BROOKHAVEN
NATIONAL LABORATORY

LDRD 2013 Annual Report

Laboratory Directed Research & Development Program Activities

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Acknowledgments

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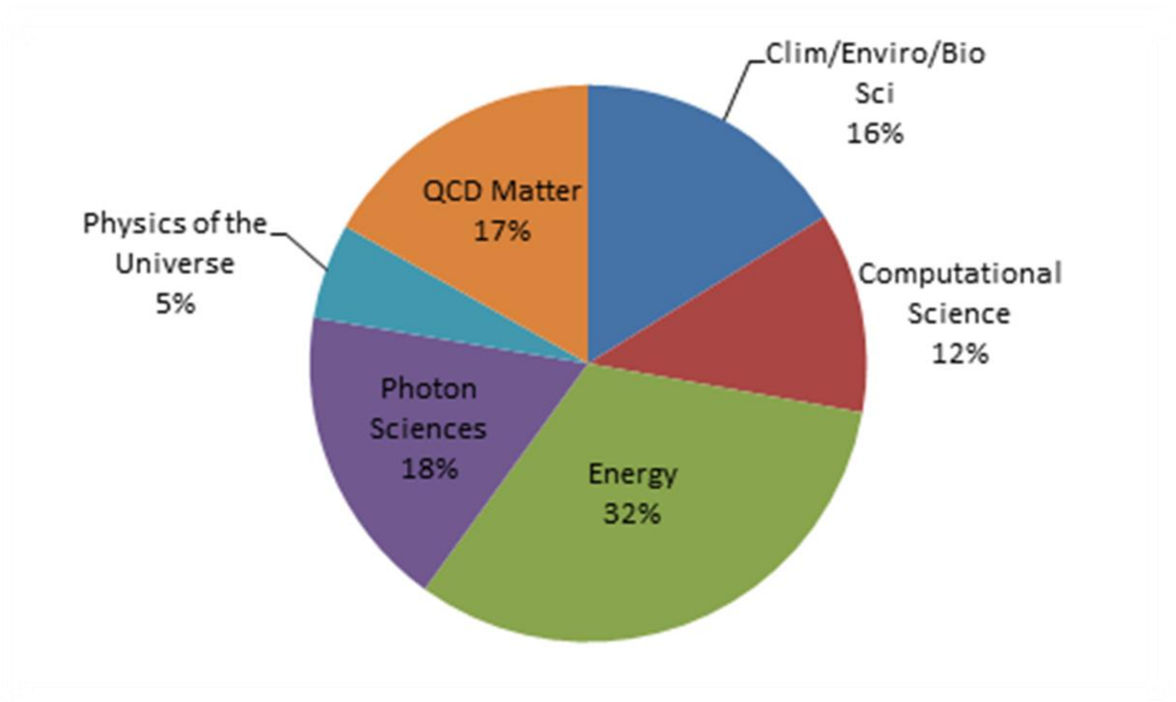
Introduction

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 in accordance with DOE Order 413.2B dated April 19, 2006. This report provides a detailed look at the scientific and technical activities for each of the LDRD projects funded by BNL in FY2013, as required. In FY2013, the BNL LDRD Program funded 42 projects, 15 of which were new starts, at a total cost of $7.6M.

The investments that BNL makes in its LDRD program largely support the Laboratory's strategic goals as outlined in the BNL Laboratory Plan. BNL has five Laboratory Initiatives; Photon Sciences, QCD Matter, Materials for 21st Century Energy Solutions, Physics of the Universe, and Biological-, Environmental- and Climate Sciences. These major initiatives support the growth and evolution of the major business lines (i.e. mission areas) of the Laboratory. In addition, there are three smaller initiatives that support growth and program development in targeted areas, i.e. Accelerator Science and Technology, Computation, and Detectors for National Security. Approximately 88% supported the five major initiatives. In total, these LDRD investments supported 64 postdoctoral researchers and graduates students in whole or in part and resulted in 118 publications and 1 award.

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



LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

2013 PROJECT SUMMARIES

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

LDRD Project # 10-040

T. Rao, T. Tsang, B. Sheehy

PURPOSE:

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

APPROACH:

The quantum efficiency (QE) of the polarized electron source is in the range of a fraction of a percent at 780 nm. In order to meet the beam requirements of the Gatling gun, the laser should deliver ~ 4 W average power at 780 nm, at a repetition rate of 704 kHz with a pulse duration of ~ 1 ns at each of the gun cathodes. Formation of the negative electron affinity surface on the GaAs is crucial for the high QE, and the preservation of the polarization. Typically the electron affinity of a very clean GaAs surface is reduced by depositing Cs and an oxidizing agent to result in a fractional monolayer of Cs on the surface. The cleanliness of the GaAs surface, Cs and the oxidizing agent determine the ultimate QE of the cathode and its sensitivity.

The scope of the program is expanded to address both the development of the laser system and understanding of the negative electron affinity of the cathode in order to increase the life time of the cathode. In collaboration with Brian Sheehy of the Collider Accelerator Department, we investigated different laser architectures, decided on the most promising design, interfaced with industry to complete the preliminary research and development and initiated the procurement process for the laser system.

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

TECHNICAL PROGRESS AND RESULTS:

The fiber laser system operating at 1560 nm has been developed by Optilab, a commercial firm. The laser system went through a number of iterations and the laser that meets the design criteria was delivered in November 2013. The performance test results delivered by the vendor are shown in Fig1-4. The ac power measured indirectly is in the range of 5-10 W, in reasonable agreement with the specification. The system is currently being configured for direct power measurement. The power distribution as a function of wavelength is shown in Figure 1. 94% of the laser power is contained in the main peak. The out of bandwidth component is due to the input spectrum from the seed diode. The non-linear effect that was observed previously has been addressed by changing the amplifier fiber. The line-width measured with fine resolution scanning, and shown in Figure 2 is 0.04 nm, well within the acceptable range. Figure 3 and 4 show the pulse duration of the amplified beam. As can be seen from Figure 4, the pulse develops a temporal asymmetry with increasing output power. This asymmetry as well as the power fluctuation need to be addressed in the final configuration for the full Gatling gun. However, these operating parameters are sufficient to test the proof of principle gun.

Optilab was unable to complete the frequency-doubling component of the laser project. We have identified another vendor capable of constructing it, but wish to wait until we can completely characterize the 1560 nm laser before issuing that contract. Depending on the timing, we may just construct the doubler here at BNL from components.

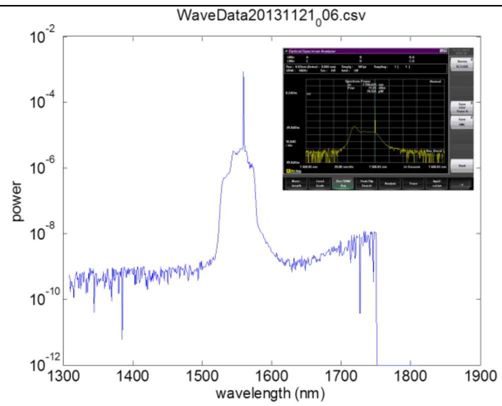


Figure 1 Power spectrum of the amplifier output. Inset: power spectrum of the seed oscillator

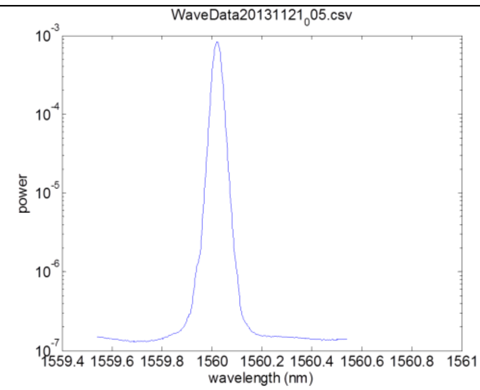


Figure 2 High resolution scan of the power spectrum showing the narrow band width

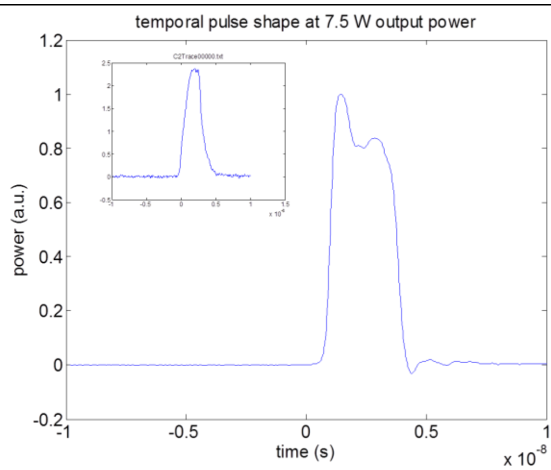


Figure 3 Temporal shape of the amplified beam. Inset: Drive electrical pulse

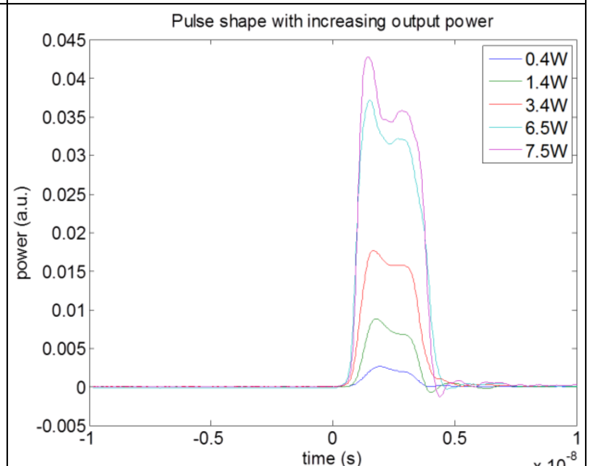


Figure 4 Temporal shape of the amplified laser beam as a function of output power

Simulation, Design, and Prototyping of an FEL for Proof-of-Principle of Coherent Electron Cooling

LDRD Project # 10-041

Vladimir N Litvinenko

PURPOSE:

Free electron laser (FEL)-based Coherent Electron Cooling [1] (CeC) promises to become a revolutionary method that will significantly increase luminosity in proton-proton colliders, ranging from the Relativistic Heavy Ion Collider (RHIC) to the Large Hadron Collider and in future electron-ion colliders such as eRHIC or LHeC. We addressed issues, theoretical and numerical, that the cooling and FEL communities have put aside for at least two decades. We also designed and fabricated a prototype helical wiggler to address possible needs of CeC. This LDRD was the front-runner project for testing the CeC mechanism in a proof-of-principle (PoP) experiment. Success of the CeC PoP will greatly benefit future eRHIC. Importantly, it will ensure eRHIC's competitive edge against MEIC at JLab.

APPROACH:

The theoretical part of our research focuses on the evolution of the e-beam phase-space distribution in the FEL, with arbitrary initial conditions and under the influence of space charge. From our findings, we should be able to simulate and predict the cooling time for a realistic CeC PoP system. We address the following theoretical and design challenges:

1. Fitting the CeC system, including the FEL, into the space between the DX magnets; 2. Evaluating the space-charge and diffraction effects on the FEL's and the CeC's performance at a relatively low energy of the electron beam (20 MeV), and a rather long wavelength of FEL (18 microns); and 3. Establishing the tolerances on the FEL design and the wiggler fields.

The CeC PoP experiment requires a new helical wiggler, suitable for installing into RHIC's Interaction Point between two DX magnets. It should have an aperture adequate to avoid imposing any constraints on RHIC's hadron beam. We are designing, and plan to build, and evaluate a short prototype of such a wiggler during our practical feasibility studies.

TECHNICAL PROGRESS AND RESULTS:

As part of this LDRD research we had developed a detailed lattice for the CeC experiment– see Fig. 1 [4,5].

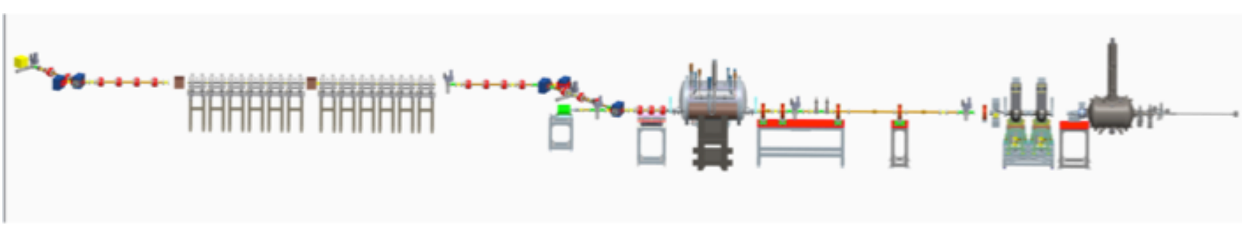


Fig. 1. Layout of the CeC PoP experiment.

We also achieved significant progress both in the theory and computer simulations of the processes in the coherent electron cooler [2-4, 7-18]. The main theoretical accomplishments are discovery of the beam-conditioning for the CeC process [1] and rigorous proof that there is only a single growing mode in the FEL [3,4,12]. In May 2011 Stephen Webb defended his Ph.D.

thesis on "Theoretical Considerations of Coherent Electron Cooling" at Stony Brook University. The other graduate student, Justin Owen, successfully defended his MSI thesis at Stony Brook University in 2013 on simulating the beam evolution in the CeC PoP accelerator.

On the experimental side, we completed the design and the manufacturing of a 50 cm prototype of the helical wiggler (Fig. 2) with 4 cm period, which was fully paid for by this project's funds. Magnetic measurements demonstrated the quality of the field exceeding the requirements for the CeC PoP system.

Fig. 2. Dr. P. Vobly demonstrating the helical wiggler prototype at the Budker Institute of Nuclear Physics (Novosibirsk).

We published three refereed and twelve conference proceeding paper on CEC during reporting period. We also were awarded in the FY11-13 period $4.18M funds by the DOE Office of Nuclear Physics competitive accelerator R&D program for experimental demonstration of coherent electron cooling. Our early start with LDRD funds in prototyping the wiggler for CeC was of critical importance for this success. Results of the wiggler prototyping were also critical for the positive evaluation of our DOE proposal.

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Cloud and Precipitation 4D Radar Science

LDRD Project # 11-001

Scott Giangrande

PURPOSE:

Deep convective clouds (DCCs) play a critical role in Earth's climate system. Understanding the properties of these clouds and simulating their impact is a major challenge for current global climate models (GCMs) and cloud resolving models (CRMs). DCCs are particularly difficult to adequately observe and model since their dynamical, microphysical and radiative feedbacks act over a wide range of scales. This LDRD capitalizes on a new cloud observing facility strategically positioned in an environment favorable for DCC development. This unique testbed provides an opportunity to overhaul traditional cloud observations and assess the environmental controls that influence the lifecycle and morphology of DCCs. Our objective is to innovate novel observations of convective cloud properties and atmospheric controlling factors to enhance our understanding of these cloud systems towards significantly improving CRM/GCM performance.

APPROACH:

A. Background and Scope: New Multi-scale Observing Facility Capability: The DOE Atmospheric Radiation Measurement (ARM) Climate Research Facility located in central Oklahoma underwent a major upgrade towards providing unprecedented observations of DCCs. Of immediate interest for characterizing DCC evolution is the suite of scanning cloud and weather radar, each tasked to operate over progressively larger and overlapping domains. These systems include first-ever scanning cloud radar (millimeter wavelength) to map initiating clouds, as well as large-umbrella weather radar (centimeter wavelength) for bulk quantification of deeper precipitating storms. The radars allow detailed microphysical insights with sensitivity to capture clouds as they form. Here, the opportunity exists to assume leadership in multi-sensor synergistic approaches to climate-cloud observations for GCM/CRM evaluation. The traditional DOE ARM model relies on individual remote-sensing platforms, but this is not sufficient since individual radar systems only capture a brief snapshot of DCC cloud life cycle. Further, DOE ARM lacks expertise in observing deep precipitation processes. Exploiting multiple radar synergies for cloud and precipitation lifecycle study has never been attempted, but has the potential to yield far more meaningful advances in our understanding of DCCs for improving model parameterizations.

B. Methodology: Deep Convective Storm Tracking and Characterization:

Scanning radar systems provide an opportunity to map cloud evolution since they can observe cloud particles at spatial and temporal scales sufficient for continuous monitoring. An individual radar platform is only sensitive to specific stages of cloud development as a consequence of the radar wavelength and other hardware limitations. We propose to observe DCC lifecycle possible as follows. (1) Capture 4D (space + time) cloud evolution by exploiting the synergy of complementary, overlapping radar platforms. This is our best opportunity for DCC monitoring, but for the observations of initiating clouds in particular, adaptive scanning of cloud systems is unique, exploratory and therefore risky since our observational capabilities may not be sufficient. The effort further requires (2) detailed tracking of initiating cloud elements using a variety of novel approaches to assess the best techniques to observe representative cloud properties. This must be performed in coordination with (3) identification of the specific cloud properties that best translate across the overlapping radar domains (e.g., radar reflectivity factor, cloud base/depths). Efforts in (2) and (3) benefit from additional support from collaboration with McGill University radar and cloud experts on an LDRD subcontract. Finally, individual case studies must (4) package the 4D observations quantities in a manner easily accessible for GCM/CRM model improvement; e.g., linking with the atmospheric conditions that forced these clouds.

TECHNICAL PROGRESS AND RESULTS:

Previous Year (2012) Progress: In year two, the PI and graduate student merged the radar dataset and forcing record for analysis and cloud modeling connectivity. Engaged in a new collaboration with Kansas University cloud modeling experts to begin detailed Large Eddy Simulation (LES) model comparisons for the May 25th, 2011 shallow cumulus event. Model-observation LDRD partnering continued into 2013 under McGill student leadership (LDRD subcontract). 2013 milestones under this partnership include associated publications on cloud radar insights to LES cloud modeling. Encouraging initial results from cloud tracking methods also provide solid justification for resubmission of a follow-on proposal on shallow cumulus cloud lifecycle. Initial journal publications from 2011 efforts towards deep convective radar processing and intensity observations accepted for release in 2013. A student-led publication on the LDRD cloud tracking algorithm and its associated results is in preparation for 2013 submission. Overview manuscripts describing the 2011 campaign and the new DOE capability for radar precipitation products and insights also in preparation.

Current Year (2013) Progress: In year three, the PI and graduate student continued this collaboration with Kansas University cloud modeling experts towards LES cloud model sensitivity studies for the May 25th, 2011 shallow cumulus event. 2012 into 2013 milestones under this partnership (an initial tracking manuscript) were met, and secondary publications for this LES modeling activity are in preparation. Multiple publications on the subject of deep convective radar processing and intensity observations were accepted and/or published in 2013 including several new community (open-source) opportunities. Year 2013 also featured an additional follow-on funding activity to engage the energy sector (distribution) on the use of weather radar datasets in convective storm environments for potential restoration activities. This included a BNL-led workshop on these subjects having website location, http://www.bnl.gov/wius2013/ .

A Novel Approach to Parameterize Sub-Grid Processes in Climate Models

LDRD Project # 11-002

Dong Huang

PURPOSE:

The purpose of this project is to develop a statistical approach that enables consistent treatment of sub-grid processes in Global Climate Models (GCMs). The new approach offers new ways to utilize high spatial resolution observations in climate models.

APPROACH:

Physical processes acting at spatial and temporal scales that are too small to resolve by the numerical grids of GCMs are presented in climate models using parameterizations. A parameterization is a statistical description of the effects of the subgrid processes and interactions in terms of the resolved-scale state. Therefore, parameterizations are statistical in nature. Conventional parameterizations used in current GCMs (e.g., cloud feedback and aerosol-cloud interaction) are developed empirically and sometimes are inconsistent with each other.

Using more rigorous statistical methods, we have developed a new framework that utilizes explicit subgrid variability, i.e., subgrid Probability Distribution Functions (PDFs), to formulate parameterizations.

As illustrated in Figure 1, two different approaches have been investigated to explicitly account for subgrid variability: a direct approach and a Monte Carlo approach. The direct approach is to analytically integrate the relevant subgrid processes over the subgrid cloud PDF. For mathematically-simple processes (e.g., autoconversion, accretion, and evaporation), this direct approach is attractive because the addition of computational cost is negligible. The second approach is a Monte Carlo approach. A statistical realization of cloud field (subcolumns) will be generated using a statistical cloud generator under the guidance of the subgrid PDF. Other subroutines then can be directly applied to the subcolumns and the grid-averaged quantities can be obtained by cleverly sampling the subcolumns. The Monte Carlo approach could be the only option for some complex processes for which analytical integration is difficult or impossible to perform.

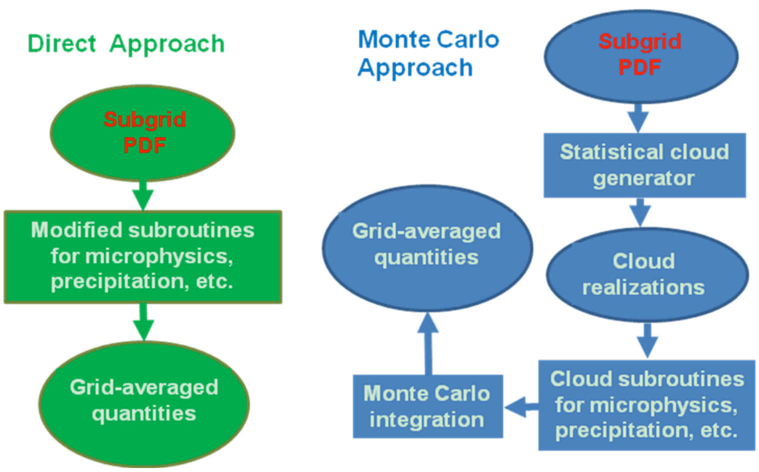

Figure 1: Two approaches for explicitly accounting for subgrid cloud variability.

TECHNICAL PROGRESS AND RESULTS:

This project officially started in October 2010 and this is the third year of the project. Dr. Michael Galletti (joined us as a research associate in August 2011) is fully supported by this project.

In FY2012, we developed a statistical (or stochastic) radiative transfer parameterization scheme that directly uses a subgrid cloud PDF and cloud spatial correlation function. In FY2013, we tested the new approach using various cloud cases simulated by Large Eddy models. We validated the new approach using the I3RC Community Monte Carlo model under several different conditions. Through the use of statistical information of subgrid-scale clouds, the grid-average radiation fluxes can be accurately computed. The statistical approach does not require the knowledge about the exact 3D spatial distribution of cloud properties and it instead uses statistical distribution function of the clouds. We also examined the improvements in the calculations of grid-average cloud microphysical process rates by including subgrid PDFs of cloud. We parameterized subgrid cloud distributions as gamma or lognormal distribution functions and used these functions to upscale the local microphysical and radiative transfer processes and obtain grid-average process rates and radiative fluxes. It is found that if cloud subgrid variability is totally ignored, the mean relative biases of autoconversion rate, upward and downward radiative fluxes are unacceptably large reaching 60% in many cases. When the gamma or lognormal distribution function is used to represent cloud subgrid variability, the calculated autoconversion rate and radiative fluxes at the three sites are reduced to within 5% (Figure 2).

