diagnostic system including the beam position monitor system, and the design of a diagnostic chamber for the measurement of beam size at the focal point. This leaves sufficient room for the next step of the development of the transition radiation measurement of the bunch length.

The following aspects of the project were realized in 2016:

For the physics design, the first work was to transform the previous simulation into a realistic model for beamline engineering design. Bunch dynamics optimization was carried out while the structure was modified to fit a realistic design. The quads required in the previous simulation turned out to be not physically realistic and cost effective. We had to reduce the physical sizes and the maximum field gradient to reach a realistic magnet design. We were able to reduce the maximum field gradient from 45 T/m to 9.5 T/m, the bore size was increased from 10 mm to 24 mm. The focal point is moved from the center of the last quad to 3 cm downstream. To accommodate the current sample chamber, we had to move the first quad downstream by 8 cm.

We also found out that the previous simulation implies a significant misalignment of the electron beam centroid from the quads center in the dispersion section, and hence we needed to find a way to align the center. All of these required a significant amount of optimization work. Based on this work, we were able to reduce the number of quads type from 4 to 2, and came up with a realistic design.

The vacuum chamber and beam profile monitor system design was carried out to fully use the narrow spaces between the quads for beam diagnostics. The engineering design strategy of the sample chamber was conceptually carried out to allow for the sample to be positioned at the focal point as close to the last quad by 3 cm only. This result provides the engineering design of the focusing system as in Figure 1.

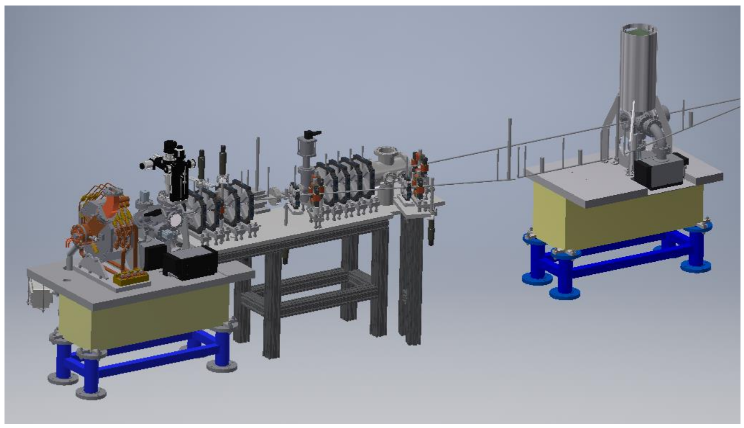


Figure 1. Engineering design of the focusing system.

An important result of all this work is that we were able to obtain a signed contract with "Everson Tesla" for $112k (unburdened). This overcame the significant difficulty with the magnet cost and met the budget deadline for 2016.

FY 2016 mechanical design and manufacture status summary: preliminary layouts were completed for the system. These included the draft system specifications, an initial lattice, system layout models, preliminary vacuum drawings and the specifications/Statements Of Work for the 24 mm quadrupole, 30 mm quadrupole, 30 mm dipole and corrector magnets. The quadrupole and dipole magnets were ordered.

Milestones

Because of a budget shortfall, we cannot expect to deliver the chicane in this period of the LDRD. Instead, our new plan is to construct the beamline with focusing and its diagnostics with sufficient tuning range for diffraction experiments in 2017. The beamline should be sufficiently flexible for us to vary, within several orders of magnitude, the focal point size, divergence angle and bunch charge, and use the diagnostics system to verify the results.

In situ Synchrotron Studies of Subsurface Material Interfaces Using X-ray Fluorescence Mapping and X-ray Tomography at NSLS-II

LDRD Project # 16-019

S. Gill, M. Elbakhshwan, L. Ecker

PURPOSE:

The dissolution and precipitation reactions that occur at solid-fluid (cement-fluid) interfaces under hydrothermal conditions as well as carbon sequestration need to be understood as they can lead to drastic loss in permeability, which may impact economic viability of well bore integrity. Hence, it is critical to study interfacial interactions to understand the degradation mechanisms involved in subsurface materials. Such knowledge will not only help predict economic viability of sequestration and well integrity, but will also help in designing next generation subsurface materials with enhanced performance under extreme geothermal conditions.

This LDRD project is aimed at utilizing high-resolution, ultra-fast synchrotron characterization tools to study interfacial interactions at cement-fluid and cement-casing interfaces. Solid-fluid interactions in well and foam cements and solid-solid interactions in cement-casing interfaces under geologic sequestration and hydrothermal conditions will be studied using both *in situ* and *ex situ* synchrotron [X-ray fluorescence (XRF) and X-ray absorption near edge structure spectroscopy (XANES) and computed tomography (CT)] studies. Such studies will elucidate the phase, chemical and microstructural changes associated with dissolution and precipitation reactions occurring at subsurface material interfaces.

The proposed research will provide fundamental understanding of subsurface material degradation of advanced cements and cement-casing interfaces from the meso- to the nano-scale using synchrotron methods, which will aid in design of next generation self-healing cements. It strategically leverages National Synchrotron Light Source II (NSLS-II) and positions BNL as a key player in characterizing subsurface materials using high resolution and ultra-fast X-ray methods. This will position BNL to be a strategic key partner in the Subsurface Technology and Engineering R&D (aka SubTER) team and to compete for the anticipated Energy Frontier Research Center call on subsurface materials as well as funding from the DOE Offices of Fossil Energy and Basic Energy Science.

APPROACH:

Characterization of cement-casing interfaces (in collaboration with Bill Carey at Los Alamos National Laboratory [LANL]): In a summary of seven years of work on the impact of CO_2-induced reactions on wellbore integrity and the viability of CO_2 sequestration, Carey *et al.* found that the primary leakage mechanism was via failures at the cement-steel and cement-caprock interfaces. Although the pathway has been identified, little is understood about how chemical reactions can initiate these defects and whether these defects grow larger or smaller in time as a result of either dissolution or precipitation in the presence of supercritical CO_2 (sc-CO_2) and brine. Our goal is to investigate chemical reactions and map mineral dissolution and precipitation reactions at cement-casing interfaces using a combination of high-resolution synchrotron methods at NSLS-II.

Characterization of microstructure and iron containing phases in foamed and polymer based cements (in collaboration with Barbara Kutchko at National Energy Technology Laboratory and Carlos Fernandez at Pacific Northwest National Laboratory): The storage of CO_2 in deep geologic formations requires the assurance of wellbore integrity, including the evaluation of the stability of wellbore cements over time. Investigations into well bore cement should include studying the effects of geologically-relevant parameters on the geochemical and geomechanical stability of existing conventional as well novel self-healing cements. Our goal is to study microstructure, chemical composition and structure of conventional and advanced, as-synthesized cements as well as after exposure to CO_2.

TECHNICAL PROGRESS AND RESULTS:

In FY 2016, three milestones were achieved:

1. Synchrotron based XRF and XANES characterization of cement-casing interfaces using the Submicron Resolution X-ray Spectroscopy (SRX) beamline: cement-casing samples were prepared using a synthetic wellbore system consisting of cement and an embedded rectangular length of steel casing with grooves to accommodate fluid flow. The system was exposed to a 50:50 mixture of sc-CO_2 and brine at 40 °C, 14 MPa pore pressure for 394 h. These cement-casing interfaces were studied using XRF mapping at the SRX beamline. XRF studies showed ''eye''-like carbonate structures formed at the cement-casing interface (Figure 1B), which consisted of Ca and Fe rich regions. These findings were aligned with Scanning Electron Microscope (SEM) studies (Figure 1A) done at LANL and provided the elemental distribution of eye-like carbonate structures at the sub-micron scale.

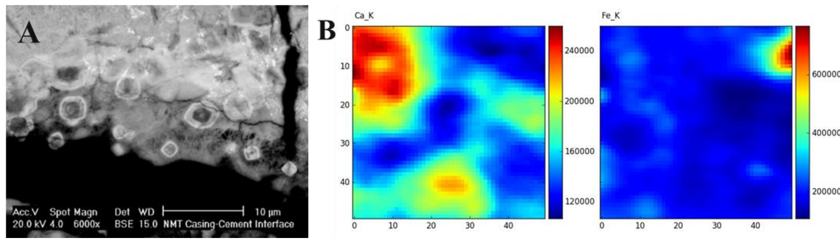


Figure 1: A) SEM image and B) Ca and Fe XRF maps showing formation of eye-like carbonate structures formed at cement-casing interfaces after CO_2–brine exposure.

2. Synchrotron based CT, XRF and XANES studies of advanced polymer cement composites using the SRX beamline: CT was used to study the internal microstructure of advanced polymer-cement composites with exceptional self-healing ability as a function of added polymer concentration. It was observed that porosity was clearly affected by polymer addition, where a polymer-cement composite with 25% polymer showed larger pores compared to a 10% sample. Further, XRF and XANES analysis of polymer cement composites exposed to CO_2 were performed at the Fe edge. The data was analyzed using linear combination fitting with different Fe compound standards measured at the same conditions. Unexposed polymer cement composites were found to contain ferrihydrite and geothite phases, while samples exposed to CO_2 showed clear carbonation and formation of siderite ($FeCO_3$).

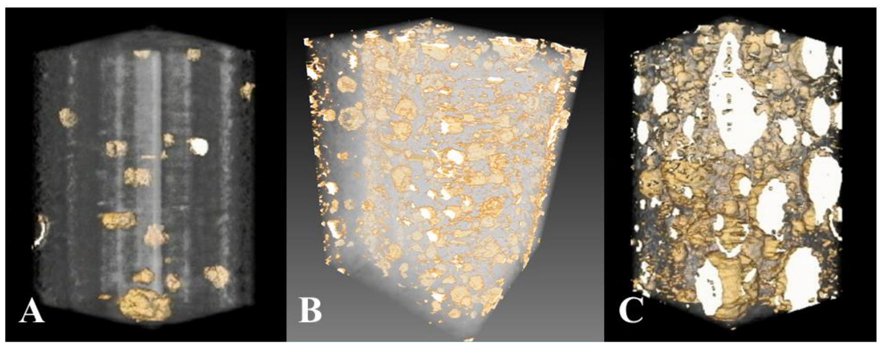


Figure 2:Tomography analysis of advanced polymer cement composites containing A) 0%, B) 10%, and C) 25% polymer

3. Development of the capability to study subsurface materials in a sc-CO_2 environment: We successfully procured a sc-CO_2 pump, autoclave and Raman set-up for subsurface materials testing and characterization.

Milestones

Test and commission CO_2 loop and publish results from FY 2016

Perform *in situ* studies of subsurface materials in a sc-CO_2 environment at NSLS-II.

In conclusion, chemical and structural changes in subsurface materials (cement-casing and advanced cements) exposed to corrosive brine and CO_2 environments were successfully elucidated at the sub-micron scale using the SRX beamline at NSLS-II. Such knowledge of chemical and structural changes is crucial to fundamentally understand dissolution and precipitation reactions in subsurface materials and design advanced well cements with good bonding characteristics.

Characterization of Gold Photocathode and Photoelectrons in Liquefied Noble Gases

LDRD Project # 16-021

T. Rao, T. Tsang

PURPOSE:

The purpose of this project is to investigate the possibility of integrating a photocathode as a part of the Time Projection Chambers (TPCs) for *in situ* charge calibration. Many large-scale liquefied noble gas TPCs are being designed and built for neutrino and dark matter experiments such as the Long Baseline Neutrino Facility (LBNF), the Deep Underground Neutrino Experiment (DUNE), and the next Enriched Xenon Observatory (nEXO). A robust and reliable electron charge calibration is crucial for these high purity liquefied noble gas detectors.

APPROACH:

In collaboration with Stony Brook University, a high purity gas xenon (Xe) purification and recirculation system is constructed to recapture the expensive Xe. A small TPC drift stack made of macor and sapphire is used to study the electron transport in noble liquids. Photoelectrons are generated by back illuminating a 22 nm thick semi-transparent gold photocathode on sapphire with time synchronized ultraviolet (UV) laser pulses. Photoelectrons drifted from the photocathode towards the anode are collected and measured. Field shaping rings and a wire grid positioned between the cathode and anode help shape the field lines and improve the charge collection efficiency. We examine the quantum efficiency (QE) of the photocathode and the photoelectron transport properties in liquefied xenon (LXe) as a function of drift field and impurity. The extracted electron lifetime depends strongly on impurity that can be used as a technique for charge calibration in large TPCs.

TECHNICAL PROGRESS AND RESULTS:

To date we have safely completed well over 50 cycles of liquefaction and measurements with improved Xe purity and many hours of stable drift electron signals in LXe. The great repeatability of the system allows us to study in detail the drift electric field dependence of the longitudinal drift velocity and diffusion. Data are collected on various LXe purification runs and on many different days to obtain reliable systematic and statistical uncertainties. Picosecond and nanosecond UV laser pulses of 4.66, 5, and 4.74 eV with pulse durations of 60 ps, 7.1 ns, and 71 ns, with peak power density ratio of 10^3, 10^1, and 1, respectively, are used to explore the role of multiphoton ionization in LXe.

Figure 1(a) shows a representative set of drift electron charge signal in LXe at the output of the anode shaping amplifier. It is clear that the electron charge clouds drift slower, thus have longer drift time, at lower drift fields; moreover, the widths of the charge signals broaden accordingly. This drift field transport information allows us to extract the field dependence of drift velocity, Figure 1(b), and the longitudinal diffusion coefficient, Figure 1(c). We derived a drift speed of 1.98 mm/μs and a diffusion coefficient of 22.6 cm^2/s for a drift field of 500V/cm. The multiphoton ionization in noble liquids is of interest in liquid argon (LAr) and LXe detectors, such as the LBNF and nEXO experiments. Although the ionization energy of LXe is comparable to LAr, ~12.1 eV versus ~15.7 eV, the 2-photon ionization cross section in LXe is expected to be ~4 orders of magnitude greater than in LAr. Therefore, multiphoton ionization in LXe is far stronger when a high peak power light source is used. Here, we explore multiphoton ionization of LXe using three different lasers of comparable UV wavelengths, but different pulse durations varied by a ratio of 1:10:1000. Figure 2(a) depicts the preamplifier signal of the charge collected at the anode, Figure 2(b) the amplitude of the multiphoton component of the signal as a function of laser intensity and 2(c) the same for linear photoemission. In addition, we estimate the multiphoton ionization cross section and compare it to the sparsely existing literature values. Such information can then be used to predict the electron bunch sizes for other laser configurations and to devise an approach to mitigate them in an electron charge calibration scheme based on photocathode technology.

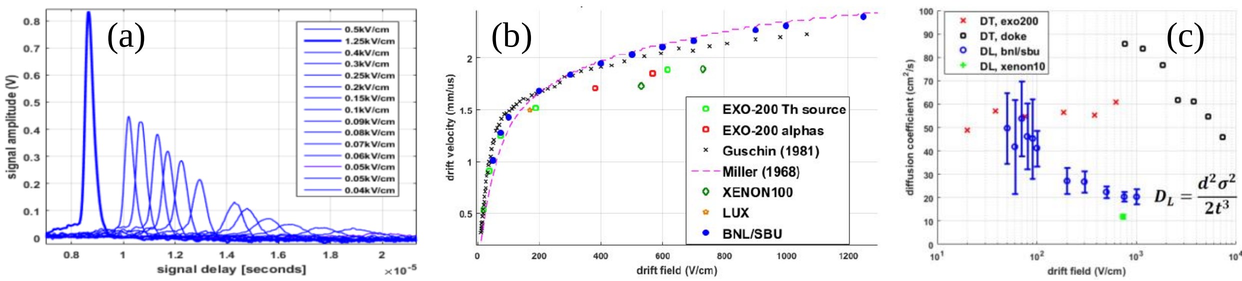


Figure 1. (a) A representative set of drift electron charge signal in LXe at the output of the shaping amplifier; the corresponding (b) longitudinal drift velocity, and (c) diffusion coefficient, as a function of drift fields, respectively.

After taking into account the lower electron yield and the higher loss of photoelectrons from the photocathode at low field, we estimated the quantum efficiency of the semi-transparent gold photocathode in LXe to be ~10^{-7}, which is comparable to that in LAr. In addition, we evaluated the electron lifetime by comparing the ratio of electrons arriving at the anode to that of leaving the photocathode at one fixed drift field. A consistent ratio of 0.6 was obtained at 0.5 kV/cm field gradient. All these results highlight the importance of minimizing impurity to extend the electron lifetime in LXe and to establish the reliability of the electron charge calibration scheme based on photocathode technology.

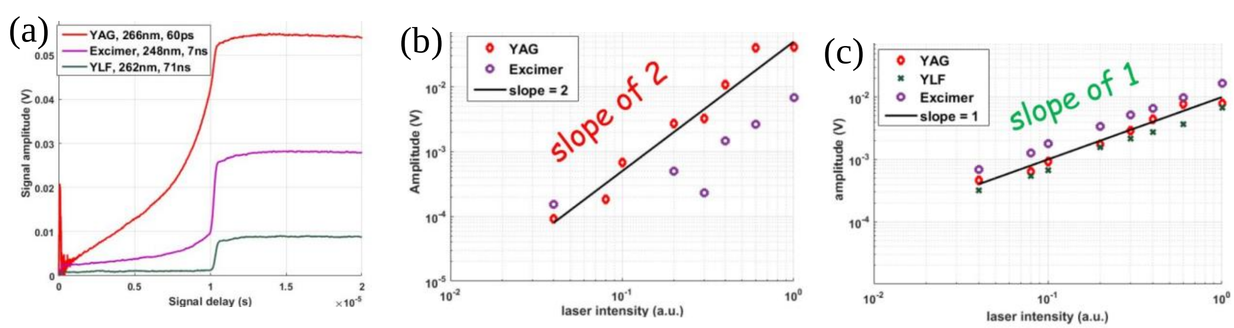


Figure 2. (a) A representative set of drift electron charge signals at the output of the anode charge sensitive preamp drifting through a 2-cm long LXe using 60 ps, 7.1 ns, and 71 ns light pulses, respectively. Log-log plot of the preamp signal amplitude versus laser intensity highlighting (b) a slope of 2 for multiphoton ionization in LXe, and (c) slope of 1 for linear photoemission from the gold photocathode by using short and long light pulses, respectively.

Milestones

FY 2016: a parts per billion purification system was constructed; expensive Xe was recovered.

FY 2017: drift velocity, longitudinal diffusion, QE, and multiphoton ionization are quantified.

Investigation of the Performance Characteristics of Silicon Photomultiplier (SiPM) Photosensors Under Extreme Conditions for Use in Nuclear and Particle Physics Detectors

LDRD Project # 16-022

T. Tsang, C. Woody

PURPOSE:

The purpose of this project is to study the properties of silicon photomultipliers (SiPMs) under extreme conditions (cryogenic temperatures and/or high radiation environments) for use with other detectors in nuclear and particle physics experiments. BNL plays a significant role in many of these experiments, such as PHENIX and STAR at the Relativistic Heavy Ion Collider (RHIC), ATLAS at the Large Hadron Collider, the Deep Underground Neutrino Experiment, and the next Enriched Xenon Observatory (nEXO). Improving their performance would benefit new programs at BNL, such as eRHIC and many others.

APPROACH:

A systematic study of the operation of SiPMs before, during and after irradiation was carried out at BNL. Devices with different pixel sizes were exposed to various doses of neutrons and gammas. Their operating parameters, dark current and single photoelectron spectra were characterized both at room temperature and cryogenic temperature. Recovery from radiation damage was also measured after thermal annealing. Material characterization of radiation damaged devices at the National Synchrotron Light Source II and the Advanced Photon Source is also being carried out in collaboration with Stony Brook University.

TECHNICAL PROGRESS AND RESULTS:

Comparison of radiation damage from neutrons and gammas: We observe different effects due to the different types of radiation when SiPMs are exposed to ~1 MeV gammas up to 1 Mrad and 14 MeV neutrons up to 10^{10} n/cm^2. Gammas produce a large dark current which disappears after the source is removed; while neutron-induced dark current remains after the removal of the source (Figure 1). This large induced dark current is indicative of bulk displacement damage in the silicon caused by defects produced by irradiation.

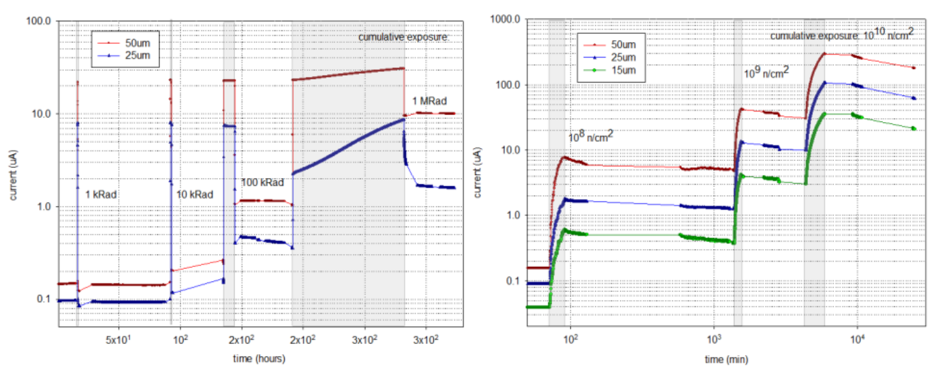


Fig. 1. Radiation induced dark current in SiPMs with different pixel sizes for increasing doses of gammas (left) and neutrons (right).

Studies of neutron radiation damage and recovery: SiPM lost its performance characteristics when exposed to a high dose of neutrons. However, the distinct hallmark of SiPMs (low dark count and excellent photon-number-resolving capability) can be recovered by thermal annealing. Several Hamamatsu and FBK series SiPMs are exposed to 14 MeV neutrons at BNL (Thermo Electron, Model MP32). After high temperature annealing up to 250^{o}C, their dark currents I-V and single photoelectron responses were evaluated using a synchronized 405 nm picosecond pulsed laser system. Figure 2 left shows the I-V plots during all stages of the experiment and

Figure 2 right shows their corresponding photoelectron spectrum. After thermal annealing, the dark current is lowered and their photoelectron resolving capability is restored. The annealing is permanent while the level of recovery scales with dosage and annealing temperature. It is effective on SiPMs from difference vendors, thus laying the foundation for extending the useful lifetime of large scale SiPM detectors deployed in ionization radiation environments.

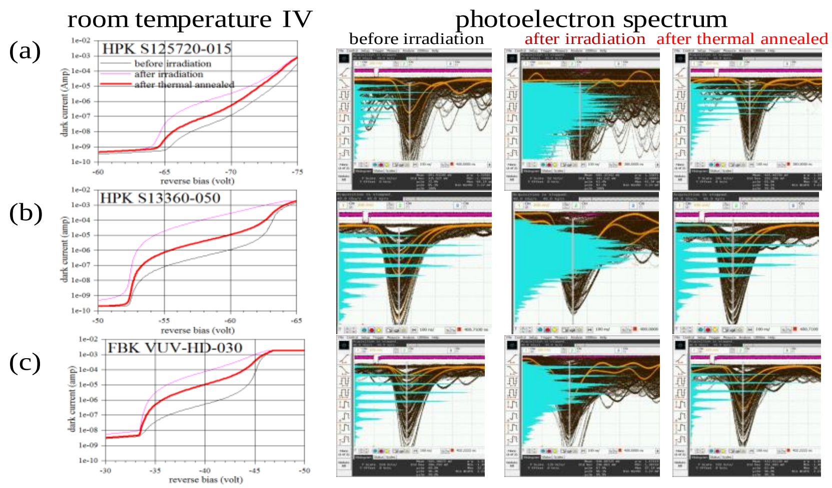


Fig. 2. Left: room temperature IV plots of (a) HPK S12572-015, (b) S13360-050, and (c) FBK VUV-HD-030 SIPMs; right: corresponding single photoelectron spectrum before, after 10^9 n/cm^2 irradiation, and after thermal annealing.

Studies at cryogenic temperatures: Scintillating photons of liquid xenon in the nEXO experiment are emitted at ~178 nm, in the vacuum ultraviolet (VUV). It is important to identify a SiPM that can meet the specifications of the nEXO detector. We have characterized the performance of the Hamamatsu VUV3 SiPM, which incorporated a trench for reducing crosstalk between neighboring pixels. Other than its ~0.5 lower fill factor, this latest SiPM design appears to meet all other nEXO requirements. Dark I-V is characterized using a Keysight B2987A electrometer, Fig. 3(a), and the single photoelectron response is evaluated using a time synchronized 405 nm picosecond laser system, Figure 3(b). At 3-volt overvoltage (OV), the charge gain, dark-count-rate, crosstalk, and the 1-photoelectron resolution are: 1.5×10^6, 5 Hz/mm^2, 0.15, and 2.6%, respectively; all meet the nEXO specifications, Figure 3(c)-(f). The photo-detection-efficiency at 178 nm is ~10% and the integration of a trench lowered the fill factor to ~0.5.