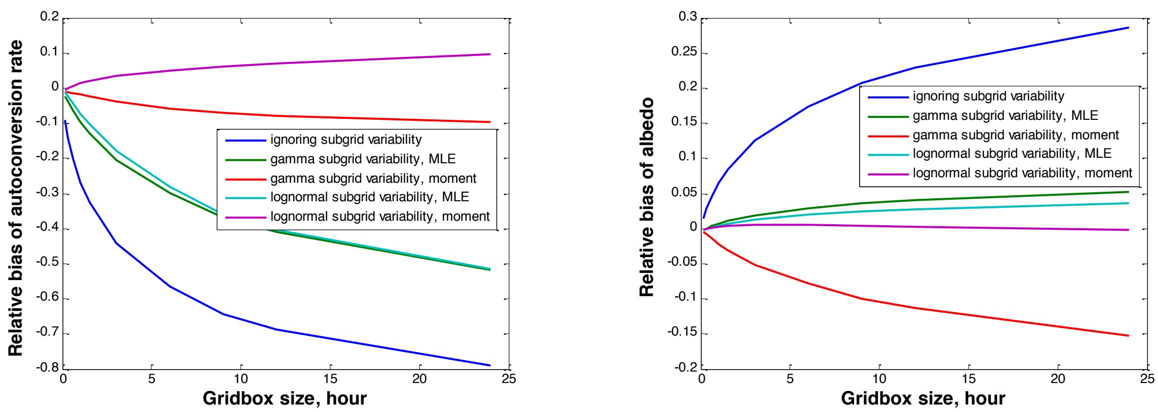

Figure 2: The improvement of calculated grid-average autoconversion rate and cloud albedo as a function of gridbox size. The calculations are performed using gamma and lognormal representations of cloud subgrid variability based on the Maximum Likelihood (MLE) and moment methods. The data from the Tropical Western Pacific (TWP) site are used.

Acoustic Touchless Serial Micro Crystallography

LDRD Project # 11-008

Alexei Soares

PURPOSE:

Our goal is to demonstrate that (i) crystallization conditions can be identified using acoustic transfer of screening compounds, (ii) crystals can be co-crystallized by acoustically transferring all needed components including chemical libraries such as fragment libraries (for drug discovery projects) and additive libraries (for improving protein diffraction), (iii) crystals can be acoustically transferred from their growth wells onto micro-meshes for data collection, (iv) crystals can be acoustically combined with chemical libraries for soaking purposes, (v) crystals can be directly injected into the x-ray beam both at X-ray Free Electron Laser (XFEL) facilities (such as the Linear Coherent Light Source) and at storage ring facilities (such as the National Synchrotron Light Source II).

APPROACH:

Our approach was to acquire an ECHO 550 laboratory acoustic instrument, and simultaneously to construct our own instrument. Both instruments are fully commissioned and in use.

TECHNICAL PROGRESS AND RESULTS:

We have completed all parts of this LDRD and have either published or submitted most of this work:

i) Acoustic identification of crystallization conditions is routine in our group, and this manuscript is in progress.

ii) Co-crystallization by acoustic methods for fragment screening has been accepted for publication in Acta Crystallographica D.

iii) Acoustic transfer has been published in Biochemistry, and a second manuscript is under review at Acta Crystallographica D.

iv) The acoustic soaking manuscript is nearing completion.

v) Direct injection at storage ring locations was published in Journal of Synchrotron Radiation, and direct injection into XFEL sources is under review in Nature.

Protein Microcrystal Dynamics by Coherent X-ray Scattering

LDRD Project # 11-025
Andrei Fluerasu

PURPOSE:
Protein function is often determined by correlated molecular motions with relaxation times ranging from milliseconds to seconds or longer, which are very hard to study experimentally. The well-developed method of X-ray Photon Correlation Spectroscopy (XPCS) employing partially coherent X-ray beams from high-brightness light sources could be used, in principle, to studies these motions but its usefulness is often hindered by practical limitations, such as beam damage or the low maximum frame rate of pixelated area detectors. In order to circumvent these problems, a new technique, namely X-ray Speckle Visibility Spectroscopy (XSVS) is developed using the laser Speckle Visibility Spectroscopy technique as the main source of inspiration. Instead of being measured from "movies" of X-rays, the sample dynamics (protein motions) can be measured by analyzing the speckle visibility resulting from the partially coherent illumination of the protein sample as function of integration time

APPROACH:
The aim of this project is to develop this method based on coherent X-ray scattering to investigate the collective motions of protein molecules. It consists of two major (and relatively distinct) parts: i) the development of the XSVS method and ii) the investigation of the protein collective motions in crystals using XSVS.

TECHNICAL PROGRESS AND RESULTS:
A semi-classical statistical method is introduced to approach the visibility factor of the scattering patterns. The scattering level is usually low due to: i) the relatively low brightness of the incident beam because the X-rays need to be collimated sufficiently to (partially) coherent beam from the chaotic synchrotron radiation, ii) the low scattering from the sample with light atoms (for example, proteins with carbon, hydrogen, and oxygen) and iii) the short integration time for dynamics with short timescales. The standard analysis from the SVS method fails. We introduced the probability density *P(K)* of a detector receiving K photons, which is described by the negative-binomial distribution (NBD) function (*L. Li et al., submitted*). NBD convolutes both the wave-like properties as well as the particle properties of light. The visibility of the speckle patterns is then extracted from the further analysis of the dynamic information of the sample motion. The XSVS method was applied to diluted and concentrated colloidal suspensions. The results from XSVS are compared to those from the more established XPCS method, and are in agreement. However, XSVS is capable of studying dynamics with a shorter timescale under the same instrumental conditions. XSVS is considered to be a single-shot experiment, so that the samples, which are sensitive to radiation dose, stand a higher probability to be studied by XSVS.

The diffuse scattering around the Bragg spots from the diffraction of protein crystals is caused by the strain and the local mosaicity of the crystalline structure. The collective atomic and molecular displacement has been studied by diffuse scattering (*J. Doucet and J.P. Benoit, Nature 325, 643, 1987*). Hence, a protein crystal is selected to be the sample form. In this research, mostly benchmark proteins, (e.g., lysozyme, glucose isomerase, and Concanavalin A (ConA),) are used to develop and optimize the experimental protocols. These proteins are crystallized in quartz capillaries using the counter-diffusive method, so that the crystals can be exposed to X-rays at room temperature without further handling and protection. The crystal quality and radiation resistance were evaluated at the X6A beamline at the National Synchrotron Light

Source (NSLS). The coherent X-ray scattering experiments have been performed at various beamlines: the ID10 beamline at the European Synchrotron Radiation Facility, and the 8ID beamline and the 34IDC beamline at the Advanced Photon Source (APS). Area detectors are used to record the diffraction patterns. Firstly, the area detector is placed close to the sample, so that it is able to capture a larger area in reciprocal space. A Bragg spot is selected at low-q region (~0.1A^{-1}) and the detector is moved a few meters away to resolve the speckles. Rocking curves are also taken to verify that the Bragg spot is recorded on the exact Bragg condition. To minimize the risk of radiation damage, the coherent X-ray scattering patterns are taken at a fresh spot on the protein crystal for a data set acquired with different integration time, and the total exposure time is controlled to be under the experimental radiation-damage threshold.

The scattering patterns of Bragg spots that have not shown any signs of radiation damage are analyzed using the photon statistics approach with the XSVS method. An ensemble of pixels is chosen in the diffuse scattering region near the Bragg spot. Fig.1(*a*) gives an example of ConA crystallized in a capillary. The long streak going through the Bragg spot is the crystal truncation rod. The pixels of interest are marked in the frame. The probability density *P(K)* of the pixels detecting K photons is then calculated by histograming the photon counts over the ensemble as well as over a series of speckle patterns. *P(K)* is then fitted by the NBD function as is shown in Fig.1(*b*). The contrast factor of the ensemble of pixels is given by one of the fitting parameters, which is the number of coherent modes of the scattered beam. The coherent X-ray scattering experiment is repeated to increase the signal-to-noise ratio. However, the mosaicity of the protein crystals is the major issue. The scattering patterns need to be acquired from different locations on the protein crystal. It is well-known that local mosaicity varies throughout the entire protein crystal. Hence, the diffuse scattering introduced by the static structure may vary from location to location, which alters the photon statistics result. Protein crystal quality is the priority for this experiment.

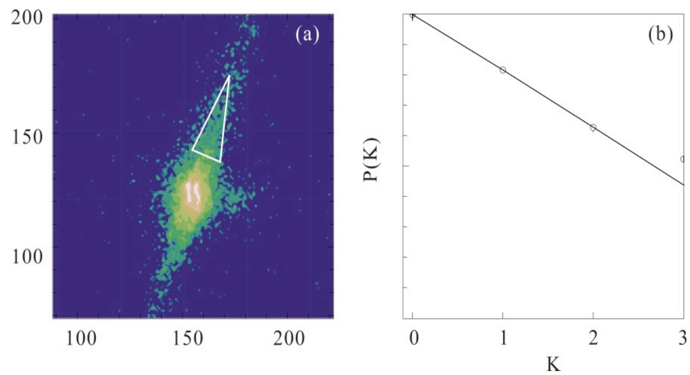

Figure 1 (a) The averaged image of the ConA (303) reflection with diffuse scattering recorded with 0.1*s* integration time over 200 frames. The experiment was performed at the 34-ID-C beamline at APS with fully coherent beam at 8keV. The crystal was orthorhombic with a space group of C222$_1$. (b) The markers are the probability density *P(K)* of receiving *K* photons over an ensemble of pixels marked in the frame in (a). The solid line is the curve-fitting using the negative-binomial distribution function. The mean count is 0.015 ph/px, and the contrast factor is 0.76 (L. Li et al., unpublished).

The coherent X-ray scattering experiment was also performed on cryo-cooled NOD (a type of kinesin) crystals, supplied by Prof. Jared C. Cochran from Indiana University. However, the crystals suffer from transportation and radiation-induced damage. Several forms of hemoglobin crystals, provided by Prof. Sam-Yong Park from Yokohama City University, Japan, have also been exposed to coherent X-rays at cryogenic temperature. So far, no room-temperature experiment has succeeded on these protein samples. The main focus during the next months is on writing several publications based on these results and on preparing the “transfer” of all the experimental techniques developed here to the Coherent Hard X-ray Scattering beamline at the National Synchrotron Light Source II.

High-Resolution Biological Imaging by X-ray Diffraction Microscopy

LDRD Project # 11-027

Enju Lima

PURPOSE:

High-resolution biological imaging is challenging; however, when successful its impact on life science is extremely fruitful. While electron microscopy (EM) delivers nanometer resolution with thin samples less than a micron in thickness, larger samples need to be cryo-sectioned, at the cost of potential artifacts or experimental difficulties, in order to achieve high resolution. The current LDRD explores the feasibility of X-ray diffraction-based imaging of biological samples in the frozen-hydrated state. Utilizing the high-penetration power of X-rays and algorithmic computation, it aims to overcome the current limitations of X-ray optics resolution and the sample thickness limitations in cryo-EM.

APPROACH:

Frozen-hydrated biological imaging by hard X-ray diffraction microscopy was previously demonstrated in two dimensions by the Principal Investigator (PI) and collaborators. Further advances, including higher resolution and 3D imaging, have not yet been demonstrated despite ongoing efforts. The current LDRD of "High-resolution biological imaging by X-ray diffraction microscopy (XDM)" is exploring high-pressure cryogenic sample preservation in order to improve the success rate. The project is also developing a method to expand the scope of cryo-XDM to image extended biological samples of tens-of-microns in size.

TECHNICAL PROGRESS AND RESULTS:

1. High-pressure Cryo-preservation Method for Cryo-XDM:

   High-pressure cryocooling has been developed as an alternative method for cryopreservation of macromolecular crystals and successfully applied for various technical and scientific studies. The method requires the preservation of crystal hydration as the crystal is pressurized with dry helium gas. Previously, crystal hydration was maintained either by coating crystals with a mineral oil or by enclosing crystals in a capillary which was filled with crystallization mother liquor. These methods are not well suited to weakly diffracting crystals because of the relatively high background scattering from the hydrating materials. Here, an alternative method of crystal hydration, called capillary shielding, is described. The specimen is kept hydrated via vapor diffusion in a shielding capillary while it is being pressure cryocooled. After cryocooling, the shielding capillary is removed to reduce background X-ray scattering. It is shown that, as compared to previous crystal-hydration methods, the new hydration method produces superior crystal diffraction with little sign of crystal damage. Using the new method, a weakly diffracting protein crystal may be properly pressure cryocooled with little or no addition of external cryoprotectants, and significantly reduced background scattering can be observed from the resulting sample. Beyond the applications for macromolecular crystallography, it is shown that the method has great potential for the preparation of noncrystalline hydrated biological samples for coherent diffraction imaging with future X-ray sources. The work is in collaboration with C. Kim and S. Gruner at Cornell University and P. Pernot at the European Synchrotron Radiation Facility, France. Publication: Chae Un Kim, Jennifer L. Wierman, Richard Gillilan, Enju Lima and Sol M.

Gruner, "A high-pressure cryocooling method for protein crystals and biological samples with reduced background X-ray scatter", *J. Appl. Crystallogr.* (2013) **46**, 234-241.

2. Cryogenic Scanning X-ray Diffraction Microscopy:

   Our group has developed cryo-scanning X-ray diffraction microscopy, utilizing hard X-ray ptychography at cryogenic temperature, for the noninvasive, high-resolution imaging of wet, extended biological samples and reported its first frozen-hydrated imaging. Utilizing phase contrast at hard X-rays, cryo-scanning X-ray diffraction microscopy provides the penetration power suitable for thick samples while retaining sensitivity to minute density changes within unstained samples. It is dose-efficient and further minimizes radiation damage by keeping the wet samples at cryogenic temperature. We demonstrate these capabilities in two dimensions by imaging unstained frozen-hydrated budding yeast cells, achieving a spatial resolution of 85 nm with a phase sensitivity of 0.0053 radians. The current work presents the feasibility of cryo-scanning X-ray diffraction microscopy for quantitative, high-resolution imaging of unmodified biological samples extending to tens of micrometers.

   This technique was developed by the PI and collaborators at the Swiss Light Source to expand the scope of XDM to larger samples. Publication: E. Lima, A. Diaz, M. Guizar-Sicairos, S. Gorelick, P. Pernot, T. Schleier, and A. Menzel, "Cryo-scanning X-ray diffraction microscopy of frozen-hydrated yeast", *Journal of Microscopy* (2013) **249**, 1-7.

3. Other Accomplishments:

   In addition to the published work outlined above, our group has made progress in achieving multiple reconstructions of cryo-XDM images on frozen-hydrated *D. radiodurans* bacteria using high-pressure cryo preservation, and reached ~25 nm resolution in two dimensions, exceeding the resolution of hard X-ray optics. A manuscript is in preparation.

   The post-doctoral fellow, Li Li, hired in FY12 on this LDRD, continued on the project until summer 2013. Based on his experience with crystal diffraction, Bragg X-ray diffraction microscopy was added as a part of LDRD. Crystal coherent diffraction simulation was carried out and this work will continue at the Hard X-ray Nanoprobe beamline at the National Synchrotron Light Source II (NSLS-II).

   Computer software for diffraction data assembly is being developed for 3D imaging of biological samples. Part of this effort will also continue at the Hard X-ray Nanoprobe beamline at NSLS-II.

Sub-10 nm Resolution Soft X-ray Microscopy of Organic Nano-materials By Novel Diffraction Methods

LDRD Project # 11-030

K. Kaznatcheev

PURPOSE:

This project is focused on the development of experimental and computational techniques which permit imaging of organic nano-materials at the spatial resolution exceeding diffraction limited performance of state-of-the-art x-ray optics. It has two aims: (i) development of quantitative ptychography and (ii) follow up investigation of meta-materials (high-resolution structure of Au/DNA crystals in various states of self-assembly).

TECHNICAL PROGRESS AND RESULTS:

Fig.1 provides a summary of 2012 success and proof that both goals set by the LDRD have been achieved. **Application of coherent diffractive imaging (CDI) indeed results in the improvement of spatial resolution and permits us to image a single layer of nano-particles (NP) as small as ~12nm.** Achieving this level of performance however requires the solution of many significant technical and computational problems. Sample positional errors, parasitic scattering (such as incoherent scattering of zone plate- optical sorting aperture, or SiN window frame) and variation of background result in artificial low frequency errors in specimen reconstruction. As ptychography provides a redundancy in the image reconstruction only among adjacent regions, accumulated errors might be significant and distort the result interpretation (Fig.1). The detector dynamic range is another restriction that significantly limits application of CDI. Close to saturation non-linear response of the CCD prevents long exposure measurements and accurate detection of faint scattering at high q. Although we gained the necessary experience, we have limited ability to improve upon experimental performance, as the measurements are conducted at different

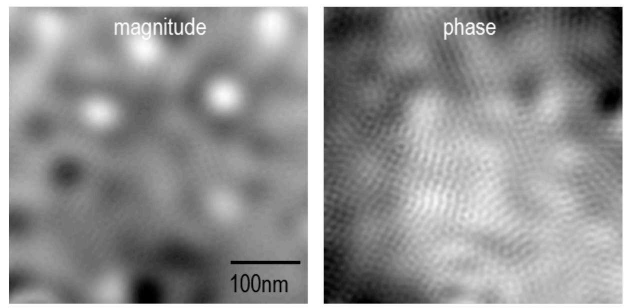

Fig.1 Ptychographic reconstruction of NP thin film. NP (γFe_2O_3: 12nm) positions can be derived from high frequency phase modulation, although low frequency background variation is likely to be artificial.

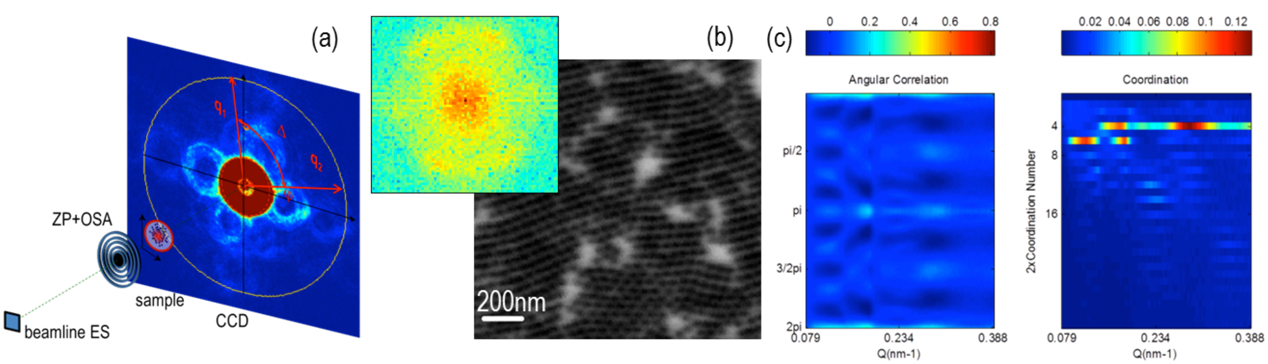

Fig.1 a) schematic representation of x-ray XCCA measurements, (b) Au 45nm NP assembly with modulus of FFT as an insert (top left, log10 scale), and (c) the result of XCCA analysis for the x-ray probe size ~60nm diameter averaged over central 10*10 (pixels):30nm (step size) portion of the sample, left image is a plot of two points correlation function $C_q(\Delta)=\frac{\langle I(q,\varphi)I(q,\varphi+\Delta)\rangle_\varphi-\langle I(q,\varphi)\rangle_\varphi^2}{\langle I(q,\varphi)\rangle_\varphi^2}$ and right- its' first 32 Fourier coefficients C_q^n, so $C_q(\Delta)=2\sum_{n=1}^{\infty} C_q^n\cos(n\Delta)$, (~coordination number).

synchrotron radiation centers. Rather that further explore CDI, we chose the development of alternative approaches to data analysis.

If one is interested in characterization of NP ordering, there is no need for full inversion of diffraction patterns. Instead, one can study the symmetry of the speckle field. Fig.2 illustrates how angular intensity-intensity cross correlation analysis (XCCA) can be used to uncover the hidden symmetry of colloidal crystals. The resulting x-ray scattering angular correlation map (Fig.2c) retains distinct peaks even when the ensemble averaged scattering intensity becomes featureless (Fig.2b). Follow-up Fourier analysis of the autocorrelation function (Fig.2c) further highlights scattering wave vector (q) dependence and reveals the NPs local coordination. As XCCA analysis is performed at each sample position during the raster scan, one can also measure an extension (correlation length) of particular ordering with the spatial resolution given by the x-ray focus size. XCCA drastically suppress arbitrary (parasitic) scattering, photon statistic noise and is not influenced by detector background. As a result the application of XCCA to the same dataset of Fig.1 yields precise quantitative results: the NPs form a dense assembly with average NP-to-NP distance of 17nm, mostly disordered ($\Delta d/d \sim 25\%$) with a small fraction of the NPs forming a square lattice (as programmed by complementary DNA strains) with a 21nm period.

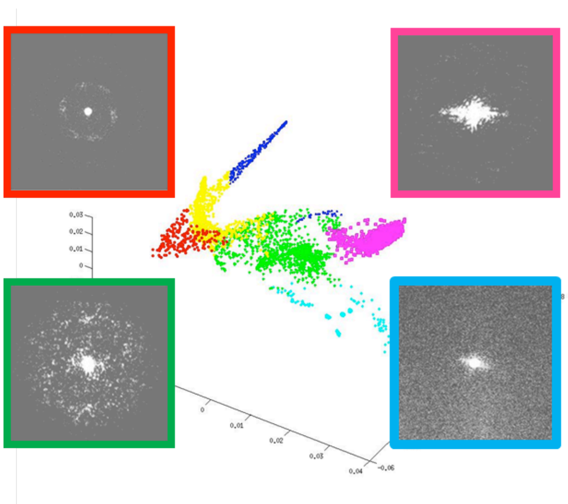

Fig.3. First four nontrivial eigenvectors of spectral clustering as applied to NP scattering data.

The potency of the correlation analysis can be enhanced even further when combined with machine-learning methods for pattern recognition and data-mining of scattering images, providing an ultimate tool for meso-scale structural characterization. Fig.3 shows how well an unsupervised method of spectral clustering can sort the scattering snapshots, uncovering patterns inherent in the data.

2013 was the last year of this LDRD with the funding extended to cover Jan.-May. This LDRD enabled Dr. S. Wang to secure a position at the University of South Florida. The approaches developed resulted in award of the NSLS-II- CFN- Computation Group joint proposal focused on "Structure and Dynamics of Discrete Meso-Architectures", which explores application of machine-learning methods for pattern recognition and data-mining of scattering images.

2013 LDRD-RELATED PUBLICATION AND CONFERENCE PARTICIPATION:

- "Diffusion-based Clustering Analysis of Coherent X-ray Scattering Patterns of Self-assembled Nanoparticles" accepted by 2013 Symposium on Applied Computing
- "X-ray Spectromicroscopy with Near Wavelength Limited Spatial Resolution" submitted to Nature
- Invited lecture at international workshop on the state and future of ptychography, May 4-7, Hohenkammer, Germany
- Presentations at "Programmable Self-Assembly of Matter" workshop, June 30-July 2, New York.

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

LDRD Project # 11-032

Lin Yang

PURPOSE:

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

APPROACH:

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

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

TECHNICAL PROGRESS AND RESULTS:

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

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

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

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

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

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

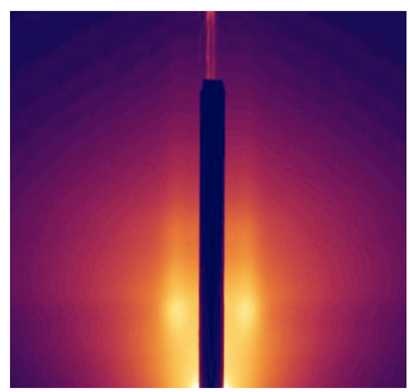

Figure 2 Grazing incident diffraction data from a frozen membrane sample that is exposed in the vacuum.

In the process of exploring rapid freezing, we learned to reduce sample mass to speed up cooling, to optimize vacuum in the cryostat to eliminate frosting on the sample, and that different cryoprotectants behave differently in the freezing process. This knowledge will be applied when we continue this research at the National Synchrotron Light Source II life science beamlines.

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

LDRD Project # 11-033
Jianwei Qiu

PURPOSE:
Quantum Chromodynamics (QCD) has been extremely successful, since it was introduced as a theory for the Strong Force about 40 years ago, in interpreting the data from the Relativistic Heavy Ion Collider (RHIC) to the Large Hadron Collider, and facilities around the world. However, we still do not know exactly how the Strong Force binds the quarks and gluons into the bound nucleons and nuclei, and we know only a little about hadron structure in terms of the quarks and gluons. Owing to the QCD color confinement, quarks and gluons, as color charge carriers, are confined to the femtometer scale and have never been seen directly in any detectors. The proposed eRHIC by BNL with the capability of colliding electron with proton (e+p) and electron with nuclei (e+A) could be a powerful femtoscope (or even an attoscope) to explore the quark-gluon structure of proton and nuclei. The goal of this LDRD project is to identify a set of observables/probes in e+p and e+A collisions that could provide direct access to the quark/glue content of a proton or a nucleus and to explore the role of glue in forming stable hadrons. Our investigations focus on two types of hard probes: jets and heavy flavor productions. The knowledge gained from this project could help articulate the physics case as well as machine parameters of a future eRHIC.

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

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

TECHNICAL PROGRESS AND RESULTS:
2013 was the third year of this LDRD project, which supported a postdoc, Dr. Yan-Qing Ma, and a Ph.D. student, Mr. Hong Zhang of Stony Brook University. We obtained a good number of research results and wrote many papers, which are either published or submitted for publication, plus several are in the pipeline. From our research, we understand much better on what we need in order to better probe the hadron structure, which is critically important for making a strong case of building an Electron-Ion Collider, such as eRHIC. We were in high demand to speak about our results at international conferences, and we delivered many invited talks.

With Dr. Kang of Los Alamos National Lab and Dr. Mantry of Argonne National Lab, we proposed a new observable, referred as Jettiness, to better probe the nuclear effect in electron-ion collisions at eRHIC [Phys. Rev. D86 (2012) 114011]. The Jettiness carries the same advantage of jet production for probing short-distance dynamics, while its inclusiveness provides a much better measurement on nuclear modification than the well-known “jet-quenching” measurement, which is too sensitive to the jet definition. With Dr. Liu of Argonne National Lab, four of us studied nuclear dependence of the global event shape 1-jettiness in electron-nucleus collisions. The inclusiveness of the 1-jettiness quantifies the pattern of radiation in the final state, and gives enhanced sensitivity to soft radiation at wide angles from the nuclear beam and final-state jet, a great advantage over jet quenching in quantifying the radiation and energy loss. We performed calculations for a variety of nuclear targets, and included resummation of logarithms at the next-to-next-to-leading log accuracy [Phys. Rev. D88 (2013) 074020]. Our findings further strengthen the rich physics potential of eRHIC, where a range of nuclear targets was planned.

Following up our early work with Dr. Kang and Prof. Sterman of Stony Brook University [Phys. Rev. Lett. 108 (2012) 102002], together with Dr. Ma, we developed an extended QCD factorization formalism for heavy quarkonium production in high energy collisions [arXiv:1401.0923]. Our work laid down a solid foundation for using heavy quarkonium production as a hard probe, and provided much needed physics insights on how a heavy quarkonium is actually produced in high energy collisions, which is very important for understanding heavy quarkonium production at eRHIC. In addition, we found that it is very likely that we could be able to explain the long-standing puzzle: why heavy quarkonia produced with a large energy/momentum do not like to be transversely polarized.

In terms of this new QCD factorization formalism, the cross section of heavy quarkonium production is made of three major parts: short-distance hadronic collision, perturbative QCD evolution of the fragmentation functions, and input fragmentation functions. Because of the short-distance and perturbative nature of the hard collision and evolution, the input fragmentation functions are the only part of the QCD calculated cross sections that are sensitive to the nature of the heavy quarkonia. With the student and postdoc supported by this project, we investigated for the first time the transition probabilities for a heavy quark pair produced in the hard collisions to transmute itself into a physical quarkonium in non-relativistic QCD, an effective theory of QCD. We evaluated the transition probabilities via an intermediate S-wave as well as a P-wave state of non-relativisitic heavy quark pair, which are the most relevant states when heavy quarks are heavy. Our results provided much needed information for understanding the formation of a bound heavy quarkonium in high energy collisions, and the value of quarkonium production as a hard probe [arXiv:1311.7078,arXiv:1312.0524].

The surprisingly large flavor asymmetry between the up and down quarks in the proton sea has provided us a very serious puzzle as well as a challenge to explain such an asymmetric sea. Working with Prof. J.C. Peng and others, we identified independent experimental evidence for a nucleon to have such an asymmetric sea of up and down quarks and antiquarks. We also presented a theoretical explanation for the momentum dependence of such a flavor asymmetry [arXiv:1401.1705, submitted to Phys. Rev. Lett.], and pointed out the future opportunities to further measure and test such a flavor dependent asymmetric sea in the proton, in particular, the measurements at a future Electron-Ion Collider, such as eRHIC.

CMOS-Pixel Vertex Detector for EIC

LDRD Project # 11-036

Elke-Caroline Aschenauer and Benedetto Di Ruzza

PURPOSE:

BNL is working on the design of a new accelerator; this new accelerator will add an electron machine to the existing Relativistic Heavy Ion Collider, a hadron collider. This will be the most cost effective solution for an electron ion collider (EIC) in the U.S. The EIC detector should include a vertex detector that covers a wide range of pseudo-rapidity ($-1<y<1$) down to very low p_T (~100 MeV) allowed by the detector geometry and needs to be capable of reconstructing displaced vertices from heavy flavor decays. Traditionally, such detectors are implemented in two separate parts – a "barrel" layer that detects tracks out to $|\eta| \sim 1$ and an "endcap" composed of disks that extend the acceptance down to smaller polar angles ($|\eta|>1$). Such detectors were tested for the first time in the WA97 and DELPHI experiments. Today they are an integral part of the tracking systems for any particle detector, i.e., ATLAS, CMS and ALICE at CERN.

Such detectors are extensively used in the Large Hadron Collider experiments and typically contain several layers of 100-300 μm thick silicon sensors and significantly more material in the separate readout chips resulting per layer in typically 3% - 10% radiation length of material. μ-Detectors based on such designs are unsuitable for an EIC, where the energy of the scattered electron can be as low as 0.5 GeV. The EIC detector requires dedicated research and design for the tracking detectors, which emphasize low radiation length.

In the last decade there has been significant progress in the development of Monolithic Active Pixel Sensors (MAPS). In these sensors, the active detector, analog signal shaping, and digital conversion take place in a single silicon chip (i.e., on a single substrate) (see [1] and references listed there). These devices are built using ordinary CMOS technology based on an epitaxial layer as the active sensing element and the charge created by ionizing particles is collected by thermal diffusion.

BNL, Columbia University, and the Institut Pluridisciplinaire Hubert Curien in Strasbourg, France (IPHC-CNRS) started a research program to investigate the use of the silicon pixel MAPS sensor "MIMOSA", designed in the IPHC, for the μ−vertex for the new EIC detector. MAPS μ−vertex detectors in the barrel of particle detectors have become more common. The unique development of **this** research is to produce for the first time a prototype μ−vertex MAPS detector disc for the detector endcaps. The main risk of this research lies in realizing a technology called stitching to combine chips in quadrants, which will be used to form the forward discs. This technology has until today never been realized.

The present goals of this research are:

1) Test the sensors already developed (Mimosa 26 and 28) and the new more radiation hard sensor technologies, i.e., Mimosa-34, currently under development, with an ion beam and with a synchrotron radiation source in order to emulate the signal and background conditions of an EIC detector.
2) Test the bandwidth limits of the readout system using the ion beam.

3) Integrate the μ-vertex detector into the GEANT model of the EIC detector to study the number and longitudinal alignment of the forward discs to achieve the needed tracking resolution.
4) Study the charge collection with a laser and a calibrated ion source.
5) Test how the performance of different chips changes as a function of their operating temperature.

APPROACH:

The main research task of this project is to develop a test stand in order to test the "Mimosa sensors" with a laser source, cosmic rays and radioactive sources (55-Iron and 90-Strontium). The starting point of this test stand is the hardware and software setup already used at DESY and CERN in the "EUDET Beam telescope" (Mimosa-26 sensors with 'LabVIEW' based data acquisition system) designed for the "Linear Electron Collider" silicon μ-vertex tracker development. The results achieved with the Columbia and Strasbourg Groups were presented in the 2012 IEEE NSS conference (Anaheim, CA, October 2012) and elsewhere.

Another key task will be a detailed GEANT simulation of all these different silicon sensor prototypes in realistic electron-proton/ion collisions. This work will be performed in collaboration with the local BNL group responsible for EIC physics and detector simulations. These simulations will give us precise constraints on the needed detector geometry and pixel-size. A first meeting on the results of the first EIC simulations was held at BNL [2]. At this meeting the general detector simulation framework was chosen.

It is very important to remember that all this R&D work, even if mainly oriented for the EIC collider detector, can be used in a wide range of other applications, e.g., new medical tracking sensors. The main advantages of the Mimosa sensors are that they are cheap to produce, easy to handle, and sensitive to both gamma rays and radioactive particles. That's why in addition to their applications to the EIC detector it is important to establish at BNL expertise for these sensors and the basic knowledge about this technology for present and future projects.

TECHNICAL PROGRESS AND RESULTS:

The test stand at BNL is working for noise tests on the Mimosa 26 and 28 sensors. Dr. Benedetto Di Ruzza, the postdoc for this project, spent four weeks in 2013 in Strasbourg working with the team, which developed the current MAPS based sensors, in order to learn how to test the current and the new Mimosa-34 sensors with a laser. This knowledge was immediately integrated into the test stand at BNL.

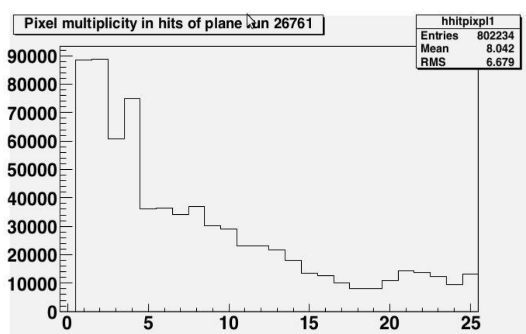

Figure 1. Pixel multiplicity for a Mimosa-26 sensor after the irradiation with a 1 GeV/u silicon ion beam

A Mimosa 26 prototype sensor was successfully exposed to different ion beams at the NASA Space Radiation Facility in order to test the limit of the DAQ system and the radiation hardness of the chip in the environment of hadron beams. Continuing analysis of the acquired data will be performed in order to study the clustering of hits in these sensors depending on the different ion beams. First preliminary results are shown in **Error! Reference source not found.**.

A first design of the barrel and the forward disk μ-vertex detectors has been integrated in the full simulation of the EIC detector. First initial tracking studies have been performed studying the momentum resolution as a function of several design parameters, e.g., the pixel size and the thickness of the individual silicon sensors.

shows the momentum resolution for pions as function of their momentum and different silicon sensor thicknesses. For the coming year the plan is to:

1) Complete the analysis of the data taken with the different ion beams
2) Extend the test with ion and laser sources and repeat these tests with the Mimosa-34 prototype
3) Test the laser charge collection as a function of operating temperature
4) Integrate a more realistic cooling system for the forward disks in the detector simulation to study the impact of its material on the momentum resolution.

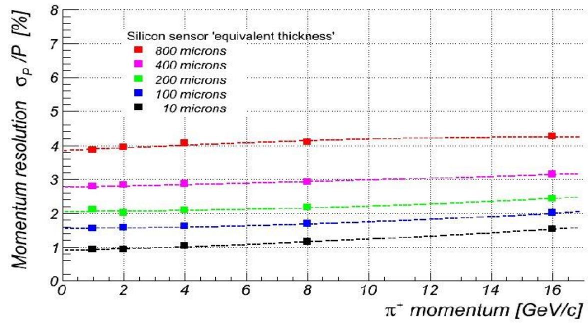

Figure 2. Simulation studies for the momentum resolution for pions as function of the pion momentum and assuming different silicon “equivalent thicknesses.”

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Study of FEL Options for eRHIC

LDRD Project # 11-040
Vladimir N. Litvinenko

PURPOSE:

The potential performance of X-ray Free Electron Lasers (FELs) driven by eRHICs high-energy electron energy recovery linac (ERL) has been studied since 2004 [1] and recently returned to focus as a potential future direction for BNL's light sources [2]. This project was focused on detailed studies of various X-ray FEL options for eRHIC, including a single pass self-amplified stimulated emission (SASE) FEL, seeded and high gain harmonic generation FELs, and X-ray FEL oscillators [3,4,5]. Advanced FEL and beam dynamics codes will be used to evaluate various FEL options, compare them, and connect them to potential applications.

APPROACH:

The goal of this LDRD project was to explore the potential of eRHIC as a driver for a farm of X-ray FELs as well as a driver for an X-ray FEL oscillator (see Figure 1).

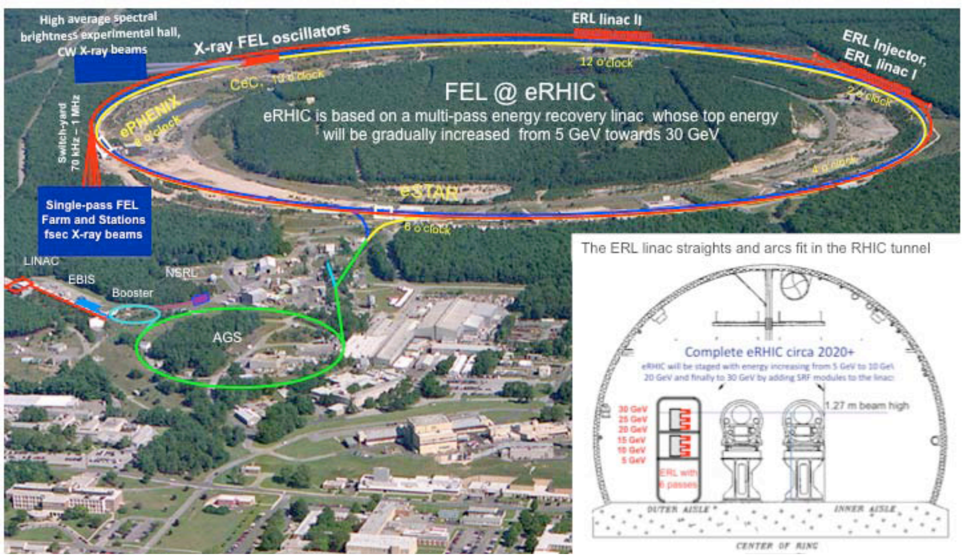


Figure 1. Schematic layout of possible FEL-based light source facilities surrounding a future eRHIC energy recovery linac [2].

TECHNICAL PROGRESS AND RESULTS:

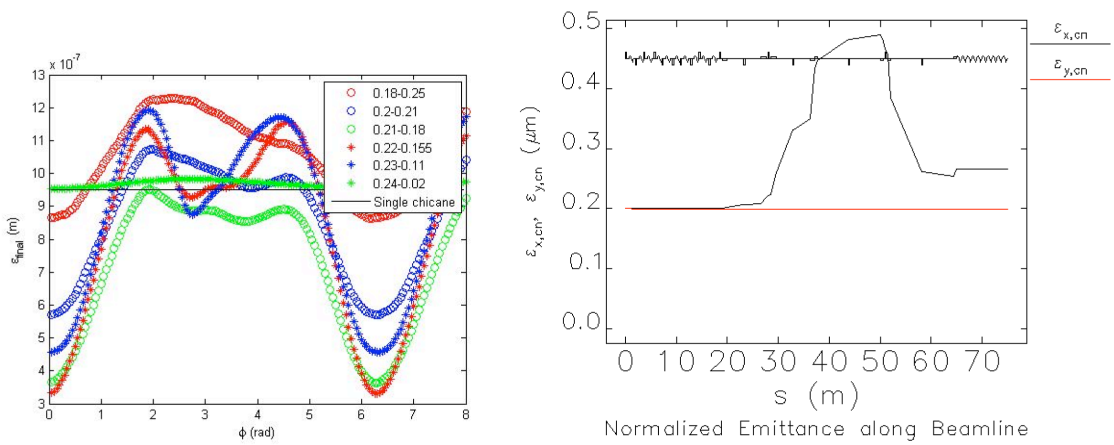
During the first part of 2010, the main focus was on the selecting appropriate software and hardware for massive simulation of beam and FEL dynamics. We also made a preliminary simulation of the X-ray FEL oscillator and found eRHIC can serve as the main FEL driver with an additional low energy ERL needed for the feedback.

In August 2011 we hired a post-doc, Dr. Yichao Jing, who actively pursued the selection of the beam parameters and bunching scheme for an X-ray FEL farm. One of the main challenges of using an ERL as an FEL driver is the effect of coherent synchrotron radiation (CSR) in the arcs and in the beam compressor. Specifically, since the electron's trajectory is bent in the ERL arcs, it is necessary to accelerate a longer bunch in an ERL compared with those in a straight linac, i.e., a buncher with large compression is required to generate kA levels of peak current necessary for X-ray SASE FELs. It can result in significant emittance degradation.

The accurate choice for the beam energy and an advanced strategy of compressing bunches are of critical importance for creating the necessary beams. We had chosen to operate the FEL with e- beam at an energy of 10 GeV to reach to the hard X-ray regime with current available undulator technology. We used a chicane to compress the bunch for a high peak current of a few kAs and tested the SASE FEL operation mode.

The bunch compressor system located at 12 o'clock and the electron beam will be guided in its second pass in eRHIC (where the beam energy is about 7.55 GeV) into the cavity located at 2 o'clock. The latter is detuned from on crest operation to induce a correlated energy spread for bunch compression with a large R56. The compressor induces CSR, which can easily blow up the beam emittance by a large factor. To address this problem, we developed an analog of the emittance preservation technique in a merger developed for space charge dominated beam – the so called ZigZag scheme [6] and use a combination of chicanes to minimize the CSR effect.

The simulation results are very encouraging and the scheme demonstrates strong suppression of the CSR affect. The results of these studies were presented at invited and contributed talks at two conferences and have been published in a refereed journal [10]. A brief summary of the studies is presented below (see Figure 2).



(a) (b)

Figure 2. (a) a scan with the dipole strengths (in rad) in the first and second chicanes. The horizontal axis is the phase advance between two chicanes and the vertical axis is the final emittance after bunch compressors (b) the normalized emittance along the bunch compressor system. The CSR effect in the second bunch compressor cancels out the CSR in the first chicane, thus final emittance is minimized.

We used a Gaussian distribution with a normalized emittance of 0.2 μm in both planes and tracked 200000 particles along the whole system using the code ELEGANT. We assume the initial energy spread is 1e-6. The CSR effect and synchrotron radiation are included in the process and random higher order field errors are also included in the dipoles and quadruples. The calculation confirmed our expectations that using one chicane causes very serious beam degradation. The CSR effect would blow up the beam emittance 4-fold. Using two chicanes with opposite bending signs (e.g. the zigzag scheme) minimizes the CSR affect. The optimum cancelation occurs with the proper choice of betatron oscillation phase advance between the two chicanes and the proper choice of the beam optics. We scanned the relative strengths of two chicanes to locate an optimal working point. Overall the 4-fold increase in the beam emittance in a traditional scheme was reduced to a mere 33% emittance growth (see Fig. 2). It means that the

CSR effects in the second bunch compressor nearly cancel out the CSR effects in the first chicane.

We used the resulting particle distribution after the compressor to simulate the FEL process using the 3D FEL code GENESIS. As shown in Figure 3, such beam will generate a 1 Å coherent X-ray FEL beam of excellent quality.