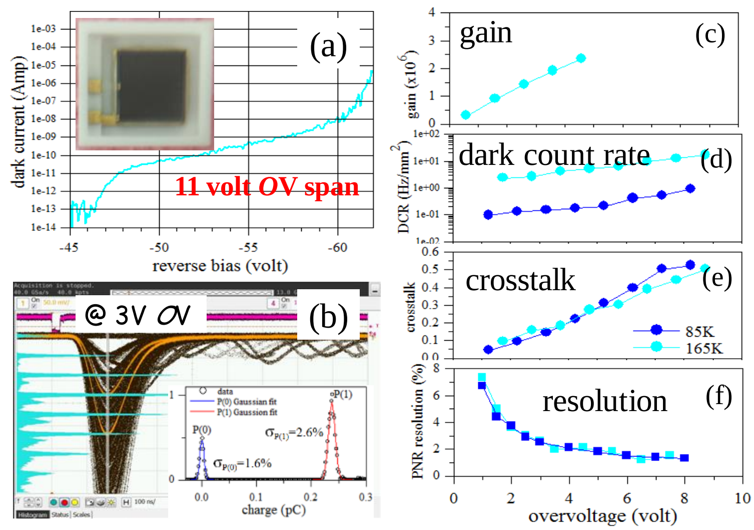


Fig. 3. (a) HPK VUV dark current IV plot at 165°K and (b) the corresponding single-photoelectron spectrum, in-set shows the resolution of the 1-pe peak and it instrument resolution. (c), (d), (e), and (f) are the charge gain, dark count rate, crosstalk probability, and the 1-pe charge resolution as a function of overvoltage.

Milestones

In FY 2016, we demonstrated that the SiPM works well in the cold and identified a technique to restore radiation damaged devices. In FY 2017, we identified that gammas and neutrons produce different radiation effects, established that thermal annealing is effective on SiPMs from different vendors, and identified SiPM that meets nEXO specifications. For the remainder of FY 2017, we will characterize the improved HPK VUV4 SiPM for nEXO and explore the difference in radiation damage, if any, when SiPMs are irradiated at cryogenic temperature.

ADC and Gbit/s Serializer/Driver in CMOS for Large Data Generation and *in Operando* Analysis

LDRD Project # 16-023
S. Li, E. Vernon

PURPOSE:

Modern radiation detectors are required to be compact with increasing demand for larger number of channels, better resolution, and faster data throughput. Low noise, low power, and high functionality front-end Application Specific Integrated Circuits (ASICs) are the enabling technology behind advances in modern radiation detector design. The purpose of this work is to develop an analog-to-digital converter (ADC) for signal processing, and an encoder-serializer/driver (ESERD) to transmit the digitized data off chip at Giga-bits/second (Gb/s) speeds. If resources allow, these circuits will be developed to operate at both room and cryogenic temperatures. Compared to conventional systems built from discrete components, if successful, two critical enabling circuits (ADC and ESERD) will be integrated into next generation front-end ASICs as systems on chip (SoC), thus directly impacting the future of micro-electronics and state-of-the-art detector developments at BNL. The applications will cover various R&D programs in Nuclear and Particle Physics, Synchrotron Light Sources (such as the National Synchrotron Light Source II [NSLS-II]), and National Security. There will be an immediate impact on large scale Liquid Argon Time Projection Chambers for the Long Baseline Neutrino Facility, large scale neutrino-less detectors for the next Enriched Xenon Observatory, dark matter detectors, and X- and Gamma-ray imagers needed at NSLS-II.

APPROACH:

The micro-electronics group in the Instrumentation Division at BNL has been developing ASICs to readout gas, liquid, and solid state radiation detectors. Conventional designs incorporate ASICs, which measure the amplitude and timing of an event and multiplex the analog data off-chip for digitization outside the detector with discrete ADCs. As the need for more channels increases, conventional designs are approaching a bottleneck in data rates and the number of feed-throughs required, which also increases the noise from cross-talk.

Alternatively, advances in low noise ASICs and direct interface with the sensor electrodes inside the detector volume have improved the noise performance and reduced the complexity of detector design by requiring less feed-through. In addition, by implementing ADCs and ESERDs on the ASIC fabric to form SoCs, the data bandwidth will be significantly improved for next generation detectors.

In phase I of the design process, the successive approximation register analog-to-digital converter (SARADC) design is under study. The approach involves: the exploration of various topologies; developing functional models for the signal chain; systematically converting functional blocks to transistor level designs; implementing the physical layout; verifying performance with post layout simulations; fabrication of the first prototype on a multi-project wafer; and bench top testing with the possibility for a design revision. In phase II, the ESERD will follow the same design trajectory to achieve parallel testing of the two circuits.

TECHNICAL PROGRESS AND RESULTS:

During FY 2016, a functional model for the SARADC was developed as shown in Figure 1. The model includes a capacitive digital-to-analog converter (CDAC) that also acts as a sample and hold circuit, a comparator, and the SAR logic. Complementary Metal–Oxide–Semiconductor (CMOS) 1.2V input/output pads along with scalable low voltage signaling pads for high speed communication (500 MHz) were also implemented. In addition, a library of digital standard cells consisting of AND, NAND, OR, NOR, XOR, D-flip-flop, multiplexer, and tri-state buffers was developed.

During the beginning of FY 2017, different topologies of the CDAC were studied to improve the energy efficiency of the ADC.

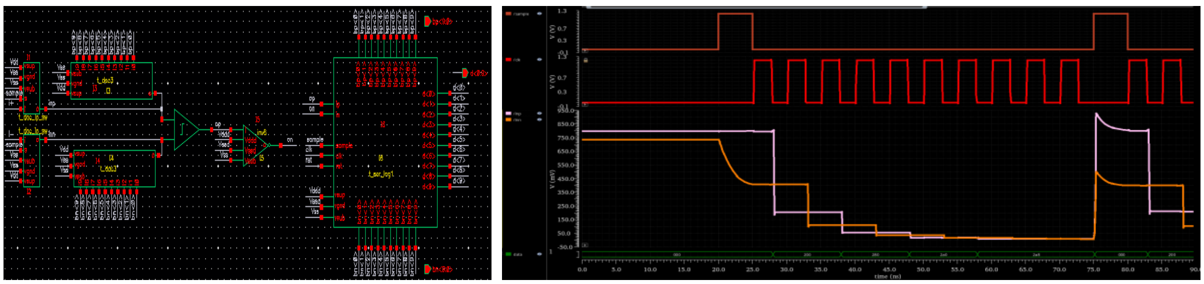


Figure 1. (Left) Functional block diagram of the SARADC and (Right) corresponding simulation.

Milestones

FY 2017

- Schematic design and simulations of the ADC
- Physical layout and post layout simulations.

FY 2018

- Fabrication of the first ASIC prototype (ADC)
- Characterization of the first prototype
- Design revisions
- Fabrication of the second ASIC prototype
- Characterization of the second ASIC prototype.

Improved X-ray Spectroscopy Detectors

LDRD Project # 16-024
G. Giacomini, D. Elliott

PURPOSE:

High-rate X-ray spectroscopy allows the determination of the elemental composition of a sample by detecting the element's characteristic fluorescence X-rays that are emitted in response to an excitation produced by the synchrotron X-rays. Nowadays, this is done by an array of p-in-n diodes, *e.g.* the BNL-developed detector called Maia, whose energy resolution is essentially limited by the noise coming from the capacitance of each diode. Such resolution allows only the detection of X-rays emitted by elements heavier than aluminum, while lighter elements are beyond detection. To extend the reach of the elemental tagging of the first elements of the periodic table, the detector must feature a better energy resolution, such as the one achieved by Silicon Drift Detectors (SDDs), which, due to the complexity of the device, exist commercially only as single channel devices. To retain the high throughput typical of the original Maia array (tens of megahertz), each diode has to be replaced by a single drift sensor. This translates to an improved energy resolution at shorter shaping times, which in turn further increases the acquisition rate (or decreases the measurement time).

Improved spectroscopic performance will allow exploring new kinds of samples; a number of beamlines at the National Synchrotron Light Source II will benefit from this new development, while generating interest from other beamlines at synchrotrons world-wide, some of them already equipped with versions of the diode-based Maia.

APPROACH:

Maia is a high-rate X-ray spectroscopic detector, which consists of an array of 384 1x1 mm2 p-in-n diodes. The sensor itself is fabricated in the Silicon Processing Facility of the Instrumentation Division at BNL; the read-out electronics and the boards have been designed at BNL and the mounting is performed here too. The energy resolution – and thus the capability of detecting X-rays emitted by light elements - is intrinsically limited by the capacitance of the p-in-n diodes, which also negatively affects the measurement times.

As a first step towards the achievement of an enhanced energy resolution and shorter acquisition times, it is fundamental to replace the sensor itself. Each 1x1 mm2 diode must be replaced by a SDD, whose small anode capacitance allows the achievement of both goals.

To carry out the development, the following actions must be undertaken and completed: design and fabrication of SDDs in the Silicon Processing Clean Room at BNL (Wei Chen); electrical characterization of the fabricated devices at the probe station to select good devices; laser scribing of wafers to identify the good devices; mounting on printed-circuit boards and connection through wire bonding to the read-out electronics (Don Pinelli); and in-lab X-ray spectroscopic measurements (Peter Siddons). Boards and electronics are the same as for the original Maia. From the results of the first characterization, an optimized design and process flow follow.

TECHNICAL PROGRESS AND RESULTS:

A first design was carried out and a first batch of silicon wafers was processed. Electrical characterization of devices at the probe station allowed selection of the best sensors (Figure 1a), which were then mounted on boards and connected by wire bonding to the read-out electronics (Figure 1b). A first in-lab spectroscopic measurement campaign was performed. From these results, a new batch – with a slightly modified design and process flow – was initiated.

FY16 Milestones accomplished

- Design of photolithographic masks
- Fabrication of a first batch of sensors
- Spectroscopic testing of a few sensors.

FY17 Milestones

- Completion of the second batch
- Electrical characterization of the wafers and selections of good devices
- Functional test of good sensors
- Design of a new mask set
- Fabrication of an additional batch, after inputs from the previous activity.

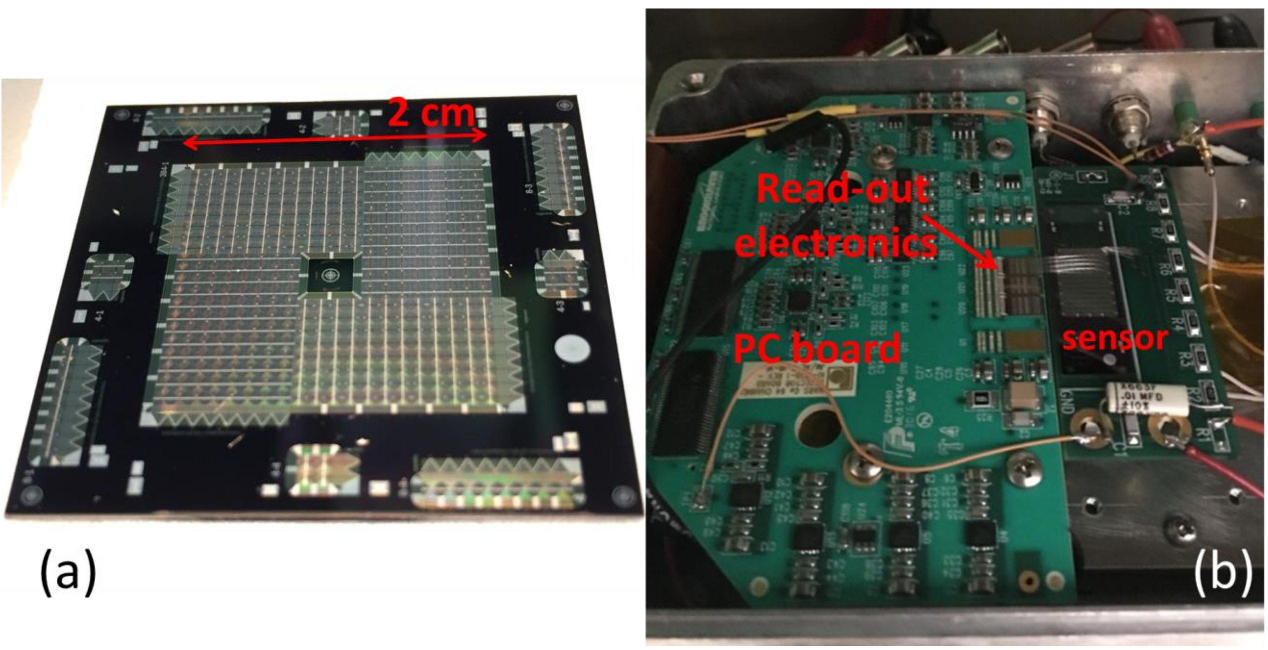


Figure 1. (a) Picture of a fabricated 384-array of a Silicon Drift Detector, laser-scribed from the 4 inch wafer. (b) Set-up for the in-lab spectroscopic measurement.