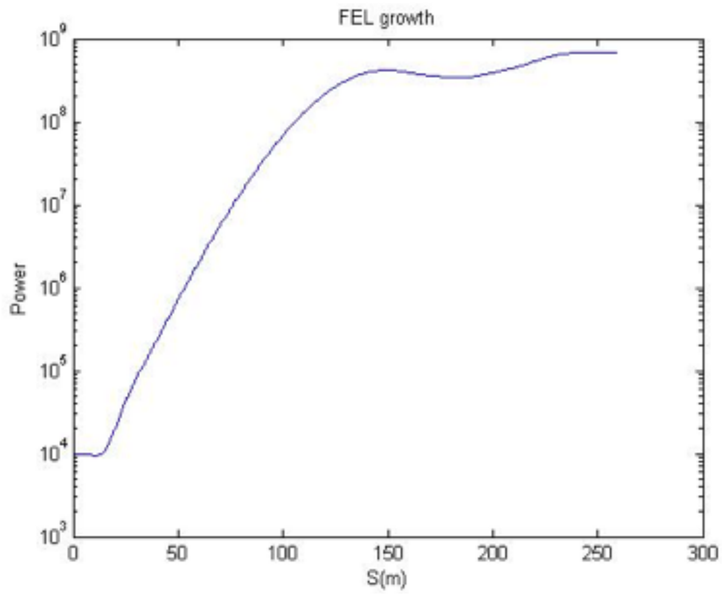


Figure 3. FEL peak along the FEL. The calculated 3D gain length is 3.1 m.

In addition, we studied the CSR suppression using a set of parallel polished conducting plates in an experiment at the Accelerator Test Facility. The result demonstrated, for the first time, suppression of the CSR induced energy loss and the CSR induced energy spread. These findings were presented as an invited talk at PAC'11 and published in Phys. Rev Letters [11].

Overall, this LDRD-supported research provided BNL with the possibility of maintain a leading position in the area of advanced coherent X-ray light sources, which could open a new area of research and application in the post NSLS-II era. If an eRHIC ERL is built, such an X-ray FEL could be added to the facility with a reasonable cost and could compete with (or exceed) any other existing or planned coherent X-ray source.

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Overcoming Electromagnetic Interference in Simultaneous PET and MRI for Biological and Clinical Imaging

LDRD Project # 11-050

Paul Vaska, David Schlyer, Craig Woody

PURPOSE:

Recently the concept of acquiring positron emission tomography (PET) images simultaneously with magnetic resonance imaging (MRI) has generated considerable excitement in biomedical science. The new possibilities engendered by this fusion of two distinct but complementary imaging modalities are numerous in medicine, relating to the accurate image alignment between the functional image and its anatomical reference frame, and to the potential for interrogation of multiple functional measures simultaneously using functional modes of MRI such as fMRI, spectroscopy, or diffusion tensor imaging. Further, this approach is being applied to the broader context of biological imaging, in particular to understand basic biochemical mechanisms in plants in an effort to develop improved biofuels and to predict the impact of climate change on critical plant species. Our group has been one of the pioneers in the area of multimodality PET-MRI imaging, having developed modular PET detectors and prototype imaging systems that can tolerate the punishing MRI environment, which consists of strong static and dynamic magnetic fields and high power radio-frequency transmission. However, the integration of the two systems has been challenging, in particular due to the interference between the modalities, each of which relies on high fidelity radio-frequency electromagnetic signals. In our prototype systems, significant interference has been observed in both PET and MRI data despite initial attempts at isolating them with electromagnetic shielding. In this proposal, we plan to investigate the generation and propagation of the electromagnetic interference (EMI) in a rigorous and methodical manner, and to develop and test technological approaches to mitigate the problem to the greatest extent possible. This will build a foundation for multiple ongoing and planned projects in simultaneous PET and MRI imaging.

APPROACH:

We aim to analyze the potentially deleterious signals in the relevant PET and MRI subsystems, and then develop ways to shield or otherwise mitigate the effects. This includes analysis of the sources of electromagnetic waves, the transmission paths, and the circuits that are sensitive to them. Building upon this analysis, we will design and test optimized electronics and various shielding configurations.

TECHNICAL PROGRESS AND RESULTS:

Funds were carried over into FY 2013 mainly to complete the purchase of MR-compatible components for our PET detectors, which have a long lead time. These components enable us to continue building MR-compatible systems which feed grant proposals going forward. There is no more funding from this LDRD project, but the results are supporting grant proposals to the Department of Defense and National Institutes of Health.

Complex Modeling of Nanostructures

LDRD Project # 12-007

Simon J.L. Billinge and Pavol Juhas

PURPOSE:

This project aims to develop data analysis algorithms and software for solving atomic structures of nanoparticles and locally disordered materials. Accurate knowledge of atomic structure is critical information for understanding, development and application of new materials. Structure determination of nanomaterials is considerably harder, because they have a more complicated structure (distortions at the surface) and at the same time produce weaker and less resolved signal 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. This is not straightforward, because data analysis tools for experimental or theoretical techniques were not designed for interoperability and because each given material may need a specialized modeling procedure, as per the available experimental, theoretical or chemical inputs. Our objective is to develop software for an easy and highly configurable buildup of such specialized structure simulations and explore computational routines that would lead to successful structure elucidations. The codes are developed as open source software to promote sharing, verification and contributions from the community. If successful, this project will be of great benefit for the data analysis of the National Synchrotron Light Source II experiments and for the characterization and development of nanostructured or locally disordered materials.

APPROACH:

Conventional crystallography can almost routinely determine the structure of crystalline materials, as their long-range periodic order and high-symmetries of atom arrangements produce highly resolved diffraction patterns and permit structure description with but a few variables. The situation is much more difficult for nanomaterials. The particle sizes are too small to form any sizable periodic order in atom positions. A significant number of atoms are at the surface where their positions relax and distort. Experimental data from nanoparticles are in general more noisy and less signal-rich than from crystals, but nanostructures have less symmetry and require more variables for their structure description. Apart from a few cases where nanoparticles crystallize in sizable domains, accurate structure information is not available.

To overcome the increased complexity in the nanoscaled structure, we combine multiple experimental inputs such as pair distribution function (PDF), small angle scattering, local chemical constraints (coordinations, allowed bond angle ranges) and theoretical energy calculations in a single optimization setup. The increased number of inputs that the solved structure has to satisfy should compensate for its higher degree of freedom and for lower resolution in the experimental data.

TECHNICAL PROGRESS AND RESULTS:

For a long time, Pavol Juhas worked alone on this project as we faced serious challenges finding staff and putting contracts in place to allow other staff to begin working. Our first attempt to hire a computational post-doc of the required quality failed. The only two candidates above threshold took competing job offers. This delayed the hiring of a post-doc by a number of months, but is now resolved with Kevin Knox joining the project in this role. Secondly, our attempts to recruit Mike McKerns, an expert in Uncertainty Quantification and in high performance computing applied to scattering problems, was not successful. We put a consulting agreement in place to acquire his services for 30% of his time. This contract took many iterations, but is now in place. Finally, Xiaohao Yang, a Columbia grad student in the group of Simon Billinge is the final member of the team. It also took a long time to get the contract with Columbia in place to fund this, but this is now in place. The project is now fully staffed and we are ramping up productivity. The personnel were only in place towards the end of the reporting period and their efforts are hardly reflected in this report.

One of our first goals is to turn the software development activity into a community open source project that we refer to as the Complex Modeling Initiative (CMI), with Brookhaven prominently identified as the main sponsor, so that others in the community can become vested and contribute. To this end we have transferred our project code repositories to GitHub, which is the leading platform for open source software development, and makes it much easier for anyone in the community to contribute. This will be rolled out as a community project early in the new year and we expect this to increase the visibility of the project. We will strongly publicize this development after its launch.

There have been significant important updates to the code-base of the project.

1) The PDF calculator in our C++ library has been optimized to allow fast-update calculations, which reevaluate only contributions from changed atoms. This produced an order of 1000 speed up of PDF calculations in a 10000 atom structure and made the library suitable for big-box modeling approaches such as reverse Monte Carlo.
2) We have completed a Python interface to the C++ library that, due to the object-oriented architecture, allows enhancements of calculations, for example, by defining custom PDF-profile shapes. The Python interface also allows adapting any Python representation of the structure data for use with the PDF, bond valence sum, and radius overlap calculators that are in the library.
3) We have set up a documentation project for each source code package in our library and configured publishing of online manuals using web hosting at GitHub.
4) We have converted the front-page web page diffpy.org for our codes from HTML to re-structured text, which will allow easier updates and maintenance of the content in the future.
5) We have prepared binary software bundles for easier installation on Linux and Mac OSX operating systems. The bundles will be released upon obtaining necessary permissions from the BNL/DOE.
6) We have prototyped the use of our SrFit CMI framework on high performance computing resources at the Lab by integrating it with the Mystic and Pathos distributed computing packages of Mike McKerns. We identified areas where codes have to be refactored for them to work in this environment and we are working on this refactoring work.
7) We have incorporated rigid body constraints into the code-base and made them operate within the CMI framework.

Since the main goal of the project is to obtain external funding to support this effort, we are also applying the Complex Modeling methods to scientific problems to demonstrate its scientific utility. There were highlights in several structure determination projects that use the Complex Modeling codes developed. First, the following papers using our Complex Modeling Framework appeared in this reporting period:

1) Christoper L. Farrow, Chenyang Shi, Pavol Juhás, Xiaogang Peng and Simon J.L. Billinge, Robust structure and morphology parameters for CdS nanoparticles by combining small

angle X-ray scattering and atomic pair distribution function data in a complex modeling framework, J. Appl. Crystallogr. , Submitted (2013).
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Current ongoing unfinished scientific projects are the following:

1) A Complex Modeling structure solution was carried out on ultra-small CdSe nanoparticles synthesized in the lab of Jon Owen at Columbia University. The approach was to take a tentative starting model candidate from a single-crystal analysis of one of the samples as a starting point and constraint in a CM fit of PDF data from uncrystallized powders of a series of nanoparticles. This was a success and the resulting paper describing the synthesis and structural characterization is about to be submitted to Nature.
2) As a follow up to the above, we carried out an assessment of the information content in the PDF data - a sensitivity analysis of fits to adding and removing individual atoms. We found that while the proposed cluster model has an excellent fit to the measured PDF, so do numerous other clusters based on the same zinc-blende lattice, but with different shapes, validating the need for a CM approach revealing that inputs from other information sources that are more sensitive to particle shape are required for reliable shape determination.
3) We are using the CM approach to solve the structure of an ultra-stable Au-144 atom gold nanoparticle that can be made in a pure sample. We determined that the published DFT-based model for the Au144 “ubiquitous” nanoparticle contradicts the measured PDF. We setup an automated scan of Marks decahedral structures and were able to find a plausible model for the particle structure. We are again investigating the sensitivity to the presence of surface structures in these models from PDF data alone; again demonstrating the need for a CM approach.
4) Finally, in the third science-application project we have greatly improved the accuracy of PDF simulations for organic crystals by separating contributions from inter and intramolecular atom pairs. In addition we were able to use the new codes to define the molecules in crystals as rigid bodies and resolve their correct orientation in the crystal from the PDF fit, even when starting from a completely random initial orientation. This was made possible by the modular and configurable code-base. This project demonstrated multiple ways of defining structures available in the CMI codes and their configurability that allowed tweaking the PDF calculations.

Milestones for next year:
1) Rollout and publicize CMI community development effort
2) Full release of SrFit end-user CM software application
3) Develop and run a hands-on SrFit workshop, possibly at the American Crystallographic Association meeting in Albuquerque
4) Publish 3 papers, targeting high impact journals, demonstrating scientific results made possible by CM
5) Publish 2 papers describing the methodology
6) Submit at least one proposal for external funding

Early Deployment of Leadership Applications on BG-Q

LDRD Project # 12-008

Yan Li, Roman Samulyak, Taku Izubuchi, Frithjof Karsch, and Chulwoo Jung

PURPOSE:

The purpose of this project is to deploy applications to the BG-Q architecture in important areas of science at BNL. The three areas that were chosen were materials, accelerator physics and lattice QCD. For materials this project is a collaboration between the Computational Sciences Center and Dr. Simon Billinge's group in the Condensed Matter Physics and Materials Science Department to demonstrate the use of a complex modeling scheme for solving the structure and properties of nanostructures. The goal is to develop and demonstrate some parts of the global optimizer scheme Billinge proposed, namely the pair-distribution-function (PDF)/theory complex. For accelerator physics, the goal was the development and deployment of highly scalable codes for the simulation of processes in particle accelerators. Our project had two main objectives: the development of an advanced electromagnetic Particle-in-Cell (PIC) code for the simulation of processes relevant to eRHIC and advanced bean cooling and acceleration methods. The other objective was the development of particle-based hydrodynamic codes for multiphase systems and their application to the simulation of liquid mercury jet targets for the DOE Muon Accelerator Project (MAP). For Lattice QCD, the purpose was numerical computation of hadron vacuum polarization contributions to the muon magnetic moment (g-2) for last few months. The muon magnetic moment is one of the unknown physics parameters which shows significant discrepancies, by 3.6 sigma, between the experimental measurement and theoretical calculation and thus very important for the next big experiment planned at Fermilab by DOE starting in 2016.

APPROACH:

For materials, we collaborated with both Billinge's group and his experimental collaborator Prof. J. Owen at Columbia University, who synthesized the nanostructures under study and carried out structural and optical characterizations. We have combined first-principles computational tools and pair-distribution function (PDF) analysis, as well as other complementary experimental techniques (optical spectroscopy, mass spectroscopy and X-ray single crystal diffraction) to determine the atomic structures of nano-sized clusters and quantum dots, and to probe into their physical properties such as energetic stability, energy gap and optical properties. Most calculations were performed using density functional theory (DFT) implemented in the VASP package. A series of calculations based on the reactive force field (ReaxFF) were also performed and compared to DFT results to explore the potential of using ReaxFF for high throughput screening during PDF fitting and reverse modelling.

For accelerator physics, the electromagnetic PIC code is based on rigorously conservative methods for fields and currents and scalable integrators for particles and fields optimized for multicore supercomputers. The multiphase hydro code is based on our novel Lagrangian particle algorithm that extends and improves ideas of smooth particle hydrodynamics and on advanced programming methods that parallelize the code for both traditional and GPU supercomputers.

For lattice QCD, the strategies are to use stochastic estimation, imposing a twisted boundary condition to gain refined momentum points which will largely decrease the number of computations which are needed for this simulation. There is a theoretical challenge due to a broken flavor symmetry at the boundary.

TECHNICAL PROGRESS AND RESULTS:

Semiconductor quantum dots have a wide variety of applications due to their tunable properties depending on composition, size and surface terminations. Recently a series of atomically precise, pyramid-shaped, CdSe quantum dots have been synthesized with the inorganic core structures solved by the atomic pair distribution function (PDF) technique. In this work, we have investigated structural and optoelectronic properties of the synthesized clusters, by combining first-principles DFT and TDDFT calculations with experimental NMR spectra, UV-vis absorbance spectra and PDF analysis. In particular, we systematically examined the adsorption motifs and binding strength of the passivating ligands on the CdSe (315nm) cluster, as well as their influence on energetic stability, core structure and electronic properties of the cluster. Two stable ligand shell arrangements, which differ in the intermolecular hydrogen bonding network, were found to yield the most stable structures and satisfy the electron counting rule of the inorganic core. A similar scheme was then used to passivate the other three clusters in the series. Overall an excellent agreement was found between the computed TDDFT optical gaps and the measured ones; the simulated PDFs also agree in general with the measured PDF curves.

For accelerator physics, the electromagnetic PIC code for relativistic particles and fields, called SPACE, has been developed and optimized on multicore supercomputers, including ones with heterogeneous communications via MPI and OpenMP. The code is currently being used for the study of coherent electron cooling, a beam cooling method important to the future eRHIC facility. The unique feature of the code is its ability to accurately resolve atomic physics transformations. Understanding of the interaction of muon beams with plasma in muon cooling devices is important for the optimization of the muon cooling process. The core code uses the PIC method for the Maxwell equations coupled to the dynamics of particles. Electromagnetic PIC methods are combined with probabilistic treatment of atomic physics processes responsible for the plasma production. Both traditional smoothed particle hydrodynamics and new Lagrangian particle methods, proposed by the authors, have been investigated. The Lagrangian particle method has demonstrated superior accuracy compared to SPH. Both codes have been optimized for traditional and GPU supercomputers. The codes are being used to provide simulation support for the MAP. Simulation studies have contributed to the target design for the proposed muon collider and neutrino factory.

Lattice gauge theory can provide a fundamental approach on the g-2 problem and the hadron vacuum polarization value is one of the error sources with the largest contribution. There have been several attempts on the lattice hadron vacuum polarization computation, but still, the theoretical error estimation is not accurate enough to find the breaking point of modern physics theories.

For more precise computation, we need to increase the size of 4 dimensional simulation spaces but to do that, numerical costs also need to be increased proportionally. Furthermore to calculate the higher order of error correction terms, so-called disconnected quark loop contributions, in principle we have to calculate the equations by a factor of the lattice volume. Currently, the development of the program for this analysis is almost done and the code is being checked in many aspects to get ready for production.

Inter-individual Variation in Radiation Induced Epigenetics

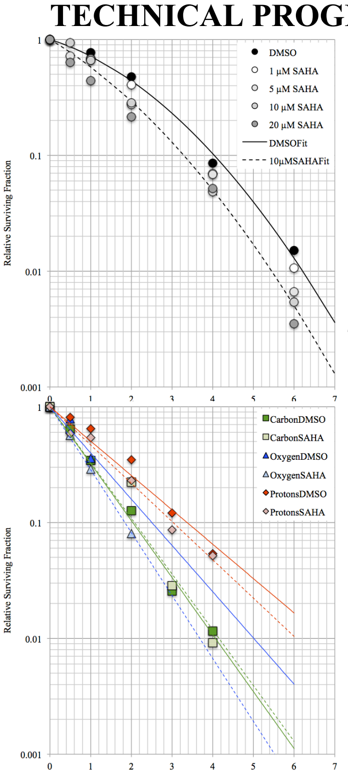
LDRD Project # 12-012

Paul F. Wilson

PURPOSE/APPROACH:

The goal of this project is to understand the impact of epigenetic modifications on *in vitro* cellular responses to photon and charged particle irradiation in terms of altered DNA repair capacity, increased cellular radiosensitivity, and translation to potential higher risks of carcinogenesis and other IR-associated disease endpoints. Inter-individual genetic variation in molecular pathways responsible for proper maintenance of cytosine methylation patterns in genes and regulatory sequences encoding critical DNA damage response pathway proteins and/or post-translational modifications (PTMs) of chromatin proteins affect IR-associated disease risks, particularly after low dose and low dose rate exposures. We have been investigating whether 5-hydroxymethylcytosine (5-hmC) levels and histone PTMs impact IR-induced DNA damage induction/processing as well as cell killing and transformation (acquisition of anchorage-independent growth in soft agar) following gamma ray and light ion irradiation in normal and tumor cell lines. Treatment of NFF-28 normal human fibroblasts, U2OS osteosarcoma cells, and U87-MG glioma cells with the histone deacetylase (HDAC) inhibitors SAHA/vorinostat, M344 and PTACH at 5–10 µM concentrations 18 h prior to gamma irradiation results in significant induction of 5-hmC (~5–10% at IR-induced break sites), delayed/impaired clustered DNA damage and double-strand break repair processing, and ≥2-fold radiosensitization assessed by clonogenic survival assays. Proton, carbon and oxygen ion irradiations at the NASA Space Radiation Laboratory (NSRL) at clinically relevant energies were completed to assess potential normal tissue cancer risks and possibility for increased therapeutic gain of employing adjuvant HDAC inhibitors for hadron radiotherapy. Unlike uniform gamma ray radiosensitization, effects of HDAC inhibitors were unexpectedly cell type and ion species-dependent, with the carbon and oxygen ion irradiations showing significantly enhanced normal cell survival and transformation frequencies.

TECHNICAL PROGRESS AND RESULTS: The following summarizes our FY13 results.



Cell Line	HDACi	HDAC$_i$ Sensitization Ratio[a]			
		^{137}Cs γ	200 MeV p	350 MeV/n ^{16}O	290 MeV/n ^{12}C
NFF28 (NHDF)	10 µM SAHA	1.31	1.29	0.42	0.62
	10 µM M344	1.26	1.31	0.37	0.71
	5 µM PTACH	1.20	1.28	0.33	0.79
U2OS (osteosarcoma)	10 µM SAHA	1.23	1.11	1.38	0.98
	10 µM M344	1.13	0.92	1.36	1.13
	5 µM PTACH	1.04	0.87	1.42	0.85
U87-MG (glioma)	10 µM SAHA	1.22	1.09	1.46	0.88
	10 µM M344	1.58	1.03	1.32	1.19
	5 µM PTACH	1.26	1.15	1.41	1.19

[a] Determined from LQ or exponential best-fit lines. Sensitization ratios calculated for exponential fits as the ration of slopes ($\alpha_{HDACi}/\alpha_{DMSO}$) and for LQ fits as the ratio of doses required for 10% relative survival.

Figure 1. Radiosensitization of U2OS osteosarcoma cells treated with the clinical HDAC inhibitor SAHA (vorinostat) 18 h prior to irradiation with cesium-137 γ-rays (top panel; 1-20 µM) and 200 MeV protons, 290 MeV/n carbon ions, or 350 MeV/n oxygen ions (bottom panel; 10 µM). Gamma ray survival data was fit with LQ-based weighted least-squares regression functions and the charged particle data with exponential functions. Table shows radiosensitization ratios for various drug/radiation combinations for NFF28 normal fibroblasts, U2OS cells, and U87-MG glioma cells (green: sensitization; red: sparing). Normal fibroblast sparing following carbon or oxygen ion irradiation was an entirely unexpected result given the ~1.25-fold radiosensitization observed following gamma irradiation, and companion transformation experiments show *significantly* increased anchorage-independent growth (data not shown). Ratios reported in black are not significantly different from unity (*i.e.*, no radiosensitization was observed), and suggest these compounds would not be effective as radiosensitizers for proton or carbon ion radiotherapy.