Microwave Kinetic Inductance Detectors: from Cosmology to NSLS-II

LDRD Project # 16-026

P. O'Connor, A. Nomerotski, A. Slosar

PURPOSE:

A principal question in the Office of High Energy Physics's Cosmic Frontier research portfolio is to understand the nature of Dark Energy (DE), the accelerated expansion of the universe. Experimental approaches to date have relied on all-sky surveys with large optical telescopes equipped with silicon detectors. In this LDRD, we are pursuing alternative technologies for the next generation of Dark Energy research. In particular, we are investigating radiofrequency (RF) wavelengths and alternatives to silicon detectors. Radio surveys have the potential to expand the survey volume by a factor of ten relative to present optical surveys, and a new class of superconducting detector (called MKID for Microwave Kinetic Inductance Detector) has attractive properties both for cosmology and photon science. In this LDRD, we hope to demonstrate feasibility of a technological approach suitable for a large-scale Dark Energy experiment follow-on to the Large Synoptic Survey Telescope (LSST), where BNL already plays a key role.

APPROACH:

Background: The universe's expansion rate is accelerating, and the origin and nature of the process (called Dark Energy) is one of the most pressing questions in fundamental physics. Experimental investigation of DE observables can only be done by measuring the properties of massive extragalactic objects on scales up to billions of light years. Today researchers use optical and millimeter-wave surveys that extend to much smaller scales, which put limits on the precision to which DE parameters can be measured.

In this LDRD, we seek to demonstrate feasibility and cost-effectiveness of an RF survey using the 21-cm emission of neutral hydrogen in galaxies by tailoring the instrument to sacrifice small-scale (*i.e.* galaxy-by-galaxy) resolution, which encodes little information on DE, in favor of survey speed, thus enabling a large volume to be surveyed in a future ten-year follow-on survey to LSST and the Dark Energy Spectroscopic Instrument (DESI).

Co-investigator Anze Slosar, visiting scientist Paul Stankus, and postdoctoral research associate Christopher Sheehy in the Physics Department are participating in a parallel LDRD which seeks to optimize the science reach of a future survey. Colleagues Jeff McMahon at the University of Michigan and Hamdi Mani at Arizona State University are helping this effort.

In conjunction with the 21-cm instrument, we are exploring properties of the MKID detector, with collaborators Glenn Jones and Bradley Johnson at Columbia University and colleagues Don Elliot in the Instrumentation Division and Abdul Rumaiz in Energy and Photon Sciences. This new detector has promise to improve the efficiency of optical surveys, while offering complementary advantages to photon science in the soft X-ray regime. Professor Johnson is a leading expert in the design and test of MKID detectors and associated RF techniques.

TECHNICAL PROGRESS AND RESULTS:

1. Prior LDRD funding allowed us to investigate MKID fabrication and testing. We made exploratory pre-MKID test structures on high-Tc material Yttrium Barium Copper Oxide

(aka YBCO) fabricated by colleagues in the Condensed Matter Physics and Materials Science Division. Tests on these structures and design studies showed this approach to be unfeasible for large-scale deployment.

2. We have made contact with colleagues at the Princeton University Physics Department who have offered us access to an 18-m steerable dish antenna in New Jersey which they control.

3. The parameters for a 21-cm RF survey were quantified and a strawman design of a demonstrator instrument was drawn up. The demonstrator will have a 4 m off-axis parabolic dish, rectangular feed horn, and dual-polarization transceiver fabricated using low-cost construction techniques. The broadband receiver electronics rely on ultralow-noise SiGe bipolar transistor amplifiers, gain calibration using tone injection, and software-defined radio back-end with low-cost Graphics Processing Units executing the required spectrometer algorithms in real time.

4. An RF interference survey of the BNL site has been conducted and we now understand the frequencies we will need to avoid the strongest interference.

5. Most of the elements of the receiver electronics have been procured and tested.

6. We have been given approval to construct the demonstrator instrument in an on-site location.

7. Modular components of the parabolic dish antenna have been assembled and surveyed, and we are initiating fabrication of the complete dish.

8. An experimental MKID maskset has been transferred from Columbia to BNL, and a prototype aluminum-based detector is being fabricated in the Silicon Detector Laboratory in the Instrumentation Division.

Milestones

In FY 2016, designs and prototypes of a complete 21-cm hydrogen intensity mapping demonstrator instrument have been successfully carried out. We expect to construct the complete instrument and begin on-sky testing in FY 2017.

Detector Calibration and Material Analysis – Expanding the Capabilities of NSLS-II

LDRD Project # 16-027

J. Smedley

PURPOSE:

The central goal of this project is to make X-ray Beam Induced Current (XBIC) a technique available at National Synchrotron Light Source-II (NSLS-II). NSLS was a leader in this research area, with two beamlines dedicated to this work, and two more also accepting proposals in this area. The project will also enable X-ray topography, which has a strong synergy with XBIC. Taken together, these capabilities allow study of both the charge motion in semiconductors and the isolation of electrically active defects, which can affect device performance.

APPROACH:

We have identified a beamline to enable topography and spectroscopic X-ray beam induced current measurements at NSLS-II (the inner-shell spectroscopy beamline [ISS]). While this capability is being constructed, we have used our initial beamline capabilities at the Cornell High Energy Synchrotron Source (CHESS) to calibrate 16 devices for NSLS-II beamlines, and have assisted four independent user groups with these techniques who will continue their work when the NSLS-II capability is available. We have secured funding for developing medical dosimetry, which is a spinoff of the detector effort and required the new capability at NSLS-II to be successful.

TECHNICAL PROGRESS AND RESULTS:

The hardware allowing XBIC mapping at ISS has been purchased and assembled in compliance with NSLS-II requirements, including use of delta-tau motion control systems. The software to allow these motion control systems to interface with the beamline has been written; we will also be able to use the data acquisition capability of the delta-tau to read the detector/sample current. The system just had its first X-ray test – the system and first results are shown in Figure 1. This system can accommodate samples up to 30 cm x 30 cm active area, and up to 10 kg, enabling it to be useful for detectors with large sensitive areas, as well as typical photovoltaic cells. This system is hermetic and can accommodate a variety of inert gas environments, with nitrogen being the most common.

While this system was being designed and constructed, we utilized a smaller, stand alone motor set at the G2 beamline at CHESS to characterize detectors for NSLS-II, including ultra-thin detectors for the Soft Matter Interfaces (SMI) beamline. We have also supported four external user groups – two from industry (one doing SiC detectors, and the other diamond detectors), and two from Los Alamos National Laboratory (LANL) (one of which was our LANL collaborator James Distel).

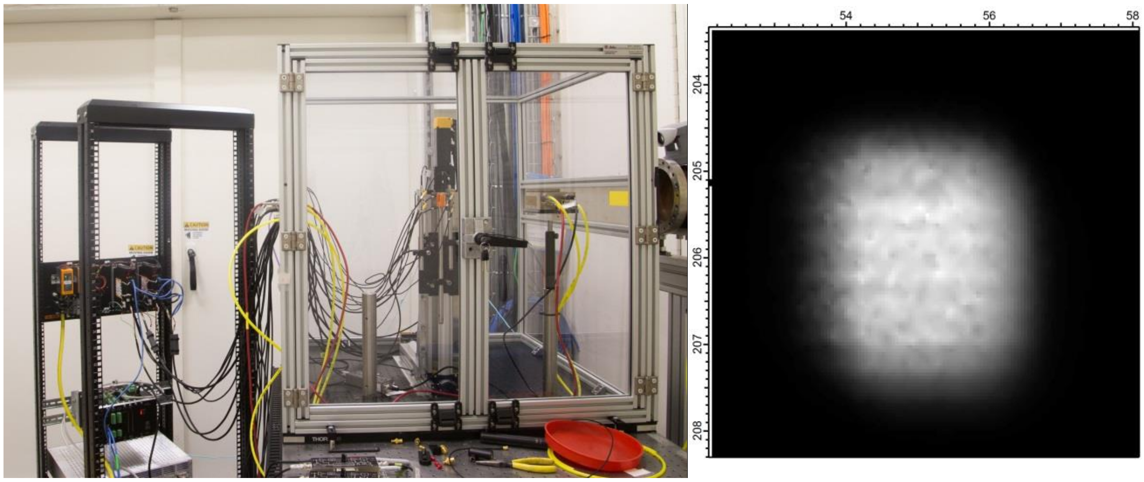


Figure 1. (Left) XBIC enclosure for nitrogen atmosphere measurements and (Right) first XBIC scan of a diamond device from this system (11 keV X-rays)

We have obtained funding from the DOE Office of High Energy Physics (Accelerator Stewardship) to develop detectors for proton and carbon ion radiation therapy ($500k over two years, half of which comes to BNL and half to Stony Brook University). This proposal relies heavily on the XBIC capability being developed, as this is the tool which allows us to understand radiation damage induced by the charged particle beams.

Milestones

- In FY17, fully automated XBIC scanning commissioned and accepting users at ISS beamline
- Microbeam scanning available (20 micron beam)
- First tests of X-ray Topography at ISS.
- Topography ready to accept users
- Vacuum environment XBIC system tested.

Higher-Order-Mode (HOM) Damping for Full Luminosity of eRHIC

LDRD Project # 16-029

W. Xu

PURPOSE:

The objective of this project is to increase the eRHIC luminosity limit, through demonstrating a high-power, full-spectrum Higher-Order-Mode (HOM) damping scheme for the eRHIC Energy Recovery Linac. The HOM damping requirement and scheme of the Superconducting Radio Frequency (SRF) linacs (electron and proton) and storage cavity for Ring-Ring eRHIC design will be studied and verified as well.

APPROACH:

The proposed HOM damping scheme for a high current SRF cavity combines waveguide HOM dampers (for low frequency HOMs) and a room temperature beam pipe absorber (for high frequency HOMs). The expected results are:

- A HOM spectrum study on a detachable copper (Cu) cavity
- RF design and simulation is the starting point of the whole project. It includes design of the ridge waveguide, waveguide absorber, and beampipe absorber
- Engineering design that includes thermal analysis and mechanical design
- A waveguide HOM damper and beampipe absorber prototype and test on the Cu cavity to verify the HOM damping results
- Modification of the Niobium (Nb) SRF cavity to attach the waveguide damper and carry out the vertical test.

TECHNICAL PROGRESS AND RESULTS:

1. The Cu cavity for the HOM spectrum study is undergoing fabrication in *RI Research Instruments GmbH* in Germany (the same company that fabricated the Nb prototype cavity). Figure 1 shows the Cu cavity model and photos of the fabricated parts.

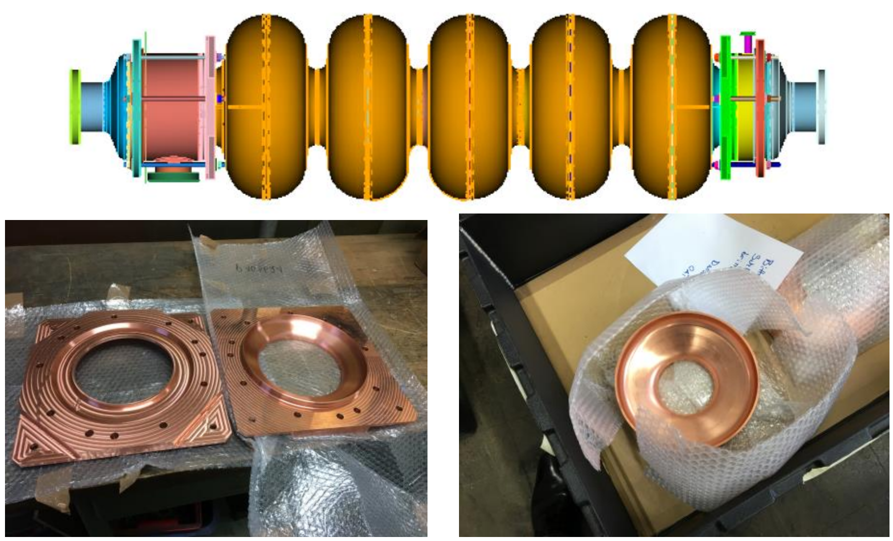


Figure 1. 5-cell 650 MHz Cu cavity model (Top) and photos of some of the parts (Bottom).

2. Version #1 of the HOM damping with six ridge waveguides and a beampipe absorber was completed in terms of the physics and engineering design. The prototype is undergoing fabrication. Figure 2 shows the damping scheme. This HOM damping scheme satisfies the HOM damping for eRHIC, in terms of monopole HOM power and beam breakup threshold for the dipole mode.