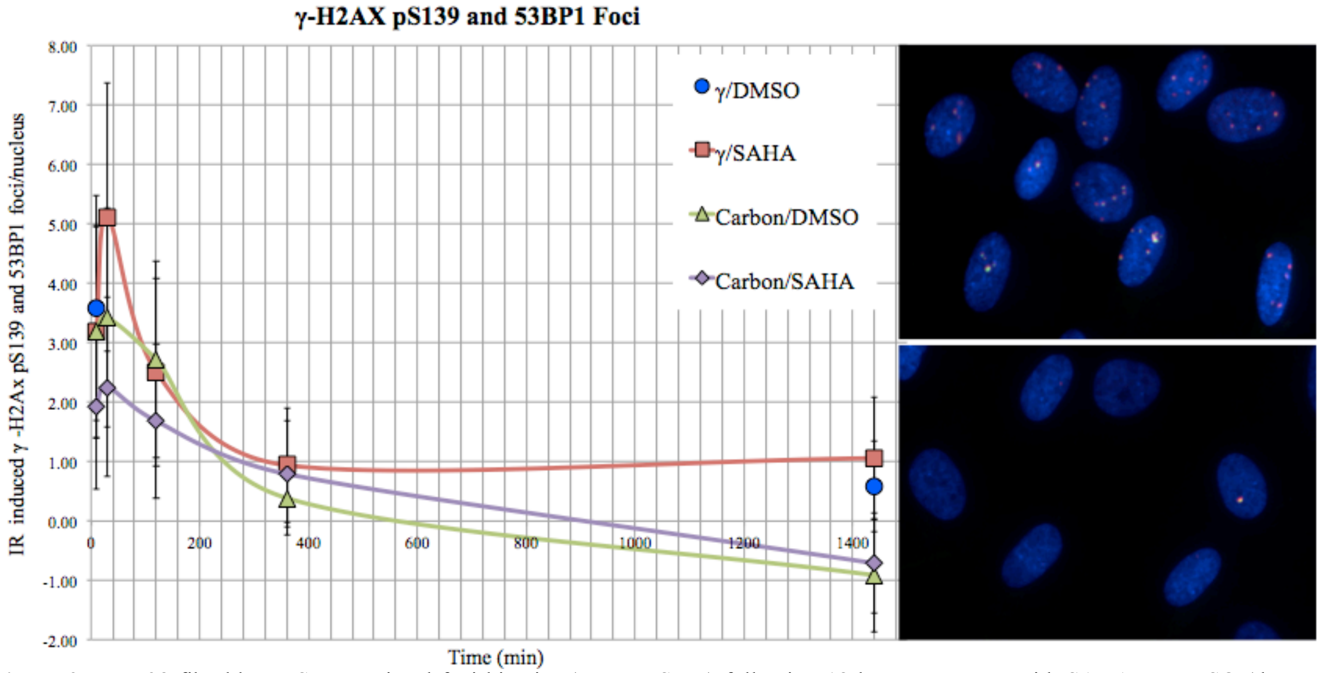


Figure 2. NFF28 fibroblast DSB-associated foci kinetics (mean ± SEM) following 18 h pre-treatment with SAHA or DMSO (drug vehicle control) and irradiation with cesium-137 gamma rays or 290 MeV/n carbon ions at NSRL. Analyses reveal that DSB-associated foci levels peak 30 min post-irradiation for all treatments. Curves for SAHA-treated NFF28 cells show lower foci induction and delayed repair kinetics more notably after carbon ion irradiation. Foci levels 24 h post-irradiation were reduced below background levels after carbon ion but not gamma ray irradiation. The low dose DNA damage signaling and repair kinetics directly correlate with higher dose cell survival assay results described in the previous figure. Right panels: immunofluorescent images of colocalized γ-H2AX/53BP1 foci in SAHA-treated carbon ion-irradiated NFF28 nuclei at 30 min (top) and 1440 min (bottom) post-irradiation (green: γ-H2AX pS139; red: 53BP1; yellow: merge; blue: DAPI).

We had additional successes this year due to the efforts of our two lab technicians A. Johnson and P. Bennett, associate scientist Dr. D. Keszenman, and SULI students K. Sanidad, L. Kolodiuk, and B. Daniels. Ms. Sanidad conducted the majority of the foci analyses, while Dr. Keszenman and Ms. Kolodiuk refined a novel 5-mC/5-hmC-specific gel electrophoresis detection system using a modified clustered DNA lesion detection assay. Ms. Bennett and Mr. Daniels optimized 5-mC/5-hmC slot blot detection using methylcytosine-specific antibodies. Several publications on our recent results and proposals to NASA and NIH to further explore these findings in an *in vivo* rodent model system (*e.g.*, U87 tumor xenograft model) are in preparation.

FY 2014 Experimental Plan

- Complete NFF28, A549, and U87 cells HDAC inhibitor gamma ray survival, foci, and chromosomal aberration induction experiments.
- Conduct final run of NSRL irradiations (NSRL-14A spring run) of NFF28, U2OS, U87 cells with 200 MeV protons, 290 MeV/n carbon ions, and 350 MeV/n oxygen ions with 5-10 µM SAHA, M344 and PTACH. Test efficacy of histone demethylase inhibitors as an alternative radiosensitization approach in limited experiments.
- Analyze cell samples for DSB and 5-hmC induction ± HDAC inhibitors with gel electrophoresis, immunocytochemistry and genomic analyses (5-hmC gel electrophoresis, 5-hmC-based loci-specific RT-PCR, ChIP-SEQ), with some mRNA samples to be analyzed offsite (Lawrence Livermore National Laboratory).
- Publish several papers in preparation. Seek funding from NASA and NIH to continue both *in vitro* and *in vivo* experiments to identify functional hadron radiotherapy radiosensitization approaches.

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

LDRD Project # 12-015
Wei Wu and Alistair Rogers

PURPOSE:

The goal is to develop an integrated model for investigating the interactions (feedbacks) between the atmosphere and land-surface ecosystems under a warming climate. As the Earth's surface temperature and atmospheric CO2 concentration increase, both the surface and atmospheric energy (i.e., radiation, latent heat and sensible heat) and water vapor fluxes will change, which will in turn influence climate patterns including cloud and radiation properties (e.g., cloud amount and optical depth), seasonal rainfall pattern, and ecosystem responsive behaviors such as photosynthesis and stomatal conductance. However, how the coupled atmosphere-land-surface-ecological system responds to the warming climate is still poorly understood. This project seeks to advance our understanding of the response of the coupled atmosphere-ecological system to the warming climate by developing an integrated coupled atmosphere-land-surface-ecological system. The success of this work will advance our capability for climate prediction and enhance our capabilities for climate-land-surface-ecosystem modeling. This will give BNL a significant edge in competing for funding in DOE modeling and ecosystem focused programs.

APPROACH:

Climate studies have indicated large uncertainties in current climate models, associated mainly with the representation of atmospheric cloud-radiation-precipitation processes. The interactions between atmosphere and land-surface ecological system (essential for the cloud-radiation-precipitation processes) are likely the culprit of regional climate variations over land. It is thus needed to advance our understanding of atmosphere-land-surface-ecosystem interactions.

The scope of the investigation includes: 1) the impacts of soil moisture and vegetation on convection and severe weather under the current climate and a warming climate; 2) the interactions between atmospheric cloud-radiation processes and ecosystem processes under a warming climate; 3) the impact of urban anthropogenic heating to regional climate variations over the Northeastern U.S.; 4) the important processes linking the coupled climate-ecological system, such as photosynthesis process and their optimal parameterizations. The methods employed to carry out the work are: 1) using and adjusting current existing coupled Weather Research and Forecast (WRF) and Community Land Model (CLM) for the investigations; 2) using observations and theories to improve the effectiveness of relevant model parameterizations. Existing collaborators: T. W. Collow, M. A. Miller and A. Robock (Rutgers University); potential collaborators: L. Ortiz Uriarte and J. Gonzalez (City College of New York (CCNY)).

TECHNICAL PROGRESS AND RESULTS:

We established a collaboration with Rutgers University to develop this project. A senior Ph.D. student has been working on the impacts of soil moisture and vegetation on convection and severe weather under the current climate and a warming climate using current existing coupled WRF and CLM model. He submitted a paper entitled "Influences of soil moisture and vegetation on convective precipitation forecasts over the United States Great Plains" to a prestigious scientific journal, which is in revision. One of the major findings is that vegetation changes had a greater impact on precipitation than soil moisture changes and removal of vegetation produced substantial drying (Table 1). He plans to submit another paper before his graduation in April, 2014. We are now making progress in establishing another collaboration with CCNY to further develop this project. A senior Ph.D. student from CCNY is expected to come to BNL during the summer of 2014 to study urban effects on regional climate over the U.S. Northeast region using the WRF and CLM coupled model. At BNL, we established our own model facility through this project by purchasing a workstation and computer servers and by downloading and installing the WRF and CLM coupled model. Testing of the new BNL model facility is nearly complete. The North American Regional Reanalysis data, which will be used as model initial and boundary conditions, have just been downloaded with the help of the NCAR Data Center. Once this step is complete, we will start several scientific model investigations as planned. We plan to co-organize a workshop with CCNY in the spring on Urban Landscapes and Regional Climate: From measurements to modeling. We have also conducted studies to examine decadal cloud variations and model parameterizations on photosynthesis linked to carbon absorptions. One paper has been published; another (revision) has been submitted. In addition, Dr. Rogers wrote a successful proposal to organize a *New Phytologist* sponsored workshop on Photosynthesis and Earth System Models (ESMs). This workshop will take place in the spring on Long Island and will bring together a group of physiologists and modelers who are engaged in studying and representing photosynthesis in ESMs. The goal is to write a road map for the discovery science and model improvements that are necessary to better represent photosynthesis in ESMs.

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

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

Papers published:

Rogers, A. (2014), The use and misuse of Vcmax in Earth System Models. *Photosynthesis research*. doi:10.1007/s11120-013-9818-1

Papers submitted:

Collow, T., A. Robock, W. Wu (2013), Influences of soil moisture and vegetation on convective precipitation forecasts over the United States Great Plains. *J. Geophys. Res.* (in revision)

Wu, W., Y. Liu, M. P. Jensen, T. Toto, M. J. Foster, C. N. Long (2013), A comparison of multiscale variations of cloud fraction from six different platforms over the Southern Great Plains in the United States, *J. Geophys. Res*. (revision submitted November 2013)

Meetings participated: Wu, W. (4 with 3 posters); Rogers, A. (4 with 2 talks and 2 posters)

Milestones for 2014-15: 1) publish the two revised papers; 2) generate 2-3 new papers; 3) prepare for applying for new funding(s).

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

LDRD Project # 12-018

Nathalie Bouet, Eric Dooryhee, Sanjit Ghose, Raymond Conley

PURPOSE:

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

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

APPROACH:

The Conical Slit is an optical element first developed at RisØ National Laboratory, Denmark. It comprises a set of conical openings positioned in accordance with the Debye-Scherrer rings of the phase to be investigated. Diffracted rays are transmitted through the slit if and only if they originate from a three dimensional gauge volume, defined by the beam size and slit opening size. To operate the slit with high energy X-ray photon beams (up to 70 keV), the challenges are the very low diffraction angles and the manufacturing of a very dense material which is effective enough to block hard X-rays. Prior to this work, wire electro-discharge machining of high Z metals (tungsten) was used to fabricate the slits. Such a process could not create features below 20 microns in size. The recent fast paced progress made in deposition and chemical etching techniques both at BNL and other facilities has come to the point where a useful conical slit can be fabricated with this method allowing slit openings of 1 micron or less to be fabricated. By pushing the fabrication technology to a state of the art aspect ratio (> 5:1) and stacking 2 slits, the absorption of diffracted X-rays originating from outside the gauge volume by the slit can easily reach 99% using tungsten.

A proof of principle experiment will soon be performed at the NSLS X17A beamline which should lead to an instrumental paper. In particular the slit system is required for collecting the diffraction signal from a sample inside a cell/device while minimizing/eliminating the spurious signal emanating from the cell/device itself. For that purpose, J. Sinsheimer has been collaborating with S.K. Gill et al. on in situ studies of interfaces under extreme environments. For high pressure/temperature in situ studies, the cell is being developed under the LDRD program for the NSLS-II X-ray Powder Diffraction (XPD) beamline. The cell has full external pressure and temperature control and can work from ambient to high temperature (up to 450 °C) and pressure (2000 psi) conditions. At the later stages of this project we shall explore the production of spiral slits so that they may take advantage of the substantial resolution increase of their conical predecessors.

TECHNICAL PROGRESS AND RESULTS:

The original LDRD proposal was awarded to begin in FY12. Control of the project was transferred to a new team in approximately July 2012. At that time, a requistion for a Postdoctoral Research Associate was drafted and posted. John Sinsheimer was selected in the fall of 2012 to fill this position. He started officially on this project on January 7, 2013.

Milestones achieved during FY13 are as follows:

- Identified and collaborated on X-ray powder diffraction experiments at the NSLS with research groups who will benefit from the conical slits: with Simerjeet Gill on an in situ corrosion study of zircaloy materials and with Lynne Ecker on investigation of structural changes induced by irradiation in steel alloys.” Both are in the Nuclear Science and Technology Department at BNL.
- Developed a new ray tracing program to evaluate requirements on slits designs, dimensions and placement respect to gauge volume of interest and energy of the X-rays.
- Completed the design of the slit system
- Started prototype fabrication using both NSLS-II optics laboratories and the Center for Functional Nanomaterials nanofabrication facility
- Defined the mechanical requirements on translation/tilt stages for slit alignment
- Started work on controls for integration of the slit system under fabrication into beamline set-up

Milestones for FY14 are as follows:

- Complete fabrication of the conical slit
- Integrate the slit system into NSLS X17A beamline set-up
- Test the capabilities of the conical slit at NSLS X17A
- Demonstrate the slit performance in several case studies, including in situ measurements using the high pressure/temperature cell.
- Fabricate version 2 of the slit (based on the above results) for implementation at the NSLS-II XPD beamline.

In situ TXM Studies of Structure and Function in Energy Storage

LDRD Project # 12-021

Jun Wang

PURPOSE:

Lithium-ion batteries are based on the principle of intercalation of lithium ions in host materials, both at the anode and at the cathode. All these materials, when subjected to the insertion and removal of lithium ions, undergo structural changes that range from minor changes in cell parameters to full-fledged phase transitions or even materials' pulverization. Understanding the dynamics of these deformation processes can provide valuable information for establishing viable high-energy and high-safety batteries. The purpose this project is to in situ monitor the electrode materials' behaviors (fundamental electrode reaction kinetics, microstructural evolution, and safety issues) within a working Li-ion battery by using the Transmission X-ray Microscopy (TXM) technique located at beamline X8C (National Synchrotron Light Source). The innovative research will substantially enhance our understanding of the fundamental mechanisms and stability of battery materials, and promote the development of advanced batteries techniques in transportation applications. This project also directly supports the key BNL mission of national energy research. Importantly, this research will develop new in situ techniques for energy studies, which will position BNL at a new frontier of energy research.

APPROACH:

The volume changes are pronounced in some high capacity anode materials in lithium-ion batteries, such as widely used silicon and tin-based anodes, leading to fracture and pulverization thereby reducing the battery capacity and cycle life. To address the mechanical degradation requires a fundamental understand of the mechanisms of microstructural change in the electrode as a function of cycling. This LDRD project will exploit the TXM technique along with in situ electrochemistry studies to observe and understand the interior microstructure evolution of these battery materials. This unique technique has an inherent advantage due to its good penetration length in the hard X-ray regime along with presently emerging techniques for chemical imaging and 3D tomography of battery materials during the battery's cycling. Combining it with the XANES technique, 2D chemical image and 3D tomography, information will be obtained to study the electrochemical reaction, electronic structure and material degradation mechanisms. Some conventional material study tools including scanning electron microscopy, transmission electron microscopy, and focused ion beam will be used to prepare, observe, and study the experimental sample to supply further information for TXM work. This multidisciplinary approach will lead to a key evolution-property-performance correlation for these battery materials in Li-ion battery systems.

TECHNICAL PROGRESS AND RESULTS:

Considering the experimental requirement of the TXM facility, design of functional batteries rather than common batteries to perform in situ 2D and 3D TXM studies is key for the success of this project. As to the 2D in situ TXM study, we successfully designed and developed coin cells with Kapton windows which allow X-rays to go through the working battery, and performed the in situ electrochemistry test (cyclic voltammogram) and tracked the morphology evolution via TXM image technique (in situ 2D study) in CuO materials. The result was published in *Chemical Communications* (a top chemistry journal) and highlighted in the inside cover page. To obtain the 3D microstructure information that completely represents the properties of a working battery, a key component is an electrochemical cell. This cell must i) allow a 180-degree rotation without blocking the x-ray beam; ii) be micron scale on the study material within the x-ray beam to meet the x-ray field of view (40×40 μm); iii) function normally as a working battery; and, iv) allow electrochemical measurement for correlating the microstructural changes with the electrochemical reaction stages. To develop such a working cell is very challenging. Recently, we overcame the challenges and presented for the first time a non-destructive in situ 3D x-ray nano-tomography method to i) monitor the 3D microstructural changes in the electrode at the nano-scale, ii) quantitatively analyze the true 3D microstructural information (volume change, feature size, specific area and curvature, etc) from the high quality 3D data and iii) evaluate the stress on the electrode particles induced by the lithiation and delithiation process and correlate the stress and 3D morphology changes (Fig. 1). This work has been submitted to *Angewandte Chemie International Edition*, a top chemistry journal.

Milestones (FY2014)

Q1: in situ 3D TXM study of lithium lithiation/delithiation mechanism within battery materials (conversion reaction and alloy/dealloy reaction)

Q2: in situ exploration and understanding the electrochemical reaction in novel battery systems such as Na-ion batteries at 2D and 3D

Q3: perform in situ TXM 3D chemical studies of battery materials

Q4: Correlate the morphology evolution to electrochemical performance/stability, and have new strategies to relieve the volume change, such as applying carbon coating or alloying methods.

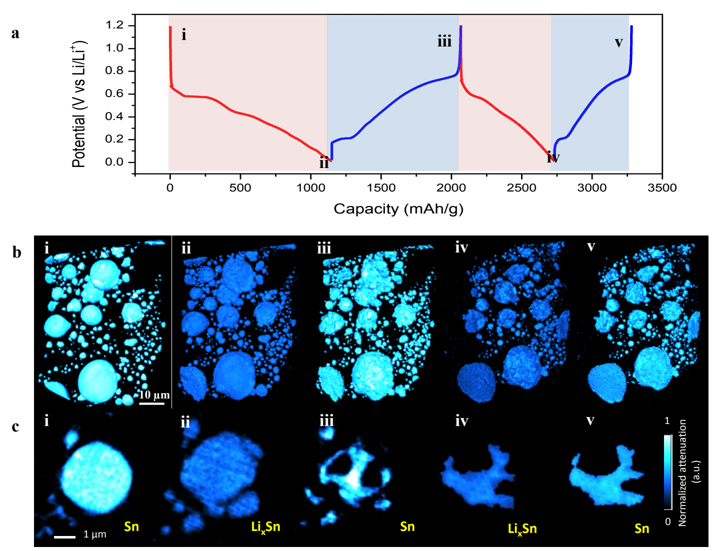


Figure 1. Three-dimensional morphology information. a, the discharge/charge profile of Sn anode at the first two electrochemical cycles

MeV-UED for Ultrafast Science

LDRD Project # 12-022
X.J. Wang, J.P. Hill & Yimei Zhu

PURPOSE:

We proposed the concept of MeV Ultrafast Electron diffraction (UED) based on a photocathode RF gun almost a decade ago [1]. The objective of the current LDRD is to develop a MeV UED at BNL, capable of producing the diffraction quality required to address the most important ultrafast scientific issues. We experimentally demonstrated high quality diffraction from a polycrystalline Al film with ~ 100 femto-second (fs) time resolution. The stringent test for any MeV-UED is the observation of a super-lattice from a strongly correlated material. The visibility of a super-lattice shows we have achieved signal to noise ratio better than 10^3. The success of this LDRD lays the solid foundation for a future ultrafast science program at BNL.

APPROACH:

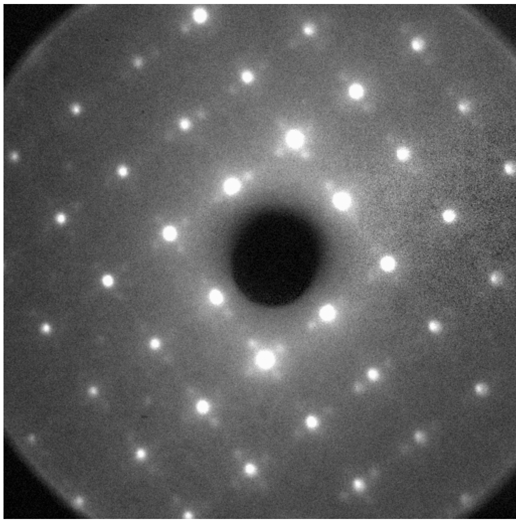
X-ray Free Electron Lasers and UED are the two most important tools for exploring the ultra-fast and ultra-small world. UED has the advantages of large interaction cross-section and compactness. A DC gun based UED system has been successfully used to investigate structure dynamics from dilute samples (gas & liquid) of strongly correlated materials. The relative low beam energy (~ 100 KeV) limits the time resolution of the DC UED to ~250 fs. To reach the 100 fs time-resolution, we pioneered the idea of MeV-UED using a photocathode RF gun [1]. The higher electric field on the cathode of a RF gun makes it feasible to extract more electrons within a shorter bunch; and the higher electron beam energy (MeV) will preserve the femto-second electron beam and eliminate the velocity mismatch between the pump and probe.

Taking advantage of the time-dependent electric field bunch compression inside the RF gun could also lead to an even shorter electron beam. One of the major challenges in realizing the MeV-UED potential is whether MeV-UED is capable of producing the diffraction quality required to address the most important ultrafast scientific issues. Another issue facing MeV-UED is the timing-jitter between the electron beam and pump laser. The mission of the BNL MeV-UED is to demonstrate high-quality electron diffraction with a sub-100 fs time resolution, and to develop a world-class ultrafast science program, particularly on the strongly correlated electron systems and transient structural dynamics. This LDRD is a collaborative effort between the BNL Photon Sciences and Basic Energy Sciences Directorates. Collaborators from Shanghai Jiao Tong University in China and Florida State University also made significant contributions.

TECHNICAL PROGRESS AND RESULTS:

After the BNL MeV UED setup was successfully commissioned, the first sample used for our MeV-UED experiment was a polycrystalline aluminum. High-quality diffraction from a gold single crystalline was also obtained. The stringent test for the MeV-UED we have built is the observation of a super-lattice from a strongly correlated material. To realize the super-lattice, a series of improvements for our MeV-UED set-up were implemented in FY 2012. First, improvement in the brightness of the electron beam was critical. The single-shot diffraction capability of the MeV-UED was explored in real time - using the diffraction quality to optimize the laser and RF parameters. Dark current reduction and improving the diffraction detector sensitivity also played important roles.

In FY 2013, we continued the MeV-UED study of the strongly correlated material-$La_{0.5}Sr_{1.5}MnO_4$ (LSMO). We simultaneously observed both orbit and charge orders (Figure 1) and its time evolution (Figure 2).



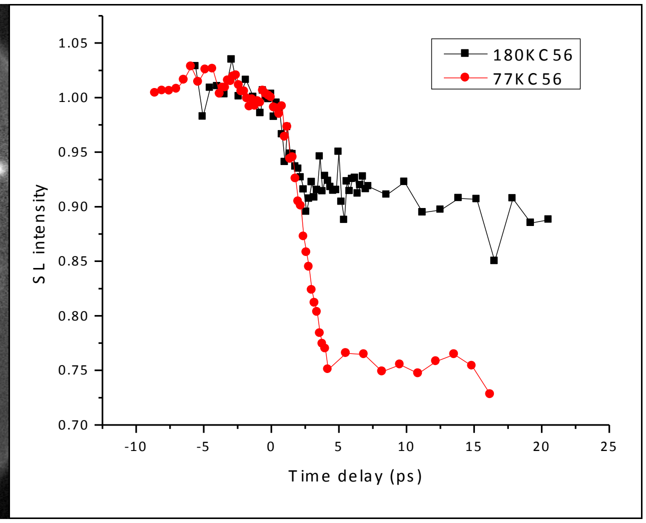


Figure 1: MeV diffraction pattern of LSMO at 77 k.

Figure 2: LSMO orbit order time evolutions at 77 k and 180k.

MAJOR MILESTONES:

- FY2012: demonstrate high quality electron diffraction.
- FY2013: 10 Hz operation; performing time-resolved experiments.
- FY2014: improve the time resolution below 100 fs, publish 2 to 4 high impact journal articles. Seek DOE funding for MeV UED operation.

REFERENCES:

[1] X.J. Wang et al., Proceeding of 2003 Particle Accelerator Conference, 420-422 (2003).

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

LDRD Project # 12-023

Li Hua Yu, T. Shaftan, F. Willeke

PURPOSE:

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

The new method has many advantages when compared to other schemes. It needs much smaller space in a storage ring for the interaction point, compared with a crab cavity, as used in the APS upgrade. The pulse length (150fs) is much shorter than the crab cavity method (1-2ps). The flux per pulse may be increased significantly compared with laser slicing (by a factor of 6-10). The repetition rate can be many orders of magnitude higher than laser slicing (about 100 kHz -1 MHz, compared with 1-10 kHz). Compared with the Linac Coherent Light Source, there is $10^2 \sim 10^3$ order of magnitude higher repetition rate, and the output is much more stable.

APPROACH:

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

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

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

Another important step towards high repetition rate is to study the performance of a low energy compressor for an electron beam generated by a high repetition rate RF-gun. We simulated such a system based on the APEX RF-gun designed by Lawrence Berkeley National Laboratory (LBNL). Since the maximum gradient for this RF-gun is 20MV/m, much smaller than the 100MV/m of the BNL RF-gun, it is a significant challenge to compress the electron bunch to 100fs and focus to a beam size of 30 micron. However, our recent simulation confirmed the feasibility.

In addition to the principle investigators, our study team also includes Guimei Wang and An He.

TECHNICAL PROGRESS AND RESULTS:
We have confirmed the feasibility of a low energy compressor at 5 MeV to achieve the desired 150 fs electron bunch of 150 pC, focused to a beam size at 30 micron in the first year of the LDRD funding.

This year we simulated the distribution of the electron beam slice in the NSLS-II ring, generated by the compressed low energy electron bunch and transported to the radiator. The distribution confirmed the feasibility of sufficient separation of the core from the slice. We also studied the achievable repetition rate and found it is possible to achieve 100 kHz. We showed that with a second low energy bunch to kick the slice back into the core bunch, it is possible to achieve 1 MHz repetition rate.

We were able hire a post-doc An He in June last year. She was able to carry out the optimization to achieve the sufficient separation of the slice from the core by increasing the linac energy to 12 MeV. She also derived the formula for an angled crossing of the electron slicing, and found the slice length can be reduced to 150 fs when the angle is 45 degree without significant reduction of the kick angle. Since September 2013, we started to study how to simulate the system using the code IMPACT with the help from Ji Qiang of LBNL, the designer of the code. This code allows the inclusion of the coherent synchrotron radiation (CSR) effect during the compression. An He was able to learn detailed information about the code, in particular the simulation of the dipole, and was able to simulate the LBNL high repetition rate RF-gun APEX. The challenge of the low gradient of this RF-gun is significant. But she was able to optimize the system to the desired parameters of 150 fs and beam size of 35 micron at 18 MeV. Thus we confirmed that it is possible to achieve the low energy compressor with 1 MHz, and the CSR effect is negligible.

In the next year we expect to study the possibility of achieving 1MHz of electron beam slicing by a second kicker in the storage ring. This will include the modification of the NSLS-II lattice to form a two kicker local bump separated by a 180 degree phase advance in both the x and y planes. The most challenging issue here will be the study of the dynamic aperture of this system, or, in other words, the optimization of the non-linear lattice. It will be an important milestone to be able to design such a lattice and recover the dynamic aperture to the design value.

Another milestone will be the simulation of the photon separation of the slice from the core. We will collaborate with Oleg Tchoubar on this issue.

The completion of these milestones will establish the feasibility of the electron beam slicing method to a highly realistic degree.

Thermochemical Conversion of Biomass to Fuels and Chemicals

LDRD Project # 12-024

Nii Ofei Mante and Suresh P. Babu

PURPOSE:

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

APPROACH:

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

TECHNICAL PROGRESS AND RESULTS:

The role of plant cell wall composition in biomass pyrolysis

A quantitative biomass structure-pyrolysis product correlation was established with 5 different NE biomass feedstocks (debarked sugar maple, willow, hybrid poplar, switchgrass and hot-water extracted sugar maple) obtained from Prof. Thomas Amidon (SUNY Environmental Science and Forestry) and Idaho National Laboratory. The principal pyrolysis oil oxygenates, such as acetic acid, hydroxyacetaldehyde, levoglucosan and others that affect its physiochemical properties were correlated with the basic components of biomass (i.e. glucan, xylan, arabinan, mannan, acetyl, lignin, and extractives). The XLSTAT statistical package was used to determine Pearson correlation coefficients. The results showed how the individual components of biomass affect the formation of pyrolysis oil components. Figure 1 correlates the biomass structure with primary pyrolysis products. The yield of acetic acid had a statistically significant correlation (0.94) with the acetyl

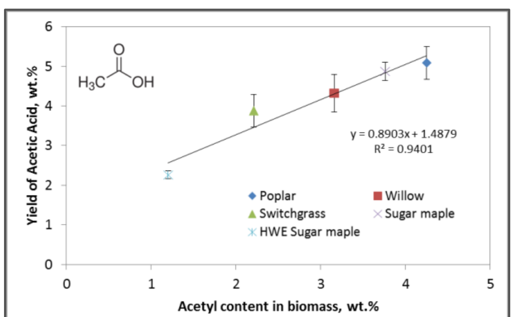


Figure 1. Relationship between acetic acid and acetyl content in biomass

contents in the selected biomass feedstocks. This finding offers useful guidance for the production of non-corrosive pyrolysis oils as well as for designing plant genomics in energy plantations of the future. Similar correlations were established for other pyrolysis oil components. The study also provides further evidence about possible interactions between the cell wall components of lignocellulosic biomass which is also useful for plant genomics.

Catalytic conditioning of biomass pyrolysis vapors

Investigations also included catalytic conditioning of primary pyrolysis vapors with metal oxides to improve the fuel properties of condensable oils. In this study, Ceria and Titania were used to selectively transform destabilizing components in the primary products such as hydroxycarbonyls, acids, sugars and multi-functional phenolics into monofunctional intermediates from biomass. Figure 2 shows that destabilizing components were transformed into C3-C6 linear ketones (acetone, butanone, pentanone, and hexanone) and cyclic ketones (cyclopentenone) as well as phenols. These ketones are desirable because they have sufficient functional moieties to undergo C-C bond forming reactions for producing aliphatic hydrocarbons. The phenols are also useful intermediates for forming aromatic hydrocarbons. With regard to catalyst performance, CeO_2 was found to be more active and selective than TiO_2. The results showed that Ni loading on TiO_2 decreased the activity and Pt loading on TiO_2 enhanced deoxygenation reactions. In a nut-shell, the intermediates produced from this process can further be subjected to aldol condensation and hydrogenation to produce a mixture of hydrocarbons that fall within gasoline, diesel and jet fuel ranges.

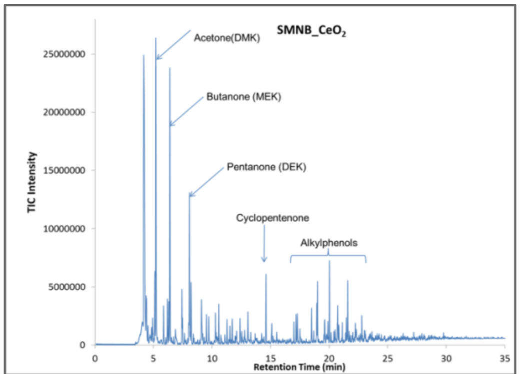


Figure 2. Monofunctional intermediates produced from biomass pyrolysis with CeO_2

Production of value-added chemicals from isolated lignin

A catalytic process was developed to selectively convert isolated lignin into chemicals that are of commercial value. Simple phenols and aromatic chemicals of commercial value were produced by selective removal of methoxy, hydroxyl, carbonyl and carboxylic groups attached to the benzene ring in monomeric phenolics by employing nanoparticles of TiO_2 at 550 ^oC at a catalyst to feed (C/F) ratio of 5 w/w%. Over 80% of selectivity was achieved to produce phenol, cresol, xylenol and alkylphenols (Figure 3). The study showed that temperature and C/F ratio are the principal process variables. For the selective production of aromatic hydrocarbons, such as benzene and toluene, a Pt/TiO_2 catalyst was used. Model studies were conducted with catechol, 2-methoxy-4-vinylphenol and coniferyl alcohol to demonstrate the selective removal of the various oxygenated substituents. The chemicals produced from the isolated lignin are useful for synthesis of phenolic resins, epoxy resins, polycarbonate, nylon, detergents, polyurethanes and surfactants.

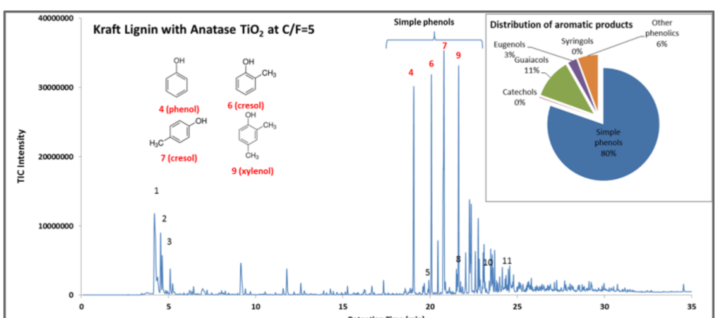


Figure 3. Simple phenols from catalytic pyrolysis of lignin with TiO_2 at 550 ^oC

Multifunctional reactor system for biomass pyrolysis and gasification
A laboratory scale multifunctional reactor system for scale-up investigation of catalytic pyrolysis and for conducting biomass gasification gas clean-up research was designed and the first set of equipment was procured. Upon receiving the remaining components of the reactor system, the bench-scale Pyroprobe-GC/MS investigations could be scaled-up for conducting continuous (up to 4 h) pyrolysis and gasification tests.

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

Flow-Based Battery Architectures for Large Scale Electrical Energy Storage

LDRD Project # 12-025
Can Erdonmez

PURPOSE:
Flow-assisted battery architectures combine features of fuel cells and battery technology. The applications that this approach targets, particularly in grid-scale energy storage, however, have extremely demanding cost and reliability requirements. Broad goals of this project are: 1) develop, at BNL, with external collaborators, platforms for advanced materials characterization to reveal processes that currently limit performance and reliability in battery chemistries targeting flow-based energy storage, 2) apply these tools to emerging/re-emerging flow-assisted technologies to guide further efforts in basic and applied research at the electrochemistry/materials science interface. The techniques developed gained will also allow us to compete for follow-on funding from multiple sources.

APPROACH:
Emerging applications in large-scale electrochemical energy storage require near-order-of-magnitude improvements in cost and lifetime over state-of-the-art, while allowing relaxation of other performance metrics (e.g. energy or power density). Flow battery technologies, utilizing liquid or dissolved species are active research areas, but the sacrifices in energy and power density are large enough to raise concerns about final systems cost. Further, the most mature systems employ materials that raise questions of resource availability and toxicity. Given this context, some combination of solid-state active materials and flow-assisted architecture may provide an improved balance of performance and reliability.

This investigation focuses on morphological, structural and chemical evolution of solid-state active materials in flow-assisted electrochemical systems. The bulk of technique development focuses on flow-assisted alkaline batteries where system architecture focuses on converting a non-rechargeable technology into a rechargeable one. A second, smaller effort is on the study of emerging electrochemical fuels.

The alkaline system is chosen for its potential for deployment, and for allowing studies targeting reliability and performance by multiple advanced materials and electrochemical characterization techniques. Participants in this project provide expertise on synchrotron characterization (Jun Wang, *National Synchrotron Light Source (NSLS), BNL*), electron microscopy (Yimei Zhu, *Condensed Matter Physics and Materials Science, BNL*), engineering and electrochemistry in flow-assisted energy storage technologies (*Dan Steingart, Princeton University & Sanjoy Banerjee, City College of New York (CCNY)*).

Technical expertise and collaborations developed under this LDRD in the flow-assisted alkaline battery field have allowed us to participate in a Princeton-led team which successfully obtained funding from ARPA-e for a seedling effort on high capacity, aqueous (non-flow) energy storage, a related but distinct area of technological research.

TECHNICAL PROGRESS AND RESULTS:
The project start was in June 2012. Therefore, this report refers to progress during months 5 - 16 of the project which fell in FY13.

Major FY13 milestones, mainly in use of electrodeposition systems developed in the previous fiscal year, for structural investigations in alkaline battery chemistry have been completed. Expanded testing at multiple NSLS beamlines (X8C: transmission X-ray microscopy, X13B: microdiffraction, X14A: time-resolved diffraction, X17B: energy dispersive diffraction, X17A: pair distribution function analysis) have yielded a number of results and capabilities, including:

1) Zinc anode deposition and dendritic growth under different conditions has been imaged, both laterally and in-plane view. These experiments constituted the first in situ electrochemical experiments performed at beamline X8C, a relatively young NSLS beamline.

2) Suppression of dendritic growth by trace additives in a flowing electrolyte, already established at CCNY, was studied using X-ray microscopy and microdiffraction. Role and distribution of trace bismuth additives in solution was revealed, leading to a joint publication. Dendrite suppression is critical for many zinc-based electrochemical energy storage systems.

3) *In operando* baseline experiments at X17B on sealed (non-flowing), commercially available alkaline batteries revealed that at high depth of discharge, cathode materials (MnO_2) undergoe irreversible changes. With shallower cycling, much longer cycle life was achieved and cycling-induced precipitation of ZnO in the anode instead was found to eventually deactivate the batteries. These results have been published and suggest delayed ZnO precipitation and shallow cycling in the extremely cheap alkaline chemistry as a path to cheaper large-scale energy storage. This result also has wider relevance to zinc-based electrochemical technologies.

4) *In situ* studies of the cathode materials (MnO_2) confirmed the structural hypothesis behind enhanced cathode lifetime in specific alkaline electrolyte compositions. These results are being prepared for publication. Follow-on electrolyte exchange and pair-distribution analysis experiments are under development.

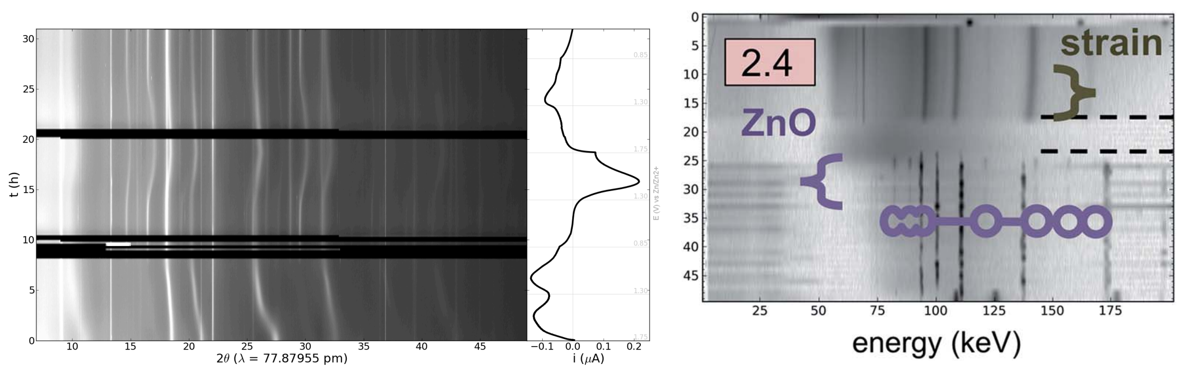


Figure –time-resolved *in situ* diffraction studies on enhanced stability of MnO_2 cathodes through changing alkaline electrolyte composition, right: published energy dispersive X-ray diffraction studies showing the role of local ZnO precipitation in cycling induced degradation in zinc anode.

Milestones for each year of anticipated funding:

FY14 – Synthetic development & characterization of doped or nanostructured active and supporting materials; extend flow capabilities to fundamental studies on cathode materials and alternative or modified material systems

FY15 – Synthesis and electrochemical efforts to focus on novel systems

Demonstration of a Grid-Wide Measurement and Control Platform for Microgrids

LDRD Project # 12-029

M. Villaran, M. Yue, R. Lofaro

PURPOSE:

This project proposes the development and demonstration of an electrical grid measurement and control platform that can be used to monitor and manage electrical distribution systems to improve their reliability and efficiency. The platform will also strive to be capable of establishing and controlling islandable microgrids from selected portions of a distribution system. The proposed platform will be based on the use of an innovative new smart grid sensor designed specifically for electrical distribution systems that can provide high-speed synchronized measurements of phasor data, power/energy, power quality, harmonics, and waveforms from various points in an electrical distribution system and also provide control capabilities [1].

The proposed platform will be developed and demonstrated using selected portions of the BNL campus electrical distribution network. As part of the demonstration, a microgrid capability will be developed at the Northeast Solar Energy Research Center (NSERC) that will include up to 1 MW of renewable generation from its new research solar photovoltaic array. The microgrid would be representative of utility distribution systems that include a high penetration of renewable energy generation sources that are becoming more common in large residential developments, industrial complexes, or autonomous Department of Energy or Department of Defense facilities with high energy demand. The experience gained from the performance of this project will help to establish BNL's capabilities in the development of future smart distribution grid measurement and control systems and renewable energy integration technologies.

APPROACH:

The proposed smart grid measurement and control platform technology will employ the innovative new Smart Grid Sensor (SGS) developed by SEI of Toronto, a collaborator on this project. This demonstration will be the first of three planned phases of increasingly scaled-up applications of the smart grid measurement and control platform that we will be developing. Besides SEI and their smart grid sensor fabricator, Hitachi High Tech of Japan, other collaborators include Electrical Distribution Design and Orange and Rockland Utilities (ORU).

In this initial project, four representative distribution circuits were selected for deployment of the SGSs: the new NSERC facility, the BNL residential area, one of the new NSLS-II feeders, and a fourth feeder to either the chilled water facility or the computer data center. Four of the SGSs will be deployed at the source end (Temple Place Substation) of the circuits and one each at the first major substation down on each of the circuits. The sensors will be integrated with communications network infrastructure along with data collection and visualization software, and tested on the BNL campus to demonstrate and validate their performance.

TECHNICAL PROGRESS AND RESULTS:

A program plan was developed [2] and BNL is designing the connection details for deploying the SGS circuit monitoring instruments on four demonstration distribution feeders. Design for the residential area feeder was completed and the instrumentation and power panels installed at Substation 616 (see Figure 1). Designs for the installation at Temple Place (4 SGSs) and the

NSERC feeder (1 SGS) are under way. Preliminary design work has started for one NSLS-II feeder and the supply circuit to the computer data center.

Figure 1 Experimental Smart Grid Sensor monitoring point installation at BNL Substation 616

Eight test-only smart grid sensors were received from SEI, Inc. and BNL is working on developing pre-installation tests for these devices. ORU has also agreed to test at least one of these test-only units to evaluate whether the SGS can be deployed effectively on their smart distribution grid circuits. The SGS devices themselves are low voltage devices so there are minimal safety concerns with them, however, the instrument transformer interfaces with the BNL system involve high voltage connections. Therefore, the design, wiring, safety features, and hardware of the experimental smart grid monitoring point installation will be reviewed and inspected by BNL electrical safety inspectors before they can go online.

Simulation modeling, using DEW/ISM software, of the demo feeders is underway; work is being coordinated with interfacing project efforts for SGRID[3] and AEGIS Center initiatives at BNL.

There was some delay in the manufacture of the first functional field-ready SGS instruments from SEI, but design and installation of monitoring point connections and hardware continued in parallel at BNL. Due to these delays, the LDRD could not be completed as originally planned before it expired in FY 2013. A request was made to extend it for a third year in FY 2014; however, this request was not approved.

Because we feel that this advanced and innovative technology will play an important role in enabling the smart distribution grid of the future, we are working to put a CRADA agreement in place with SEI so that the demonstration project may continue. SEI is considering providing funds to continue work on this project under a CRADA agreement.

REFERENCES:

1. Smart Energy Instruments, SEI Smart Grid Sensor Technology Brief, 2011
2. Program Plan: Development and Demonstration of a Smart Distribution Grid Measurement and Control Platform, Rev 0. Brookhaven National Laboratory, April 26, 2012.

Laser-driven Proton Accelerator

LDRD Project # 12-032

Igor Pogorelsky

PURPOSE:

The main goal of the project is to optimize ion beams generated by the interaction of a high power laser pulse focussed in a gas jet. The maximum proton energy is expected to increase from 2 MeV to ~10 MeV with proportional increase in the CO_2 laser driver intensity. These developments will serve as steps to the next-generation of ultra-fast mid-IR lasers; provide insights into the fundamentals of laser/plasma interactions; and verify energy scaling laws for laser driven proton acceleration. The research will also provide necessary arguments to obtain funding for the BNL/Stony Brook (SBU) initiative aimed at developing a compact and economical alternative source for hadron cancer therapy.

APPROACH:

By a string of innovations, we plan to increase the CO_2 laser intensity by one order of magnitude. This includes: femtosecond optical parametric generator based on a Ti-Sapphire laser and the Chirped Pulse Amplification (CPA) technique that has never been attempted with molecular gas lasers. Concurrent to the laser improvements, we are engaged in the optimization of the proton beam generation process. We introduce a novel method of enhancing the acceleration process by using two laser pulses with a variable time delay. The first low-energy pulse is used for hydrodynamic steepening of the plasma profile before the main laser pulse arrives. The team of investigators assembled to conduct this project includes: M. Polyanskiy, M. Babzien, O. Tresca from the Accelerator Test Facility, C. Maharjan and N. Cook (both from SBU), and N. Dover and Z. Najmudin (both from Imperial College London).