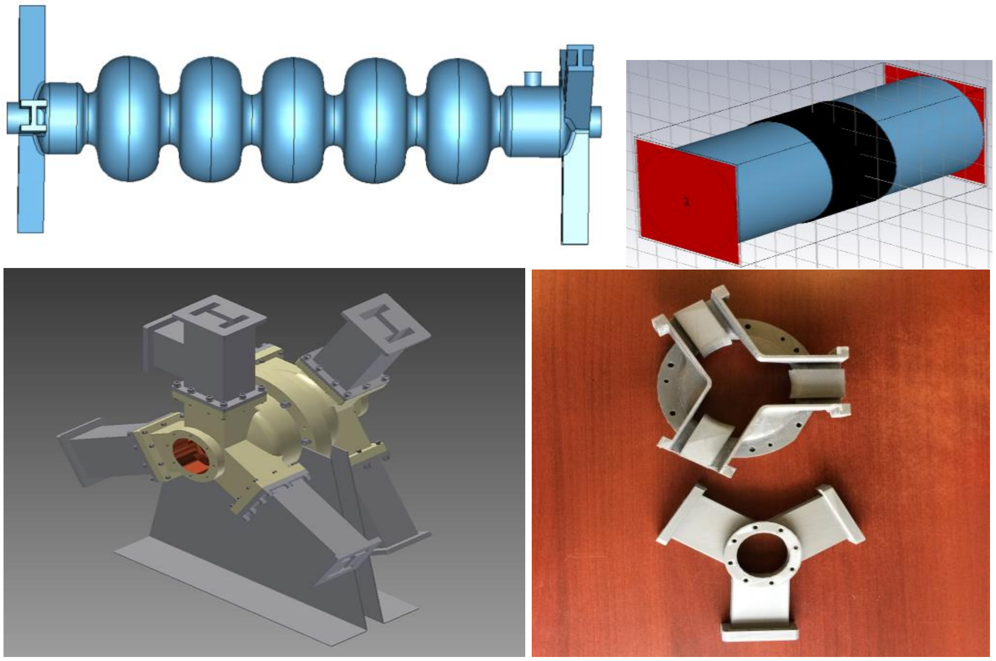


Figure 2. HOM damping scheme (Top left); Beampipe absorber (Top right); Measurement setup (Bottom left) and Photo of prototype parts (Bottom right).

Milestones

While the first version of HOM damping is being prototyped, another idea of the HOM damping scheme with a coaxial-line plus a round ridge waveguide design has evolved and is under study. This potentially allows us to have less HOM dampers per cavity, which makes the system cheaper. The plan is to finish the RF design of this version of the HOM damper in early April, 2017. This version will be prototyped and tested with the Cu cavity as the version #1 HOM damper.

One version of the HOM damper will be fabricated out of Nb material and welded to the Nb cavity for a vertical test, to verify the fundamental mode’s property. The decision of which version to fabricate will be made by the end of 2017. The vertical test will take place in June 2018.

Advanced Silicon Detectors R&D

LDRD Project # 16-034

F. Lanni, H. Chen, G. Giacomini, H. Takai, A. Tricoli

PURPOSE:

The focus of this project is on the development and characterization of three innovative Silicon (Si)-based technologies for their potential application in tracking and calorimeter system upgrades of current experiments (*e.g.*, ATLAS and CMS at high luminosity Large Hadron Collider), and of future experiments at the next generation of colliders in nuclear and particle physics (*e.g*. eRHIC and a Future Circular Collider). These are high voltage/high resistivity CMOS hybrid sensors (HV/HR-CMOS), ultra-fast Si detectors through Low Gain Amplification Devices (LGAD), and Monolithic Active Pixel sensors based on HV-CMOS (HV-MAPS). These technologies will be evaluated in terms of performance, reliability and radiation tolerance. In the process, we will take advantage of the existing facilities at BNL for understanding material properties in detectors and electronics, specifically at the Instrumentation Division. The ultimate objective of the project is the exploration of fully monolithic sensors, which integrate both sensor technologies and readout devices mentioned above. The advance of these technologies may also impact other fields, such as high precision/fast read-out sensors for dynamic structural analysis for time-resolved crystallography and beam monitoring at photon science facilities and medical applications, such as precision timing-based Positron Emission Tomography. The project, if successful, will heighten BNL's reputation as a leading organization in Si sensor R&D cutting-edge technology.

APPROACH:

Precision measurements of multi-hadronic final states at high energy colliders will require larger and larger areas of Si detector coverage and readout channels and miniaturization of feature-size. Today's available technology is limiting this capability because of cost implications and the amount of service that these detector require, which ultimately will compromise the performance in reconstructing charged particles and the underlying events to be measured.

The motivation of this project and the strategy that we have pursued is to advance technology in the following directions:

- Research the development of sensors through industrial fabrication
- Maximize integration of front-end electronics on sensors in small feature size processes
- To enable the discovery of rare events, very high luminosity colliders are needed; therefore experimental measurements are complicated by the number of primary vertices per bunch collision. Silicon detectors with high precision timing reconstruction of a track, together with the vertex information, enable identification and discrimination of particles emerging from the hard scatter vertex.

TECHNICAL PROGRESS AND RESULTS:

The milestones and the achievements for FY 2016 are:

M16-01: Establish measurement capabilities of the sensor qualification using HV-CMOS and LGAD designs from existing Multi-Wafer Projects

M16-02: Contribute to the design of the monolithic front-end of AMS prototype submissions (submission of both HV-CMOS and LGAD prototypes in FY 2017)

M16-03: Perform baseline measurements of the HV-CMOS and LGAD first prototypes.

The main achievements are:

- Setup a dedicated laboratory in the Instrumentation Division for characterization of Si-based sensors using top and edge-TCT (Transient Current Technique). TCT is based on a controlled laser injection to study charge transport and collection in the Si sensors. Commissioning of the Top-TCT has been completed.
- Manufactured LGAD structures, designed by G. Giacomini, using processing at the Si fabrication facility in the Instrumentation Division. Preliminary characterization of those structures is on-going
- Established two international collaborations for HV-CMOS (U. of Geneva; U. Bern; U. Liverpool; Karlsruhe Institute of Technology) and for LGAD (U. California Santa Cruz; U. Paris VI; Laboratoire de l'Accélérateur Linéaire Orsay; Centro Nacional De Microelectronica (CNM) Barcelona; Jožef Stefan Institute Ljubliana; CERN; Istituto Nazionale di Fisica Nucleare Turin)
- Design, fabricate test fixtures of first LGAD sensors (design of CNM in 50 um devices)
- Participate at testbeam campaigns at CERN in August – as part of the High Timing Detector Proposal in the ATLAS experiment, of which I was the proponent and coordinator until December 2016.
    - Demonstrated capability of achieving expected timing performance with resolution below 50 ps (Figure 1)
- HV-CMOS testbeam characterization for non-irradiated and irradiated large area sensors achieving excellent minimum ionizing particle efficiency above 99.7% (Figure 2).

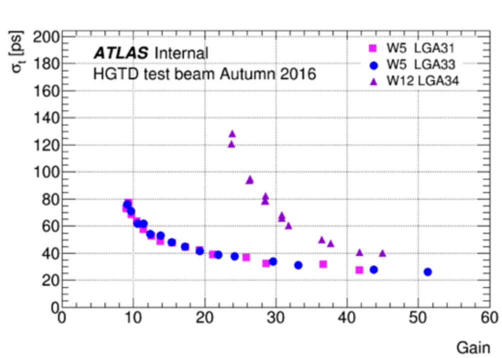


Figure 1. HV-CMOS prototype efficiency.

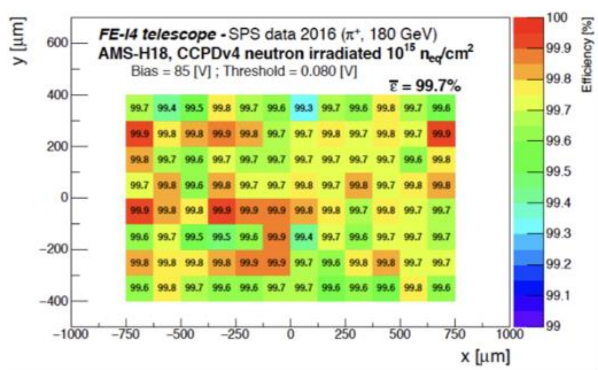


Figure 2. LGAD prototype time resolution

The excellent results allowed us to define priorities and the milestones for FY 2017, continuing the program outlined in the original proposal:

Milestones

- Iterate design for both LGAD and HV-CMOS prototypes. First HV-MAPS designed submission and preliminary test characterization
- Laboratory characterization at BNL and through testbeam at Fermilab and CERN (October 2016, May-July 2017, September 2017)
- Irradiation of devices for radiation damage studies with pions
- Completion of irradiation studies. First annealing studies at BNL

Resolving Technical Issues of a Compact Time Projection Chamber for Use at both RHIC and a Future Electron Ion Collider

LDRD Project # 16-035

E. O'Brien

PURPOSE:

The purpose of the project is to develop a concept for building a compact Time Projection Chamber (TPC) that could be implemented as a detector for both the Relativistic Heavy Ion Collider (RHIC) and a future Electron-Ion Collider (EIC). The challenges are: the mechanical footprint of the detector must be only minimally larger than the active volume of the TPC; the design of the high voltage field cage must minimize field distortions, especially at the inner radius; the readout plane must minimize ion feedback and space charge build-up; and the electronics chain must be able to handle both the high multiplicities during RHIC heavy ion operation and the high luminosities during RHIC polarized proton running. At the end of the LDRD, we plan to have completed a conceptual design compact TPC design that could operate at both RHIC and EIC.

Time Projection Chambers are an excellent technology for RHIC and EIC. They measure the momentum of all charged particle with good precision. They are generally low mass devices, meaning that they do not significantly scatter the particles that they are measuring. Their limitations include that their performance degrades at high particle multiplicities and high rates due to field distortions from ion build up, and they have trouble tracking at radii close to the interaction point, at radii less than 60 cm. If the space charge effects could be reduced at low radii and high multiplicity, then their utility at RHIC and EIC would be markedly improved. A TPC with a smaller outer radius than those currently employed at RHIC and the Large Hadron Collider would enable the installation of calorimetry at a much smaller radius and result in calorimeters with significantly smaller volumes, which translate to significantly lower costs.

APPROACH:

I have been involved in the design, construction and operation of tracking detectors for use in both High Energy Physics and Nuclear Physics experiments for over three decades. As a member of the sPHENIX project, I have become interested in solving a number of challenges associated with compact Time Projection Chambers that would allow for their use in both a RHIC and EIC detector. I also have a number of colleagues that share this interest and are collaborating with me on this project including: Craig Woody, John Haggerty, Takao Sakaguchi, Jin Huang and Bob Azmoun at BNL, Tom Hemmick and Klaus Dehmelt at Stony Brook University (SBU), and Alexander Milov at the Weizmann Institute of Science (WIS). We will use design studies, simulation studies, bench tests and fabrication of prototypes to test our ideas on how to solve the challenges previously described.

TECHNICAL PROGRESS AND RESULTS:

In 2016, we advanced the conceptual design of a full-scale prototype of a compact TPC. The design of the prototype field cage, central membrane, end caps and external support structure is advanced. Construction of the field cage for the prototype started at SBU and will be completed in mid-2017. The software simulations made good progress and were used to develop schemes to minimize space charge effects. The simulated solutions look very promising. We have identified the preferred gas option for the detector through work at WIS and BNL. We completed a preliminary design study for the readout electronics chain, created a block diagram and identified key components in the chain.

In 2017, the construction of the prototype field cage will be completed. We will produce a small number of readout modules for the TPC and install them in the prototype field cage. The main goal of the Research & Development work for 2017 is to complete the prototype TPC and begin testing. Testing will likely take place first at SBU and eventually at BNL. We will test the new design features of the TPC prototype, especially the voltage integrity and field quality of the field cage. The scheme for the mechanical support, the low profile gas seal, field distortion minimization, signal feed-through, and gas electron multiplier readout module will all be tested. The TPC will be tested with the preferred gas choice for minimum ion feedback as determined by our simulations.

Milestones

- The TPC prototype field cage and end cap will be completed and ready to assemble in May 2017.
- The detector will be tested to compare its operation to the simulated performance parameters stating in June and running to September 2017.

Exploring Hadron Structure with ab initio Lattice QCD Calculations and Making Predictions for eRHIC

LDRD Project # 16-037

T. Izubuchi

PURPOSE:

The ultimate goal of the project is to provide reliable theoretical guidance for the future eRHIC experiment in terms of the nucleon's internal structure. We aim to compute the parton distribution function (PDF) and transverse momentum dependent (TMD) PDF, which describe the dynamics of quarks and gluons (collectively called partons) inside hadrons. We recently proposed a formalism to extract PDFs using first principle lattice Quantum Chromo Dynamics (Lattice QCD) in terms of both theoretical principles and practical numerical calculations. This requires thorough understanding of QCD factorization and related theoretical topics as well as Lattice QCD technologies. Synergetic collaboration of researchers from two subareas, perturbative QCD and Lattice QCD, are established for this purpose.