TECHNICAL PROGRESS AND RESULTS:

Significant progress was achieved in the process through simulations and experiments:

- Temporal evolution of the plasma density under irradiation by a low energy laser pulse, corresponding to the first pulse of our dual pulse scheme, has been studied using 2D hydrodynamic simulations. The results have then been used as input for 1D particle-in-cell (PIC) simulations to identify the optimal plasma conditions for ion acceleration. The best results have been obtained between 2 and 5 ns after irradiation of the gas jet by a 100 mJ laser pulse. The simulation findings have been reproduced experimentally using hydrogen and helium gas, shown in Fig. 1.
- The second or main pulse parameters for proton acceleration from the H_2 jet have also been identified experimentally. As shown in Fig. 2, only a narrow range of laser energy, for both pulses, results in the production of ions, between 100 and 200 mJ for the first pulse and around 11 J for the second pulse. PIC simulations are currently being performed to confirm these findings.
- Successful generation of proton and He+ ions have been achieved. Protons have been accelerated up to 3 MeV with a broadband spectrum (Fig. 3a) and up to 1.6 MeV with a narrow energy spectrum (Fig 3b). Acceleration of He+ ion has also been achieved for the first time, up to 2 MeV (Fig 3c).

UPCOMING WORK:

- Note that the delay used in our previous experiments was fixed at 25 ns, which is not optimum according to our more recent simulations. A variable delay stage, 1 to 5 ns, is being installed now to control the time interval between the two laser pulses. This should allow us to better shape the plasma profile. This set-up will be used during our next experimental run to further investigate the laser conditions needed for monoenergetic ion acceleration.
- Recent progress on the laser amplification chain will enable us to irradiate the gas jet with a shorter laser pulse (3 ps instead of 6 ps), increasing the laser intensity by a factor two. This will also be tested during our next experimental run.
- The knife edge technique has been tested to shape the gas density profile. The obtained density steepening looks promising for improving the ion generation. This approach will be tested later on.

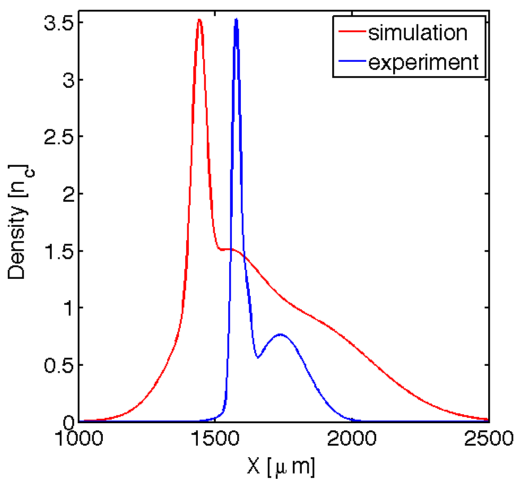


Fig 1: Plasma density profiles from hydro simulations (red) and measured experimentally by optical interferometry (blue).

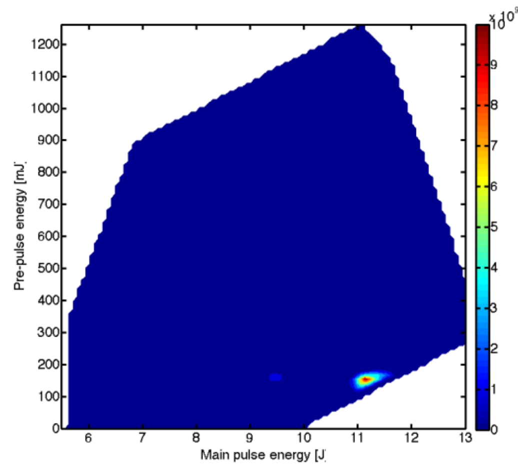


Fig 2: Mapping the laser parameter range. Number of ions detected (color-scale) as a function of second (main) pulse and first (pre-pulse) laser energy.

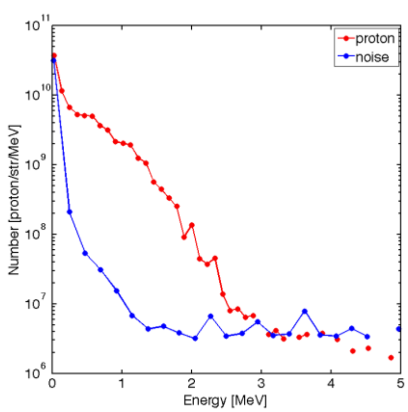


Fig. 3a: Proton spectrum showing the maximum recorded energy, 3 MeV.

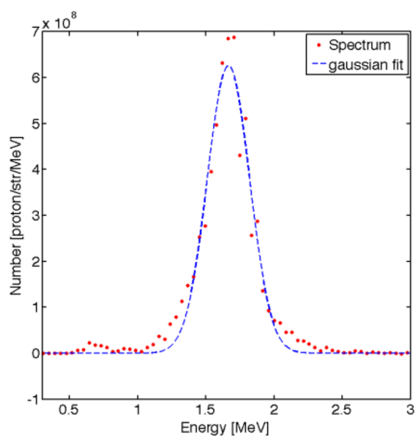


Fig. 3b: Mono-energetic proton spectrum with a peak energy of 1.6 MeV

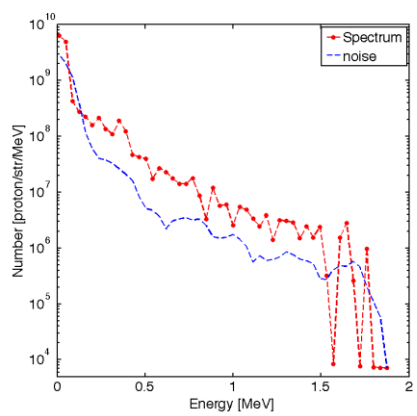


Fig. 3c: He+ ion spectrum with a maximum energy of approximately 2 MeV

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

LDRD Project # 12-033

David E. Jaffe

PURPOSE:

We are evaluating water-based liquid scintillator (WbLS) as a detection medium using prototype detectors and simulation. New techniques developed by the BNL electronic detector and neutrino and nuclear chemistry groups for making WbLS allow the fraction of scintillating liquid in water to be varied. The primary goal is to measure the light yield for different WbLS formulations with various types of particles with a range of incident energy. The results will allow an assessment of WbLS for potential particle physics experiments, such as the search for proton decay ($p \rightarrow K^{+}\nu$) in a large volume detector, improved knowledge of neutrino-nuclear interactions, low energy neutrino detection using inverse beta decay, and dosimetry monitoring.

APPROACH:

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

We fabricated small (~1 liter) prototype detectors and a data acquisition system to understand the light yield of different WbLS formulations to a low energy proton beam at the NASA Space Radiation Laboratory (NSRL) at BNL. The production of optical scintillation light depends on particle type and ionization density. Particles that travel faster than the speed of light in the medium also produce optical light by the Cerenkov process. The relative rates of light production of these processes in WbLS can be assessed by varying the proton beam energy.

We also developed a simulation to assess the feasibility of a large volume WbLS-based detector for a search for proton decay. The results of the NSRL data and simulation show that a ~1% scintillator concentration in water would yield nearly an order of magnitude improvement in proton decay sensitivity compared to an identical large volume water-based detector such as the Super-Kamiokande (SK) detector. SK has a diverse program based on the ability to reconstruct particle trajectories based on the distinctive Cerenkov light pattern. We designed a modest scale (~1000 liter) prototype detector to assess the capability of a WbLS-based detector to image the distinctive Cerenkov light pattern in the presence of isotropic scintillation light.

Collaborators on this work are D. Beznosko, a postdoc hired with LDRD funds, M. Diwan, H. Themann, E. Worcester, B. Viren, and C. Zhang of the BNL Physics Department and S. Hans, R. Rosero, and M. Yeh of the BNL Chemistry Department. D. Beznosko left in July 2013 to become an Assistant Professor at Nazarbayev University in Kazakhstan. We have hired a new postdoc, L. Bignell, who is scheduled to begin mid-January 2014.

TECHNICAL PROGRESS AND RESULTS:

Results obtained in FY2012 show that the light yield scales linearly with scintillator concentration in WbLS for 1% and 4% concentrations. In FY2013, a prototype detector was fabricated and deployed at NSRL during April 2013 for approximately four hours of proton beam time. The new detector was designed to enable measurement of the relative light yield from Cerenkov and scintillation light with minimal effects due to reflected light. Results confirm the earlier measurements and indicate that roughly 50% of the Cerenkov light is absorbed and re-emitted as scintillation light in 1% WbLS. Detailed analysis and subsequent publication of results has been delayed due to the departure of D. Beznosko and inability to promptly hire a new postdoc.

The positive results encouraged us to undertake a detailed design for a modest scale (~1000 liter) detector to determine the ability to distinguish Cerenkov and scintillation light produced by cosmic rays. The detector will be a cylinder 1.1m high and 1.1m in diameter of 1" thick ultraviolet transmitting acrylic. We have also designed and purchased materials for a dark room with secondary liquid containment to house the detector in the Physics Department. The design is flexible in that we can position multiple (6 or more) photomultiplier tubes on the outer acrylic surface to detect the produced light. The new postdoc (L. Bignell) will commission and operate the new detector as well as undertake measurements to characterize WbLS absorption length using existing equipment in the Chemistry Department.

Emboldened by the results already obtained with this LDRD, we are pursuing three new opportunities for WbLS.

We (D. Jaffe, B. Viren and M. Yeh) have entered into a Small Business Innovation Research (SBIR) proposal entitled *An Active Water-Based Liquid Scintillator Phantom for Proton Therapy Quality Assurance* with Principal Investigator Steven Vigdor, Senior Vice President of Phenix Medical and former BNL Associate Laboratory Director. The SBIR proposal was submitted in October 2013 and, assuming approval in January 2014, we expect to participate in the production, modeling and early testing of water-based liquid scintillator samples. We expect L. Bignell to contribute to the early development. The SBIR provides partial support to hire a post-doctoral assistant by Summer 2014 to aid in data analysis and simulation software development for the WbLS Quality Assurance system. We anticipate Intellectual Property (IP) being divided between Phenix Medical and BNL: BNL will retain IP for the WbLS development.

We (S.Hans, D.Jaffe, R.Rosero, M.Yeh and C.Zhang) have also begun discussions with members of the T2K long-baseline neutrino experiment concerning an upgrade of the T2K near detector (ND). At present neutrino oscillation measurements compare interactions in the ND (mainly neutrino-carbon) with those in the water-based Super-Kamiokande far detector (mainly neutrino-oxygen). Replacing the inactive water targets of the ND with active WbLS detectors would potentially allow the experiment to reduce a major systematic uncertainty due to the difference between interactions of neutrinos with carbon and oxygen nuclei.

We (S.Hans, D.Jaffe, R.Rosero, M.Yeh) have also been invited to participate in the possible phase-II operation of the WATCHMAN collaboration, an advanced 0.1%Gd-loaded water-based detector (phase-I) to measure neutrinos from low power reactors over large distances. With the addition of WbLS, the sensitivity of low energy neutron detection and reach of proton-decay lifetime will be significantly improved. A DOE briefing for the WATCHMAN experiment was given in Oct. 2013.

Quantum Electrodynamics for QCD Precision Studies at an EIC

LDRD Project # 12-034
Marco Stratmann, Elke Aschenauer, Hubert Spiesberger

PURPOSE:
The main purpose of the LDRD project is to develop and provide a comprehensive and reliable set of computational tools to control additional photon radiation to a level of precision necessary to meet the objectives of the physics program laid out for a future electron-ion collider (EIC), such as eRHIC at BNL. Quantum Electrodynamics (QED) radiative corrections are known to often reach a level of 100%, affect all measurements with electromagnetic probes, and greatly complicate the experimental reconstruction of relevant kinematic variables and the extraction of vital new information on the structure of hadrons. The anticipated results of this LDRD project will help to understand in detail the limitations due to QED radiative effects on key measurements at an EIC and will have impact on certain detector performance requirements.

APPROACH:
The key element of devising strategies to systematically unfold QED radiative corrections from the physics observables of interest is the availability of flexible Monte-Carlo simulations of additional photon radiation in electromagnetic processes that can be easily merged with programs simulating the detector acceptance and response. Programs and results existing in the literature can serve only as a starting point as they lack a number of potentially important effects and contributions for the EIC physics program. The main part of this LDRD project is devoted to filling in these gaps by developing comprehensive software implementations of QED radiative corrections tailored to the needs of a future EIC physics program.

Among the most important issues, which require detailed studies, we have identified QED radiative corrections for lepton-nucleon scattering with polarized beams and the role of two-photon processes in measurements of deeply-virtual Compton scattering (DVCS). DVCS is one of the key processes at an EIC to obtain a three-dimensional image of the nucleon structure. To provide missing analytical calculations and to turn them into Monte Carlo event generators are the milestones for our LDRD project. Based on the numerical codes, we will study whether kinematic variables can be reconstructed in such a way that QED radiative corrections can be unfolded with the required precision to achieve the goals of a future EIC in spin physics and the three-dimensional imaging of the nucleon.

The project benefits greatly from having H. Spiesberger from Mainz, Germany, as one of its investigators. He is one of the few leading experts on simulations of QED radiative corrections and has developed several of the existing codes used in the past at DESY-HERA. In FY13, also one of his former students (Till Martini) collaborated with us. The EIC task force at BNL led by E. Aschenauer provides the necessary matching expertise with detector simulations. In particular, the ability to detect the hadronic final-state is critical to reduce QED radiative effects at an EIC.

TECHNICAL PROGRESS AND RESULTS:
The project is in its second half of funding. A postdoctoral researcher (Martin Hentschinski) was hired in June 2012 to work mainly on two-photon processes relevant for future precision measurements of DVCS.

In FY12, we have completed the development of a new event generator for polarized lepton-nucleon scattering by extending the capabilities of existing software for corresponding unpolarized processes. Based on these results we have studied the impact of future EIC measurements on our knowledge of the spin structure of the nucleon (published paper in Physical Review D). We have also started to compute two-photon processes in the context of DVCS and worked towards implementing them in an event generator package.

In FY13, we fully exploited the event generator for polarized lepton-nucleon scattering developed in FY12 in several detailed numerical studies of QED radiative corrections to determine how well the unfolding procedure works for various processes relevant at an EIC. A particular emphasis in FY13 was put on high momentum transfer, charged-current electroweak processes, which require a full reconstruction of the hadronic final-state to determine the relevant kinematic variables. The completion of these studies was a milestone of our LDRD project. Detailed results were published in Physical Review D recently.

We also continued our work towards analytical expressions for two-photon processes and their implementation into a novel event generator. The numerical implementation for QED corrections to the Bethe-Heitler process, the major background to DVCS, is in its final validation stage and can be readily linked with detector simulation tools. First quantitative studies were performed.

In FY14 (funding for the postdoctoral researcher is only available until the end of May), we plan to complete our studies of two-photon processes and start to perform some quantitative studies of their impact on measurements of DVCS. This is the final milestone of our LDRD project.

Investigating eRHIC Beam-Beam Effects with CeC Linear Accelerator

LDRD Project # 13-003

Vladimir N. Litvinenko

PURPOSE:

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

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

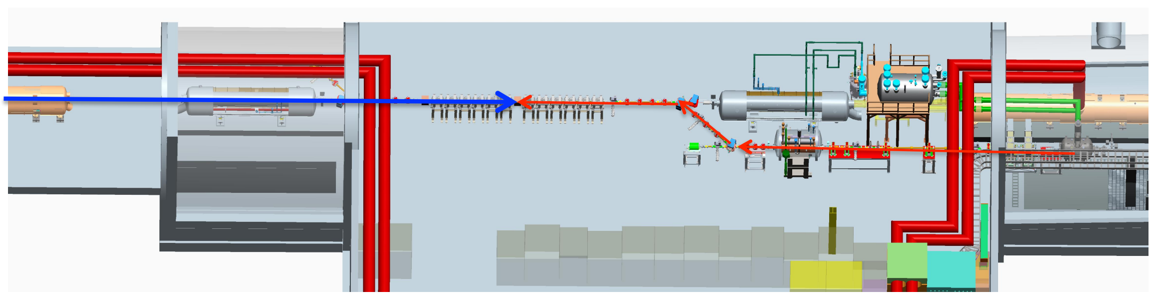


Figure 1. Layout of the experiment: 22 MeV electron beam from the SRF linac (red arrow) will collide with the circulating ion beam in the blue RHIC ring (blue arrow)

APPROACH:

We will use the coherent electron cooling (CeC) proof-of-principle (POP) accelerator to supply the electron beam. Our CeC-POP experiment was initiated by an LDRD proposal and it is now funded by the DOE Office of Nuclear Physics competitive accelerator R&D program and BNL's Program Development funds.

A low energy electron beam (~22 MeV) would propagate along the yellow beam at the intersection point 2 (IP2) of the RHIC complex. For our studies of electron-ion collisions, the electron beam will collide with the blue beam at IP2. The beam-beam effects on both beams will be controlled by varying the beams' intensities, their optics at the collision point, and the ion-beam's species and energy.

By using the CeC accelerator and RHIC beams, and with modest additional experimental equipment, we could study most of the unique features of beam-beam effects in the energy recovery linac-based EIC. The effects we would study with this set-up are the following:

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

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

TECHNICAL PROGRESS AND RESULTS:
The construction of the CeC superconducting RF (SRF) linac, supported by funds outside of this LDRD, progresses according to the plan with earliest operation at 22 MeV during RHIC Run 15 (e.g. winter – spring of 2015). As soon as the electron beam would become available, we will use it for conducting beam-beam experiments.

Currently we are developing and procuring the electronics and the diagnostics necessary for detecting and analyzing beam-beam effects in this configuration. We purchased a significant part of the beam position monitor (BPM) diagnostics (BPM buttons, the rest will be procured in FY14), which will be used for detecting the kink instability. We also developed and procured beam-profile (beam viewers) measuring diagnostics to characterize the beam disruption and pinch effects.

Figure 2. Progress with installation of 2 MeV electron gun and the transport line of the linac.

We continue theoretical studies of the beam-beam effects and published one refereed and three conference papers related to the linac-ring effect. One of the collaborators on this project (Dr. Y. Hao) submitted a proposal for a Young Investigator DOE award for advanced studies of the beam-beam effects.

REFERENCES:
A.1 *Mitigation of the kink instability in the energy recovery linac based electron-ion collider*, Yue Hao, Vladimir N. Litvinenko, and Vadim Ptitsyn, Phys. Rev. ST Accel. Beams 16, 101001, 22 October 2013, http://prst-ab.aps.org/onecol/PRSTAB/v16/i10/e101001

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

LDRD Project # 13-005
Dejan Trbojevic

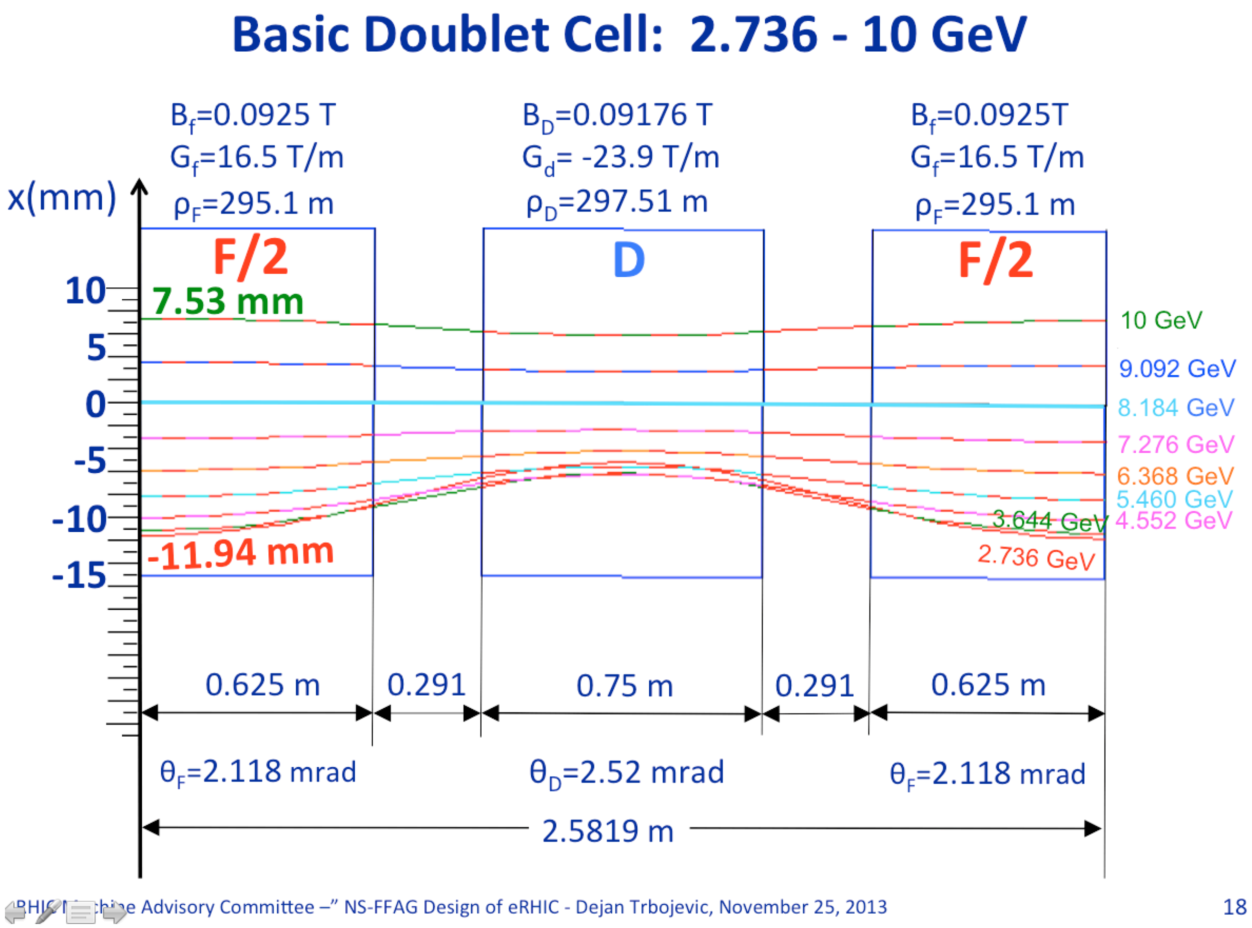
PURPOSE:
The Laboratory has previously defined a new electron-ion collider "eRHIC" as its highest priority project. To get the project approved, it is necessary to show clear scientific benefits and not to exceed $500 million for the overall cost. The Laboratory Directed Research and Development (LDRD)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

APPROACH:
The Principal Investigator of the project came to the principle of NS-FFAG independently and presented it on September 30, 1999 during a muon collider workshop. The main property of the concept is very large momentum acceptance of three, four, or five times the energy of the beam. This allows a reduction of the previous six rings with fixed energy with two NS-FFAG rings accepting multiple energies. By allowing more passes through the linac, the energy can be reduced. To achieve electron energy of 20 GeV with six rings of fixed energies, the total energy of two linacs needs to be ~3.3 GeV. With 11 passes through the linac, the energy can be reduced to half.