APPROACH:

The complex internal structure of the nucleon is studied in terms of the first principles theory of physics (QCD), which describes the quantum motion of elementary particles - quarks and color force mediator gluons. Due to the confinement nature of QCD, quarks cannot be directly isolated from hadrons and one needs theoretical descriptions of the quarks and gluons inside a hadron to interpret results from collider experiments, such as eRHIC. Parton distribution functions are an example of such quantities, which describe how the large momentum of a nucleon is carried by quarks and gluons (partons). Using the framework of QCD factorization, the PDF is related to experimentally observable cross sections of hadrons. As quarks and gluons are mutually coupled very strongly, one needs a non-perturbative analysis of QCD to be able to predict the PDF, which especially at both large and small momentum fraction, x, is poorly understood so far. Lattice QCD that has now become a reliable tool in solving QCD with high (sub-percent) accuracy for basic hadronic quantities, is applied to PDF calculations along the line of the recent proposal by Ji [1] (also see [2]). This new approach computes quasi-PDFs from equal-time QCD matrix elements of a bi-local operator (or Wilson line) for the nucleon states with high momentum. The quasi-PDF is related to the normal PDF by a convolution integral.

TECHNICAL PROGRESS AND RESULTS:

FY 2016 is the first year of this LDRD project. The project started with the arrival of our newly hired postdoc, Dr. Luchang Jin from Columbia University. He is the key player of the project. The project has been moving forward as proposed, with the following progress/achievements:

1) We organized an inter-disciplinary workshop that involves expertise from lattice QCD and perturbative QCD communities. 2) We organized a discussion group that meets every two weeks about lattice calculations of the hadronic structure. 3) We discussed and studied the renormalization of the operators used in the proposed lattice calculations. Extended discussions were also held with visitors from other institutions, *e.g.*, Andreas Schaefer (Regensburg), Tomomi Ishikawa (Shanghai), and Huey-Wen Lin (Michigan). 4) To be able to compute a PDF qualitatively, renormalization of the bi-local operator for the quasi-PDF is an important step. So far, such a renormalization process has not been carried out. We found that there are two non-perturbative approaches to compute the renormalization factors. The two approaches are the

"RI/MOM" (regularization independent momentum subtraction renormalization scheme) approach and the "renormalization factorization" approach. 5) We so far focused on the "renormalization factorization" approach. The key step of this approach is to determine the mass renormalization of the Wilson line. 6) We tried to determine the mass renormalization constant with two different methods by using lattice calculations. The first method is using a Wilson loop and static quark-antiquark potential. The second method is using a Wilson line in a Laudau gauge. A paper on the first calculations of the one-loop matching factor between the lattice QCD calculation of the quasi parton distribution functions, numerically on a discretized lattice, and the analytical calculation of the same function in a continuous perturbative QCD approach, was recently completed. This is necessary for extracting PDFs from the lattice QCD calculation of the quasi parton distribution functions. The paper was submitted to the Journal of High Energy Physics for publication. Members of the project have given a number of invited talks at major conferences.

Milestones

FY16/17:

- Establish the methodologies of the lattice calculation using a less expensive lattice with Wilson fermions and focus on the control of both statistical and systematic errors
- Apply for computer resources to USQCD, a collaboration of U.S. lattice QCD and RIKEN in Japan.

FY17/18:

- With the establishment of the methodologies and computer resources, compute with a more realistic lattice, which has a fine lattice spacing while keeping an adequate volume size
- Perform global analysis of the generated lattice "data" in terms of the QCD factorization formalism to extract the PDFs, as a function of x, to establish in practice a complete example for extracting PDFs from lattice QCD calculations based on QCD factorization
- Quantify the improvement from the first exploratory work.

FY18/19:

- Perform a realistic lattice based calculation of the ratios of PDFs, such as d(x)/u(x) at large x (> 0.1) and compare it with calculations from various models and existing data
- Extend the program to cover polarized PDFs, in particular the gluon helicity contribution to the proton's spin: DG(x), which is one of the key measurements at eRHIC
- Identify new lattice computable hadronic matrix elements, which are also factorizable to PDFs, TMDs, and generalized parton distributions, in order to establish a full program to extract the hadron's quark-gluon correlation functions from lattice QCD calculations, complementary to the ongoing worldwide efforts using data from high-energy scattering experiments.

[1] X.-d. Ji, Parton Physics on Euclidean Lattice, Phys. Rev. Lett. 110 (2013) 262002.
[2] Y.-Q. Ma and J.-W. Qiu, QCD Factorization and PDFs from Lattice QCD Calculation, Int. J. Mod. Phys. Conf. Ser. 37, 1560041 (2015), and references therein.

Preconceptual Design Study for Large Scale Structure Experiment post LSST/DESI

LDRD # 16-038

A. Slosar, P. O'Connor, A. Nomerotski

PURPOSE:

The main purpose of this LDRD is to develop "know-how" for 21-cm cosmology within the DOE laboratory complex. With its sister LDRD in the Instrumentation Division (16-026), we are building a small radio-telescope prototype. This prototype will test several novel techniques for radio astronomy that could be used in an eventual instrument with the aim of developing a systematically very clean experiment. The second goal of the LDRD is to determine the science reach of a possible future DOE experiment and work towards a design that could become a real DOE project in the 2020s.

APPROACH:

The Principal Investigator was a member of the Cosmic Visions Dark Energy committee, which was created by the DOE to find possible directions for a future survey experiment in the cosmic frontier of DOE. A report was written which suggests four possible experimental approaches in the post Large Synoptic Survey Telescope (LSST)/Dark Energy Survey Instrument (DESI) era. One of these is the 21-cm radio experiment, which relies on measuring the hydrogen spin-flip transition (with rest-frame wavelength of 21-cm) by galaxies in the universe. With the goal of developing a future DOE funded experiment in this field, we are: i) building a small in-house prototype to learn relevant techniques in order to be considered as a lead-lab in this field, ii) studying the synergies between DOE expertise and radio astronomy; iii) further developing the science case for such an experiment. On the experimental side, we collaborate with Jeff McMahon (Michigan), Daniel Marlow (Princeton) and Phil Mauskopf (Arizona). Paul Stankus, an Oak Ridge National Laboratory (ORNL) employee stationed at BNL, spends approximately 25% of his time working on this project (agreed with his ORNL management). Chris Sheehy, the postdoctoral research associate, funded by this project is also a Goldhaber Distinguished Fellow. In addition, we have one Stony Brook University undergraduate student working on it and are looking for a Ph.D. student at Stony Brook.

TECHNICAL PROGRESS AND RESULTS:

This LDRD formally started with the arrival of Chris Sheehy, our newly hired post doc. We have made significant progress in terms of actually bringing the prototype to fruition. In order of significance:

1. We have designed a low-cost 4m reflector made of off-the-shelf aluminum parts that should offer excellent accuracy in the reflecting surface, despite being relative low-cost. Studying a cost-effective way of building the experiment was part of this LDRD.
2. We have designed a horn antenna (element that receives radiation focused by the dish reflector and converts it into electrical signal) based on a published VLA (Very Large Array, a radio telescope) design. It is currently being built at University of Michigan.
3. We have designed a front-end system that is currently being tested. If employs a digitizer card and a Graphical Processor Unit that process the signal at the full rate of 2.5Gsamples/s and gives us almost unlimited flexibility compared to field-programmable gate array-based designs. We are currently in the process of testing it.

4. We have designed the rest of the infrastructure to be used in the experiment, such as the tower that holds the instrument, etc. and obtained all relevant safety approvals and estimates. The system is currently being built and should become operational in a few months.
5. We have discussed the possibility of testing it on the Princeton 18m dish. We will proceed with this once we debug the system currently being designed and tested at BNL.

Milestones

The near term goal is to build our prototype system and extensively test it and understand its properties. Our main design novelty is tone injection, which allows real-time calibration of gain fluctuations. We plan to spend a year in data taking and hope to submit first results in early 2018. We are also working on generic forecasting for 21-cm experiments of what a 1000 times bigger instrument could achieve.

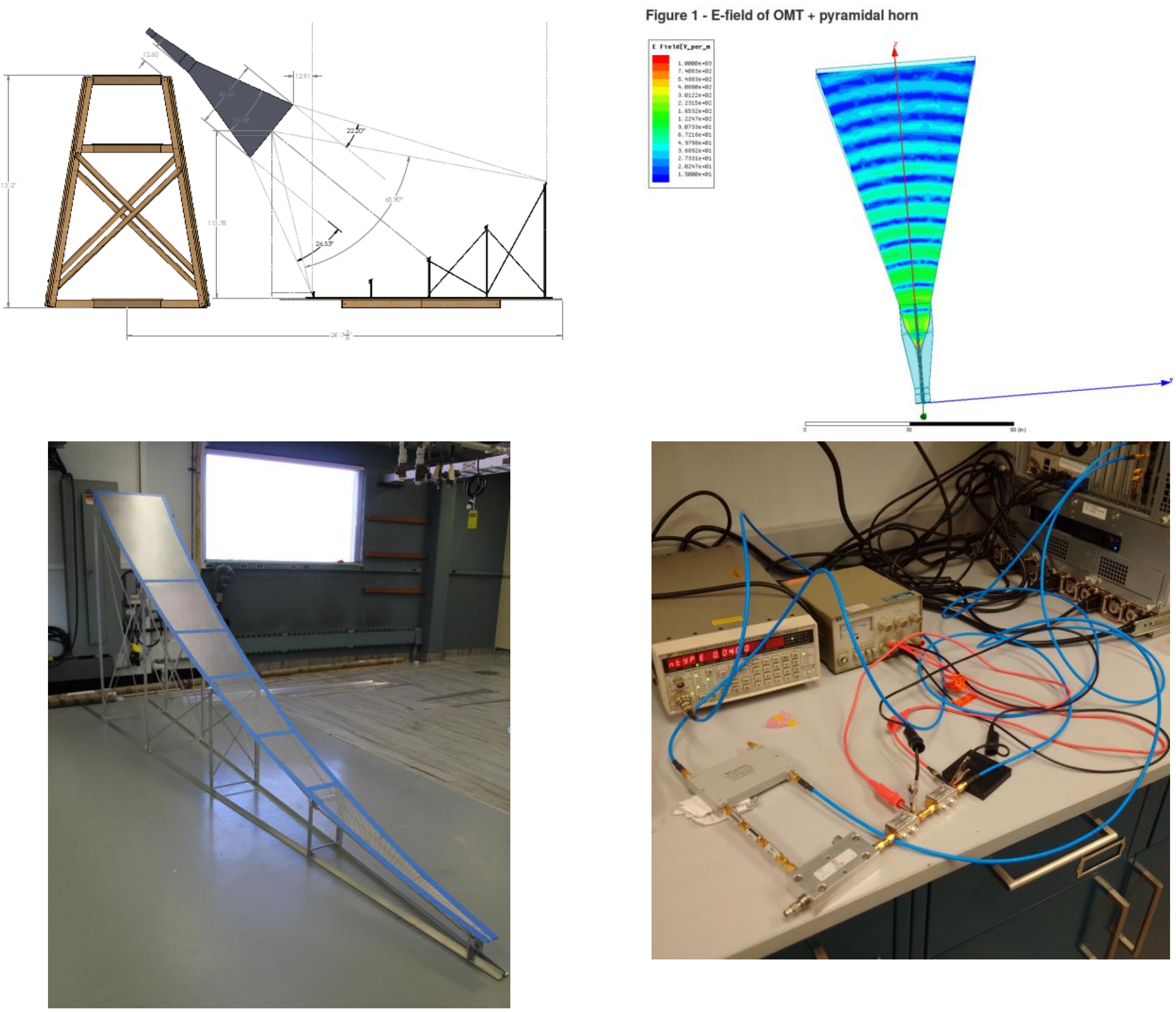


Figure 1. Designing the prototype, clockwise from top left: tower assembly, electromagnetic horn design simulations, readout system testing, reflector petal with photogrammetry maskings.

Machine Learning Assisted Material Discovery

LDRD Project # 16-039

S. Yoo, D. Lu, D. Zakharov, E. Stach, A. Frenkel

PURPOSE:

X-ray and Transmission Electron Microscopy (TEM) based imaging and spectroscopies are powerful tools to characterize structures and electronic properties in materials. Our objectives are three fold: 1) develop image analysis methods enabling near real time analysis of TEM images from a 3GB/s image stream, solving a general problem that will soon be seen at multiple beamlines at National Synchrotron Light Source II (NSLS-II); 2) develop a Spectroscopy Genome that allows deep insights into the atomic-scale changes that occur in complex dynamic processes in *operando* conditions; 3) combine the activities in 1) and 2) with first principles calculations in a robust, integrated manner to describe the dynamic structural changes. This project provides the quantitative information needed to rationally design functional materials for energy applications. These techniques exploit both *in situ* and *operando* approaches, which generate high rate data streams. Automatic real time analyses and data driven discovery have been identified as critical Laboratory goals as BNL is developing a diverse array of characterization techniques at both NSLS-II and the Center for Functional Nanomaterials to provide the quantitative information needed to rationally design functional materials for energy applications.

APPROACH:

For TEM image analysis, most of the image analyses are done manually or limited image processing tools are applied. We investigate the diverse material (semi-)automated quantitative image analysis difficulties and develop novel near real-time approximated computer vision algorithms customized for TEM to enable *in situ* analysis.

In the Spectroscopy Genome project, we propose to develop and apply a robust first principles approach for inverse modeling of core-level absorption spectra. With the focus on *in situ* and *operando* probes, the correlation between atomistic details of key structural motifs (*e.g.*, atomic position, coordination, and bond length) and core-level spectral features is systematically investigated for exemplary systems, with close cooperation from theory, simulation and machine learning algorithms. The proposed study involves constructing experimental spectra standards, extracting significant spectral signatures, developing corresponding high-quality computational spectra standards, and identifying relevant local structural descriptors. Success will allow us to interpret the changes to key local structural motifs due to stochastic or dynamic effects under *operando* conditions using the corresponding experimental spectral features.

TECHNICAL PROGRESS AND RESULTS:

For TEM image analysis, we built the first prototyped pipeline, and automated detection and tracking of nanoparticles on physical vapor deposition of a 1 nm iron film on top of a few nanometers thick titanium oxide film (Figure 1). Considering several challenges including high noise, non-uniform brightness, sensor artifacts, image drifting, etc., the implication of the first prototyped pipeline is that it showed the

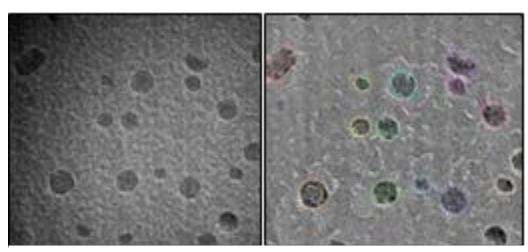


Figure 1. Raw image left and processed image with detected particles.

feasibility of fully automated detection and tracking of nanoparticles [1]. To enable near real time analysis, we investigated streaming data analysis algorithms, including streaming dimensionality reduction and clustering analysis, which enable data analysis with limited memory and processing powers. Our proposed algorithm is significantly faster than batch algorithms and yet produced two times better accuracies than the other streaming analysis algorithms. Such algorithm developments put us in a better competitive position in big data challenges and enabled us to receive two Office of Advanced Scientific Computing Research awards.

In the Spectroscopy Genome project, Lu and Frenkel started with *ab initio* X-ray Absorption Near Edge Structure (XANES) modeling to understand the impact of structural refinement of local atomic environments around metal impurities. The method we developed enables both direct modeling, where the candidate structures are known, and inverse modeling, where the unknown structural motifs are deciphered from the experimental spectra. We analyzed systematic errors and their influence on the stability and accuracy of the obtained results. As a proof of principle, we modeled palladium (Pd) K-edge XANES with FEFF and applied the blind signal separation (BSS) method to reveal the local environment of Pd atoms in Pd-doped gold thiolate clusters upon chemical and thermal treatments (Figure 2) [2].

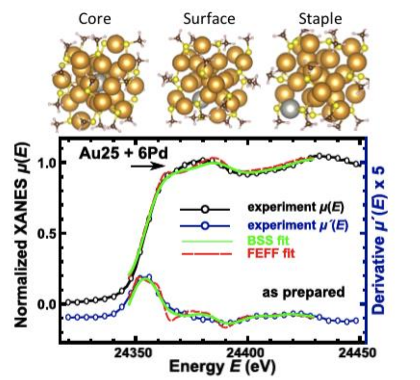


Figure 2. Pd K-edge XANES spectra of Pd-doped thiolated Au_{25} clusters: experimental spectra and their fits using linear combinations of standards (Pd in the core, on the surface and at the staple site of the gold cluster) [2].

Milestones
FY17

- A core level spectra database of metal nanoparticles
- Investigation of the the Li^+ migration mechanism and pathway in $Li_{4+x}Ti_5O_{12}$ with XANES modeling
- Particle size distribution and attaching the developed algorithms to distributed framework
- Analytical correlation between the structure database and spectra database.

FY18

- Distributed approximated image analysis algorithms
- Identification of relevant structural attributes exhibiting the right spectral features measured in allyl alcohol hydrogenation
- Understanding the reaction mechanism.

References:
[1] R. Megret et al., "Analysis of nanoparticle growth in Environmental Transmission Electron Microscopy" New York Scientific Data Summit, 2016.
[2] J. Timoshenko, et al., "Solving local structure around dopants in metal nanoparticles with ab initio modeling of X-ray absorption near edge structure", Physical Chemistry Chemical Physics, 18, 19621-19630, 2016.

Dynamic Visualization and Visual Analytics for Scientific Data of NSLS-II

LDRD Project # 16-041

W. Xu

PURPOSE:

This project aims to establish a prototype system that visually represents, explores and interacts with extreme-scale scientific data to empower future science research at National Synchrotron Light Source II (NSLS-II) and the Center for Functional Nanomaterials (CFN). To our knowledge, there are no existing visualization and visual analytics solutions satisfying the unique requirements of NSLS-II i.e., the visual analytic environment for extreme-scale data and complex analyses so that scientists can better understand and interact with their raw/analyzed data, the analysis methods and their relationships. On the success of this project, we expect to secure funding from the DOE Office of Advanced Scientific Computing for programs including scientific data management, analysis and visualization at extreme scale, and performance and productivity tools. The project will foster cross-disciplinary collaboration by extending research outcomes into other BNL programs, such as climate sciences, biology, and nuclear physics.

APPROACH:

An online visual analysis tool that can process, manipulate and display extreme-scale data is critical for scientists to make the right decision while onsite and adjust their measurement strategies during the experiment. Therefore, we identified three pilot projects that, according to our scientific collaborators, cause extreme difficulties in 2D/3D/high-dimensional data visualization, because the capabilities for interactive strategic exploration of raw data, metadata and analyzed results are lacking, thereby impeding the desired scientific insights.

- **Enable visual comparisons and integrations of multi-modal imaging techniques:**

Co-investigators: H. Yan and Yong Chu (NSLS-II), Klaus Mueller (Stony Brook University)
We devise an interactive visual analytics tool that can combine, correlate and process different image datasets so as to enable scientists to fully understand relationships among the chemical, elemental, structural and physical quantities being imaged. In specific, we investigate visual analytics methods targeting two tasks: 1) integrating and analyzing fluorescence microscopy data with multiple elemental distributions; and 2) integration and correlation analysis for multiple image modalities.

- **Automatic large-scale image set organization, summarization, and analysis:**

Co-investigators: K. Yager (CFN), M. Fukuto (NSLS-II), Klaus Mueller (Stony Brook)
Optimizing the functionality of material design requires strategic exploration of the vast parameter spaces associated with complex materials. We thus develop visualization tools ideally suited to managing and exploring large collections of X-ray scattering images, in particular providing the tools necessary to efficiently summarize and explore correlations and trends in large scattering datasets. We focus on three specific tasks: 1) multi-level display of the 2D scattering maps; 2) data summary and arrangement for large-scale data analysis; and 3) parameter space exploration and meta-data display.

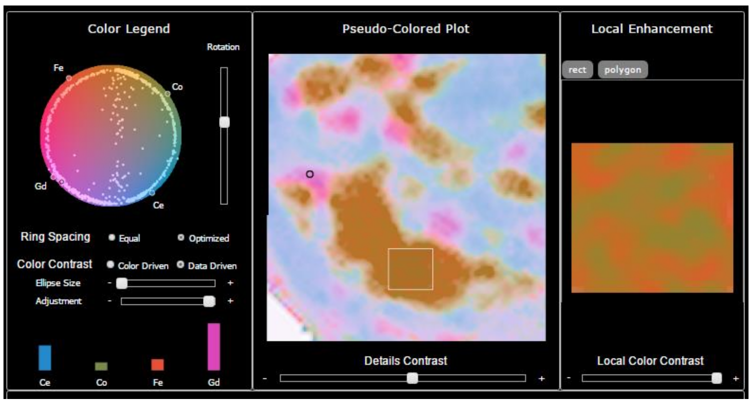
- **Dynamic 3D visualization and interaction:**

Co-investigators: W-K. Lee, Yong Chu, and Dan Allan (NSLS-II), Klaus Mueller (Stony Brook)
For 3D tomographic datasets, we propose a dynamic way to visualize data in different data channels while the raw data keep screaming in. Assisted plots illustrating the angle coverage of the sample, as well as a meta-data display will also be implemented.

TECHNICAL PROGRESS AND RESULTS:
During the first year of this project, we met all the planned goals, published good quality journal/conference papers, and made the following progress.

- **Color-mapping for a multivariate dataset**

We developed a new color mapping algorithm for a 2D multivariate dataset that needed to be integrated into one display (Figure 1). We provided two color spacing methods: the equal distance and correlation-driven methods. Users can freely reassign the colors as they like. The integrated view and the separate data channels are linked. Moreover, we provide additional tools such as a ratio map and focus lens to enhance the detail exploration.



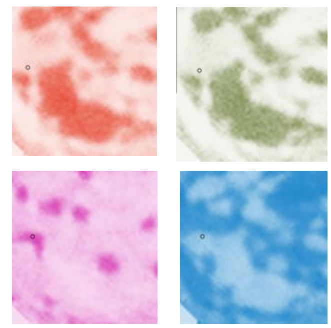
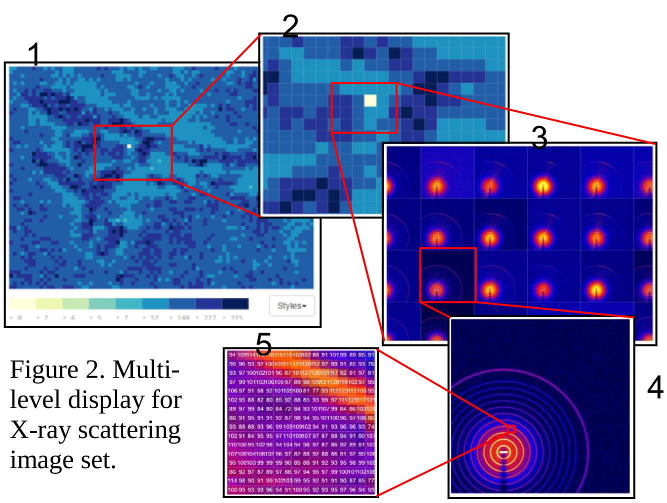


Figure 1. Color mapping for a multivariate dataset.

- **Multi-level display for X-ray scattering image set**

We developed a new interactive framework that provided semantic zooming through multiple levels of details for a multivariate X-ray image set (Figure 2). The correlation display for these variables was also linked. Additionally, we plotted a treemap to show metadata information.



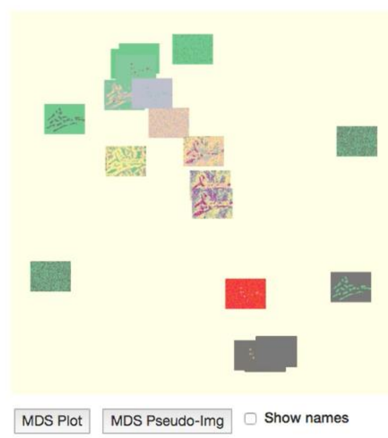


Figure 2. Multi-level display for X-ray scattering image set.

Milestones

- Extend colormapping to support 3D datasets (FY17)
- Enhance the multi-level display to support irregular distributed datasets (FY17)
- Complete correlation and metadata display to assist multi-level display (FY17)
- Devise a method to visualize streaming volumetric datasets (FY18)
- Put three software tools into the production phase (FY18).

Deep Structured Analysis for Image Datasets from CFN and NSLS-II

LDRD Project # 16-043

K. Yager, D. Yu, M. Fukuto

PURPOSE:

We are building towards a transformative new paradigm for scientific research, where experimental acquisition, analysis, and decision-making, are all automated, thereby liberating scientists to focus on high-level scientific questions. Our approach involves exploiting recent advances in machine learning to massively automate data analysis. We are adapting machine learning methods to the problem space of scientific data and thereby developing "physics-aware deep learning" methods. The ultimate goal of this project is to develop an automated data-analysis pipeline for x-ray scattering experiments and to deploy this software at National Synchrotron Light Source II (NSLS-II) beamlines.

APPROACH:

Modern scientific instruments are now generating data at unprecedented rates. In particular, 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. It is now evident that a crucial complement to high-throughput instruments is automated analysis methods, which can categorize, tag, and analyze scientific data without human intervention. This automation liberates the scientists to concentrate on high-level scientific questions and focus their attention on the subset of the data most meaningful for a given problem. This extreme automation, in turn, enables more ambitious scientific projects. In particular, these methods enable streamlined materials discovery, where new materials with desired performance (mechanical, light-harvesting, energy storage, etc.) can be efficiently found.

This project is building automated, streaming analysis pipelines for extracting scientifically-meaningful insights from datasets relevant to materials discovery, especially x-ray scattering images (Figure 1). We are developing data-analysis pipelines that serve a dual role: providing experimenters with useful (physically-meaningful) intermediate results and using these analysis results as inputs to machine learning methods. In particular, we are leveraging the recent successes in "deep learning," where carefully structured neural hierarchies are trained to identify hierarchies of structures in data. By using multiple crafted input channels (raw data, data after physics-based decomposition, analysis outputs) into a deep learning network, the machine learning can be strongly optimized to a particular problem space (collaborations with Minh Hoai Nguyen, Stony Brook University (SBU); Hong Qin, SBU; and Dantong Yu, New Jersey Institute of Technology/BNL). Thus, we are creating both efficient analysis pipelines and new physics-aware machine learning algorithms. These methods are being applied to a variety of "images": the raw detector images generated by instruments, reconstructed maps of sample structures, and the abstract phase spaces of materials science. This deep-learning centric analysis will be exploited to automate the scientific experiment itself, by providing feedback to algorithms that can efficiently explore scientific problems and make decisions about what experiments to conduct next. Overall, this project aims to deliver a data analysis pipeline for x-ray synchrotron instruments, empowering more ambitious materials discovery experiments.

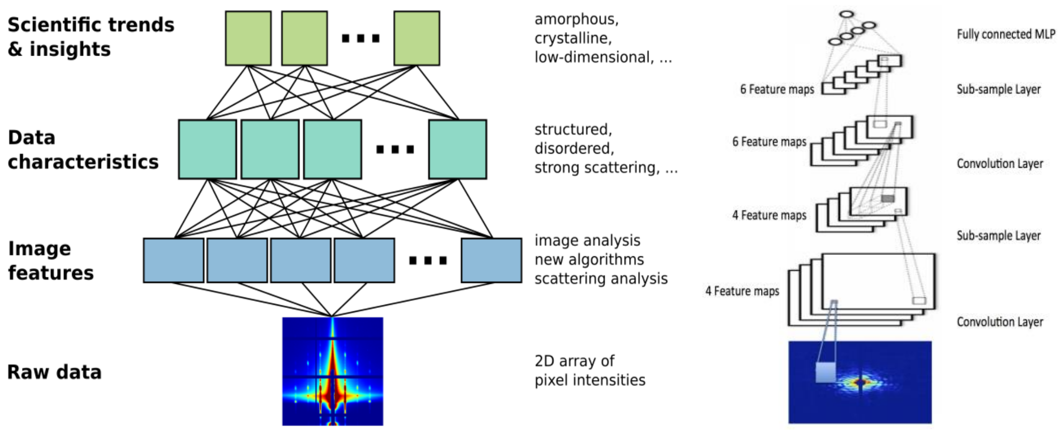


Figure 1. This project is exploiting machine learning methods to analyze x-ray scattering data (bottom). Using structured deep learning methods (right), scientifically-meaningful insights will be automatically extracted from the data (left).

TECHNICAL PROGRESS AND RESULTS:

In the first year of this project, we have designed the required analysis pipeline and created a preliminary software framework for these data-analysis modules. Several required modules have been coded: estimation of background signal in x-ray scattering data, peak identification and fitting, and symmetry & angular correlation analysis. We have also combined these modules to yield a new, powerful capability for x-ray scattering images: a method for “healing” x-ray images by filling in any gaps in the data. This “physics-aware in-painting” goes well beyond conventional image analysis methods, by exploiting measured correlations inherent to this kind of data. This image healing is useful for human inspection and as a pre-processing step in machine learning. A manuscript on this work is in preparation.

Simultaneously, we have investigated the use of deep learning networks for analysis of x-ray scattering images. We explored different deep learning hierarchies, as well as different means of pre-processing the data, in order to maximize accuracy in the prediction of scientifically-relevant tags. This work was presented at the *New York Scientific Data Summit* and was accepted for publication for *the IEEE Winter Conference on Applications of Computer Vision* (*WACV 2017*). We have also developed a new “Fourier/Bessel decomposition” method, which encodes scattering data into a reduced form, in a way that is finely-tuned to the nature of scattering data (e.g. extracting symmetry). By combining this autoencoder with deep learning methods, we have achieved unprecedented performance (including 95% precision for certain attributes).

Looking forward, we will continue our foundational development work, publishing papers on our new physics-aware deep learning algorithms. We are now beginning the work of implementing the aforementioned software (analysis pipeline and deep learning methods) on the Complex Materials Scattering beamline at NSLS-II.

Milestones

Our FY17 milestone is to have this pipeline functioning for user experiments. The final phase of the project will be dedicated towards refining all of these methods and deploying the pipeline more broadly at other NSLS-II beamlines (especially Soft Matter Interfaces, Coherent Hard X-ray Scattering, and Life Science X-ray Scattering).

Catalysis Program in Sustainable Fuels

LDRD # 16-045

J. Chen

PURPOSE:

This LDRD project established a research program led by Jingguang Chen as a Joint Appointee between BNL and Columbia University. 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. At present, ~95% of H_2 is produced by processing hydrocarbons; producing CO_2 is a byproduct. This LDRD program also explores two alternative ways to convert CO_2: (1) the discovery of active and low-cost electrocatalysts to produce CO_2-free H_2 from water electrolysis and (2) the reduction of CO_2 directly by hydrocarbons without using H_2.

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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.

The LDRD project established a research program at both BNL and Columbia University. At BNL, the Chen group is collaborating with the existing BNL catalysis and electrocatalysis research groups. The FY 2016 research effort under this LDRD was carried out primarily at BNL. The project will strengthen the BNL catalysis science program through linked research thrusts on CO_2 activation. The projects are carried out using a combination of theoretical and experimental work and *in situ* techniques at the Center for Functional Nanomaterials and the National Synchrotron Light Source II.

TECHNICAL PROGRESS AND RESULTS:

During the past year of LDRD funding, the Chen group at both BNL and Columbia University focused primarily on obtaining proof-of-principle results for CO_2 conversion using light alkanes, such as ethane and propane. The combined theoretical and experimental results have identified two classes of promising catalysts, transition metal carbides and bimetallic alloys, which are active and selective catalysts for CO_2 conversion.

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. We explored the utilization of transition metal carbides and metal-modified transition metal carbides as effective electrocatalysts for water electrolysis to produce CO_2-free H_2. We also explored the stability of these electrocatalysts by performing water electrolysis in the presence of typical impurity ions in tap water. If successful, these efforts might lead to a cost-effective way to produce CO_2-free H_2, which will be required for large scale conversion of CO_2 to fuels without generating unwanted CO_2 as a byproduct.

In the past year, we designed and installed an electrochemical cell that is directly connected to a catalytic reactor. This setup allows us to identify and quantify products from the electrochemical reactions to more efficiently evaluate metal carbide electrocatalysts.

Milestones

The initial research in this LDRD focused on conversion of CO_2 to CO using light alkanes, such as ethane and propane. Some of the results have been used to demonstrate the proof-of-principle for the renewal of a DOE Field Work Proposal. The renewal proposal was submitted to DOE in December 2016.

Oct. 2016 – Sept. 2017:

The future research efforts will continue to focus on two areas: (1) catalytic conversion of CO_2 using light hydrocarbons instead of H_2 and (2) discovery of low-cost and impurity-tolerant electrocatalysts to produce CO_2-free H_2 from water electrolysis. In the first area, we will identify design principles for identifying catalysts of selectively converting CO_2 to CO by light alkanes, which are becoming more abundant from the shale gas. In the second area, we will explore the utilization of transition metal carbides as cost-effective and stable electrocatalysts to replace the state-of-the-art platinum group metals for water electrolysis.

Strong-Strong Beam-Beam Interaction Studies for a Ring-Ring Based Electron Ion Collider

LDRD Project # 16-046
F. Willeke

PURPOSE:

The interaction between particles of opposite beams colliding in high luminosity storage rings is strongly nonlinear and the densities of the beams in collisions, which provide high luminosity, is limited by a number of coherent and incoherent instabilities and nonlinear dynamic effects. This effect, if it occurs in eRHIC, would limit the luminosity below the design values and could prevent stable high luminosity operations. It must therefore be considered as a risk, which deserves to be studied thoroughly before a decision on the scheme of the eRHIC electron hadron collider is made. The purpose of the project is to assess the feasibility of high luminosity operations of the eRHIC ring-ring option with computer simulation that will use computer codes based on a strong-strong interaction model, in which the mutual nonlinear forces of the two beams upon each other are assessed.

APPROACH:

A simple and computationally inexpensive approach to characterizing the impact of the beam-beam interaction on the beam stability is to model the interaction assuming one of the colliding beams is “frozen”, or not affected by the other beam. Within this approximation, the beam-beam interaction is studied with weak-strong beam-beam simulations, where the strong beam, not affected by the weak beam, acts as a source of the electromagnetic interaction perturbing the weak beam. Weak-strong beam-beam simulations can be very fast, at the price of neglecting any self-consistent effect or mutual interaction between the colliding beams.

In our case, numerical studies of the beam-beam interaction are to be done with strong-strong beam-beam simulations, which provide the self-consistent evolution of the colliding beams, thus the study of instability mechanisms acting simultaneously on both beams. The price to pay for strong-strong simulations is a heavy computational load, both in terms of computational speed and memory requirements. While weak-strong simulations can efficiently run on a single processor, strong-strong simulations require multi-processor programming and parallelization.

Our strategy is to perform the strong-strong beam-beam simulations using K. Ohmi’s BBSS multi-particle tracking code. The code allows the study of the beam-beam interaction of colliding beams with arbitrary crabbing and crossing angles, via slicing the beams longitudinally and then reducing the beam-beam interaction to “slice collisions”, where the electromagnetic fields are obtained by solving the two-dimensional Poisson equation. Recently, the BBSS code was used for numerical simulations compared with experiments to study the performance of crab-cavities at KEKB (the particle accelerator used in the Belle experiment at the High Energy Accelerator organization in Japan, known as KEK) and for studies of the luminosity degradation due to incoherent emittance growth and coherent beam-beam instability in the Large Hadron Collider.

The project work plan includes: procurement of a powerful computer and its integration in the National Synchrotron Light Source II (NSLS-II) Accelerator Physics (AP) computing cluster as a dedicated node for beam-beam simulations; installation of the BBSS computer code with the developer’s help; run the simulation for the Hadron-Electron Ring Accelerator (HERA) case and compare with experimental data to benchmark the code; run strong-strong simulations for the eRHIC ring-ring option, analyze the results; and write a contribution to the eRHIC Conceptual Design Report.

TECHNICAL PROGRESS AND RESULTS:
The LDRD work plan includes installation of a simulation code on the NSLS-II computing cluster; use of HERA experimental data to benchmark the simulations; and eRHIC beam-beam simulations for all center-of-mass energies. We have purchased a dedicated computer for the beam-beam simulations in the strong-strong approach. This is a 1U rack-mount server, 2x22 cores, 512 GB RAM, 2x600GB HDD. The computer was incorporated into the NSLS-II AP computing cluster as one of its nodes. Dr. K. Ohmi (from KEK) was invited to BNL to discuss simulations of beam-beam effects in eRHIC using his code BBSS. During his visit, the code was installed on the computer and a series of test runs were done. G. Bassi (NSLS-II AP group) worked together with Dr. Ohmi to get expertise in beam-beam simulations using the BBSS code. A series of simulations were done for HERA parameters and compared with experimental data. No instabilities caused by beam-beam effects were observed with the HERA working parameters. A tune scan for the electron ring of eRHIC was done to find an optimal working point and a 2D diagram of the luminosity as a function of electron tunes was presented. The simulations were done with the nominal proton tunes of 0.31/0.32 for the highest-luminosity configuration: 250 GeV proton energy and 10 GeV electron energy. The simulation results were also compared with weak-strong simulations. A chapter "Beam-beam Effects and Luminosity" was written for the eRHIC Conceptual Design Report.

Milestones
October 1st 2016: Complete initial tool set up and bench marking phase
Deliverable: benchmarked computer code and eRHIC input data sets

December 31 2016: Complete first interaction of strong-strong beam-beam parameters with two different strong-strong computer codes

March 31, 2017: Compare systematic weak-strong and strong-strong beam-beam simulations for different settings of tunes, beam-beam parameters
Deliverable: collection of corresponding simulation data
Compilation of data and interpretation in form of a comprehensive presentation

April 5-6 2017: Present results to international committee of experts during eRHIC ring-ring review

June 30: Complete systematic beam-beam simulation including crab crossing effects

September 2017: Conclusion of the Study
Deliverable: Final report, publications