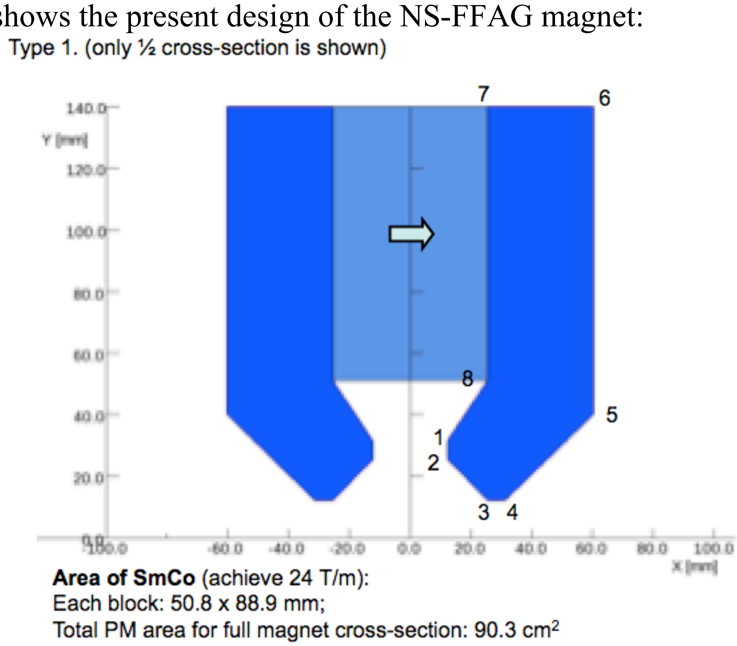
TECHNICAL PROGRESS AND RESULTS:
With the financial support obtained from the LDRD, we have succeeded in developing NS-FFAG designs with new tools "muon1" from our new scientific associate (S1). This allowed us to explore a few new directions in FFAG design: one was Vertical Scaling FFAG. The advantage of this approach is a single ring in the tunnel to cover the whole energy range from injection to the maximum electron energy of 30 GeV. Unfortunately a few disadvantages of this design were found, such as large synchrotron radiation due to the large opposite bend requirement of the design. The project design continued with the Non-Scaling FFAG lattice, which requires two or more rings for the same energy range.

A plan for the Phase I of the LDRD was to provide a basic eRHIC NS-FFAG design with the preliminary magnet design. PHASE I was extremely successful as it was confirmed and given support by the International Advisory Committee during the eRHIC design review from November 25 – 27, 2013. The LDRD funding enabled us with new tools to compare results of five different programs: SYNCH, MADX, ZGOUBI, muon1, TRANSPORT and obtain the same results. The LDRD plan for phase II is to build and test a permanent NS-FFAG magnet. This will be a proof of principle and will provide a more realistic cost estimate.

A few results from PHASE I of the LDRD were shown during the Machine Advisory Committee Review:



The next picture shows the present design of the NS-FFAG magnet:



Electrochemical Reduction of Carbon Dioxide on Surface-Modified Metal Electrodes

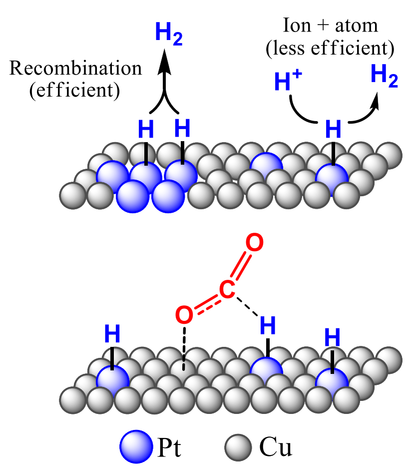
LDRD Project # 13-013
Dmitriy Polyanskiy

PURPOSE:

The objective of this project is to explore a new strategy for more efficient electrochemical catalytic conversion of carbon dioxide to reduced carbon products such as carbon monoxide, formic acid, alcohols, and methane. Our approach is based on the tailoring of a catalyst's surface properties to improve the efficiency of CO_2 electroreduction. Mechanistic understanding of chemical transformations on catalyst's surfaces and insight into the structure/reactivity relationship are the key driving factors in designing new catalysts. The employment of advanced characterization methods including those available at the National Synchrotron Light Source, (NSLS), the Center for Functional Nanomaterials (CFN), and through collaboration with other BNL groups will play a critical role in establishment of such mechanistic insights. Building upon gained knowledge and strong collaborative ties, new funding opportunities in the area of renewable energy research will be targeted. These funding opportunities include, but are not limited to the DOE Early Career program and participation in a DOE Energy Frontier Research Center.

APPROACH:

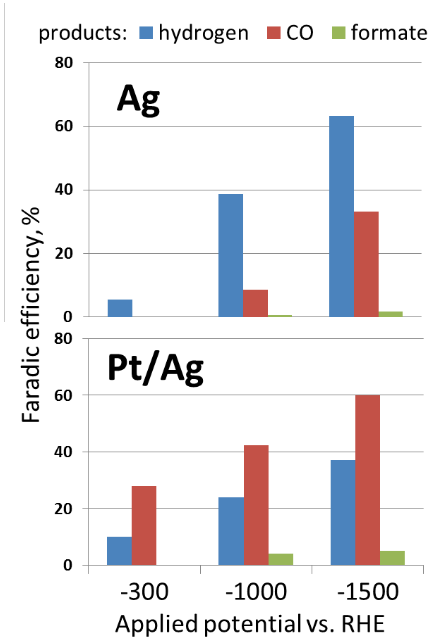
A wide variety of materials were studied for electrochemical reduction of carbon dioxide in the condensed phase; however no system was found to be efficient for potential application. The major challenges identified with the chemical reduction of CO_2 are the incredible thermodynamic stability of this molecule and the requirement to transfer multiple electrons and protons in the course of the chemical reaction. As a result, reaction pathways involving transfer of a single electron proceed through the formation of highly energetic intermediates and these processes are kinetically unfavorable. This in turn significantly diminishes the overall efficiency of CO_2 reduction and can manifest itself in, e.g., high overpotential for the electrochemical process and low yields of the most desired reduction products (e.g., methanol, methane or C2 hydrocarbons).



Our proposed approach relies on designing composite electrodes through surface modification of Cu, Au, Ag, or their alloys, with adatoms of Pt, Pd or Ni with submonolayer coverages to study the potential synergetic effect of the bimetallic surface for CO_2 reduction. In the proposed systems, electroreduction of protons on adatoms will generate hydrogen atoms under low overpotential, while Cu (Ag, Au) will provide CO_2 binding sites and suppress the hydrogen atom recombination (see figure on the left). Proposed systems will be prepared by depositing adatoms or a small adisland of Pt, Pd or Ni on Cu, Au or Ag using methods available in the Principal Investigator's (PI) lab or employing deposition tools at the CFN. The structural and chemical composition of these surfaces will be characterized by electron microscopy and x-ray spectroscopy methods available at the CFN and in the groups of our collaborators: Radoslav Adzic and Michael White (Chemistry Department). The catalytic performance will be assessed from analysis of catalytic current as well as product analysis using chromatography techniques (also available in PI's lab). In situ XAS measurements (NSLS) will provide better understanding of the catalytic site (e.g. oxidation state, atomic coordination) under catalytic conditions.

TECHNICAL PROGRESS AND RESULTS:

Since the beginning of the project in July 2013 the following milestones were achieved:



a. After a thorough search, a new research associate, Yu-Chi Hsieh was hired (start date July 15, 2013), with extensive expertise in electrochemistry, electrocatalysis, synchrotron methods, and the knowledge of other advanced characterization techniques.

b. New synthetic and characterization protocols were rapidly developed and implemented. A range of catalytic systems were prepared using two approaches: metal immobilization on high surface area carbon support (Vulcan) and surface modification of flat metal cathodes. Vulcan based catalysts demonstrated high current densities; however the major product was hydrogen. On the other hand, surface modified flat cathodes in particular, Pt/Cu and Pt/Ag systems have shown promising reactivity. Preliminary results point to: i) significantly enhanced activity toward CO_2 reduction under moderate applied potentials; ii) carbon monoxide and formic acid are produced as major products (see figure on the left, RHE is reversible hydrogen electrode). These results serve to validate our approach. Low catalytic currents and less than 100% faradic efficiencies for observed products were attributed to the build-up of CO_2 reduction products on the surface. Current efforts are focused on resolving these complications.

c. A proposal for the Center for Chemical Storage of Renewable Energy (University of Illinois Urbana-Champaign) is under preparation. This proposal stems directly from the currently funded LDRD project; it is focused on the development of more efficient and durable electrocatalysts for CO_2 reduction and their integration into functional devices.

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

a. Optimization of catalytic performance through variation of adatom coverage, solution acidity and CO_2 concentration.
b. Obtaining mechanistic insights into the reduction process using in situ XAFS studies (pending NSLS proposal), surface characterization by TEM (CFN) and XPS (White's lab), and impedance measurements (PI's lab).
c. Development of high surface area nanostructured metal supports to improve electro-catalytic currents.
d. Implementation of non-aqueous electrolyte systems, such as ionic liquids in order to explore the effect of an extended range of CO_2 concentrations and temperatures on the catalytic process.
e. Integration of optimized catalytic systems into functional devices through collaboration with groups with chemical engineering expertise (e.g. above mentioned University of Illinois Urbana-Champaign center).

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

LDRD Project # 13-017

Chu Yong and Dantong Yu

PURPOSE:

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

APPROACH:

Our system will leverage the open-source workflow technologies, including the well-established biology workflow systems, such as Galaxy and VisTrails. Their incorporation into our system will support the point-and-click execution of complex workflows, starting from raw stream data generated by detectors, the experiment metadata, log information obtained from various databases and sensors, to processed images that can be further studied off-line at selected data centers or users' home institutions.

In addition to being highly accessible with user-friendly interfaces, this system includes automatic provenance tracking to ensure highly transparent and reproducible beamline experiment and data production. We will enhance the existing workflow systems with intelligent scheduling engines and data coordination modules to maximize the efficiency of the online data processing for the first six NSLS-II project beamlines, and extend our improved workflow systems to all the remaining beamlines that will operate after 2014. Our proposed system consists of three components: user interface; workflow manager; and the underlying resource layers to host data, tools, and computing resources.

We will work with several other LDRDs to incorporate their data analysis modules and standard data access interfaces into our workflow platform. In addition, we will collaborate with the scientific computing teams from other light source facilities, such as the Advanced Photon Source and the Advanced Light Source to leverage their existing job processing system, and contribute our workflow system to the wider user community.

TECHNICAL PROGRESS AND RESULTS:

We successfully hired one highly talented scientific programmer and one beamline research associate to do the research and development work proposed in the LDRD. We collaborated with six early beamlines in NSLS-II and one existing beamline at the National Synchrotron Light Source (NSLS) to implement a prototype system, including an easy-to-use web interface, integrated high performance computing cluster, and highly optimized analysis algorithms and modules for three representative pipelines Difference Phase Contrast (DPC) Imaging for the Hard X-ray Nanoprobe beamline, tomography for the Full Field X-ray Imaging beamline and spectroscopy for X8C, an NSLS beamline). Our project team members were productive in generating publications in peer-reviewed computer science conference proceedings and in journals.

1. Database-Assisted Low-dose CT Image Restoration, Wei Xu, Sungsoo Ha and Klaus Mueller, *Medical Physics*, 40(3), 031109, pp. 1-7, 2013
2. A Comparative Study of Neighborhood Filters for Artifact Reduction in Iterative Low-Dose CT, Wei Xu, Sungsoo Ha, Ziyi Zheng and Klaus Mueller, Proc. of *12th Fully Three-Dimensional Image Reconstruction in Radiology and Nuclear Medicine*, pp. 185-188, Lake Tahoe, CA, Jun. 2013
3. Accelerating Differential Phase Contrast Imaging for NSLS-II Data Analysis, Cheng Chang, Wei Xu, Hanfei Yan, Li Li, Yong S. Chu and Dantong Yu, CEWIT conference 2013 (Oral presentation).
4. A Workflow System To Facilitate Data Process at NSLS II, Li Li, Wei Xu, Hanfei Yan, Xiaojing Huang, Cheng Chang, Wah-Keat Lee, Dantong Yu and Yong S. Chu, *NSLS/CFN Joint Users' Meeting 2013*, Brookhaven National Laboratory, Upton, May 2013 (poster)
5. Accelerating Chemical Mapping in Full-field Hard X-ray Spectroscopic Imaging on Multi-core Cluster, Cheng Chang, Wei Xu, Yu-chen Karen Chen-Wiegart, Jun Wang and Dantong Yu, SPIE Electronic Imaging 2014, in Submission.
6. H. Yan and L. Li, X-ray dynamical diffraction from single crystals with arbitrary shape and strain field: A universal approach to modeling. Submitted to Phys. Rev. Lett.

We gave three talks about our workflow system:

1. "PyLight, A Common Architecture for Composable Workflows to Facilitate Data Acquisition and Analysis at NSLS-II", Workshop Advanced Analysis of X-Ray and Neutron Scattering Data: Getting from data to science, August 14-15, 2013, Brookhaven National Lab
2. Invited talk: "PyLight, Data Processing in NSLS-II", 2013 Smoky Mountains Computational Sciences and Engineering Conference, Integration of computing and data into instruments of science and engineering, Oak Ridge National Laboratory
3. Scientific Workflow to Facilitate Data Process at Hard X-ray Nanoprobe NSLS-II. Presentation at Advanced Photon Source, April 2013, Chicago, IL.

In summary, a workflow prototype was implemented. It integrated various analysis tools and modules: tomography, DPC image processing, spectroscopy, and ptychography. This workflow system offers several key capabilities for beamline scientists: expedited data processing and analysis with high performance clusters, automated and easy-to-manage data analysis pipeline, and easy-to-learn Graphical user interface. It met and exceeded the original yearly milestones proposed in the LDRD proposal.

Synthetic Control of Lipid Biosynthesis in Plant Vegetative Tissue

LDRD Project # 13-020
John Shanklin

PURPOSE:

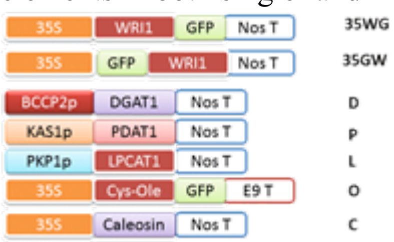
This proposal addresses the issue of increasing plant oil yield by engineering plants to accumulate oil in non-seed tissue. The eventual target for such engineering will be biofuels crops such as sugar cane, energy cane or sweet sorghum. However, work to establish proof of concept will be performed in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

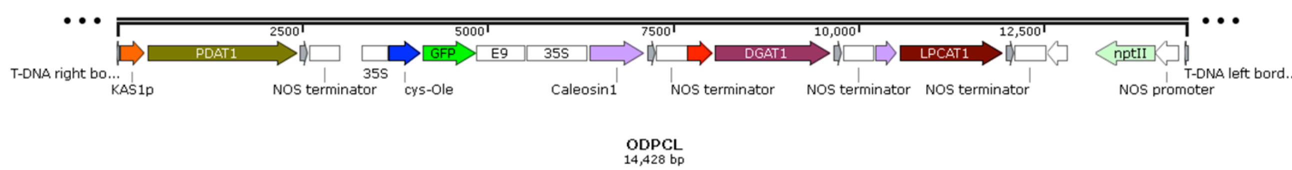
APPROACH:

The project essentially involves two parts, 1) expanding the WRI1 regulon, and 2) controlling the expression of the transcription factor wrinkled 1, (WRI1). WRI1 can be thought of as a master switch that turns on a set of genes. It is a transcription factor that controls the coordinate expression of approximately 18 genes that encode enzymes from central metabolism through to fatty acid synthesis by binding to a DNA region upstream of the coding region of the genes that it regulates. This causes them to become transcribed into RNA, and hence turned on. WRI1 thus controls the synthesis of fatty acids by regulating the expression of enzymes that direct carbon compounds of central metabolism to fatty acid synthesis. The conversion of fatty acids to TAG requires the action of an additional set of TAG assembly proteins, comprising enzymes and other factors, which are not expressed in vegetative tissues. Thus, to accumulate TAG in vegetative tissues we would need to express both WRI1, and an additional set of TAG assembly enzymes. This proposal is designed to provide a synthetic solution to this problem, i.e., to expand the constellation of (18) genes that are controlled by WRI1. To achieve this we have identified regions of DNA that have previously been shown to become activated upon the binding of WRI1, and we chose the three promoters from the 18 candidate promoters that showed highest levels of expression when coupled to marker proteins using a short (~300) base pair fragment of the promoter. These promoters will be fused with our TAG assembly genes and the genes will be transformed into Arabidopsis using Agrobacterium mediated gene transfer. Together this part of the workplan will generate an extended WRI1 regulon in which 24 genes will be under the control of the WRI1 transcription factor rather than the naturally occurring 18-gene regulon.

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

TECHNICAL PROGRESS AND RESULTS:
Binary transformation plasmids suitable for these experiments have been identified and customized. A strategy for assembling the multiple gene constructs has been devised. Custom oligonucleotides have been designed and synthesized for each key gene including lysophosphatidyl choline acyltransferase (LPCAT), diacylglycerol acyltransferase 1, (DGAT1 – AT2G19450), phospholipid:diacylglycerol acyltransferase (PDAT1 AT- AT5G13640), oleosin 1 (OLE1–AT4G25140), caleosin (CLE1–AT4G26740) and promoter segment (PI-PKβ1, BCCP2 and Kas1). Individual promoters and genes have been amplified. See schematic below for DNA elements in both single- and multi-gene DNA constructs.





FY 2014 Milestones. Assemble binary vector constructs for key genes including LPCAT, DGAT1 –AT2G19450, PDAT1 AT-AT5G13640, OLE1 –AT4G25140, CLE1 –AT4G26740, under the control of specific WRI1-responsive promoter elements. Perform transient co-expression experiments expressing single genes with constitutively expressed 35S:WRI1. Test the multi-gene expanded WRI1-controled regulon by performing quantitative analysis of samples using silica thin layer chromatography, gas chromatography coupled mass spectrometry. Transform WRI1 expression cassettes into various Arabidopsis mutant backgrounds.

FY 2015 Milestones. Use knowledge gained from analysis of *N. benth.* single- and multiple-transient expression experiments to design optimal stable transformation combinations of genes and promoters. Construct stable expression constructs. Transform into Arabidopsis lines expressing WRI1 created in FY 2014, and supplied by June Medford. Perform quantitative analysis of samples using silica thin layer chromatography, gas chromatography coupled mass spectrometry.

Tracking Lithium Electrochemical Reaction in Individual Nanoparticles

LDRD Project # 13-022

Feng Wang

PURPOSE:

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

APPROACH:

In situ synchrotron x-ray techniques are powerful for *real-time* probing of electrochemical reactions in batteries, but limited in spatial resolution to the micrometer scale. The recent development of *in situ* TEM techniques pushes the resolution down to nano scale. However electrochemical cells for TEM, due to the use of solid electrolyte and an open cell configuration, are different in the settings from real batteries. It would be desirable to develop an electrochemical cell that allows for correlative *in situ* synchrotron and TEM studies of electrochemical reaction of electrodes under real electrochemical conditions. A novel sealed electrochemical cell with flexibility of using liquid electrolyte, along with a full suite of biasing systems, will be developed for both TEM and synchrotron measurements (as illustrated in Figure 1a). Advanced *in situ* TEM imaging techniques (*i.e.* aberration-correction, energy filtering) 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. In addition, a previously developed solid-electrolyte based *in situ* cell (Fig. 1b) will be further modified for tracking lithium reactions more precisely *via* atomic imaging and spectroscopy. [1] Those developed *in situ* techniques and capabilities will be applied for *real-time* probing of electrochemical (de)lithiation of individual particles, and in a combination with computational modeling, to determine the possible *non-equilibrium* reaction pathways during battery operation [2].

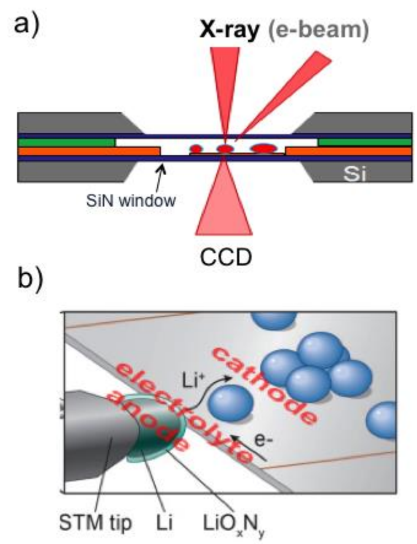


Figure 1 Schematic illustration of two types of *in situ* electrochemical cells, based on (a) liquid and (b) solid electrolyte, to study single-particle electrochemistry by TEM and synchrotron x-ray techniques.

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

TECHNICAL PROGRESS AND RESULTS:

The lab and equipment have been set up for this project, and a new postdoc was hired and trained on TEM, synchrotron and electrochemical characterization of battery materials. Originally, the proposed effort was to procure a Hummingbird Scientific *in situ* liquid-flow holder with biasing option. However, at the initiation of the project, the liquid-flow holder was still under development. In order to maintain progress on the project, BNL entered into a Cooperative Research and Development Agreement to assist in the development and testing of the electrochemically active liquid cell. The holder and accessories (i.e. optical microscope and pumping system) were installed and tested at the Center for Functional Nanomaterials (CFN). Some preliminary results are given in Figure 2. Electrode materials were directly loaded onto a patterned chip and further assembled into a liquid cell. A spatial resolution down to nano-scale was achieved under optimized imaging conditions. As shown in Fig. 2c, reasonably good contrast of nanoparticles in the liquid electrolyte was obtained by annual bright-field STEM imaging.

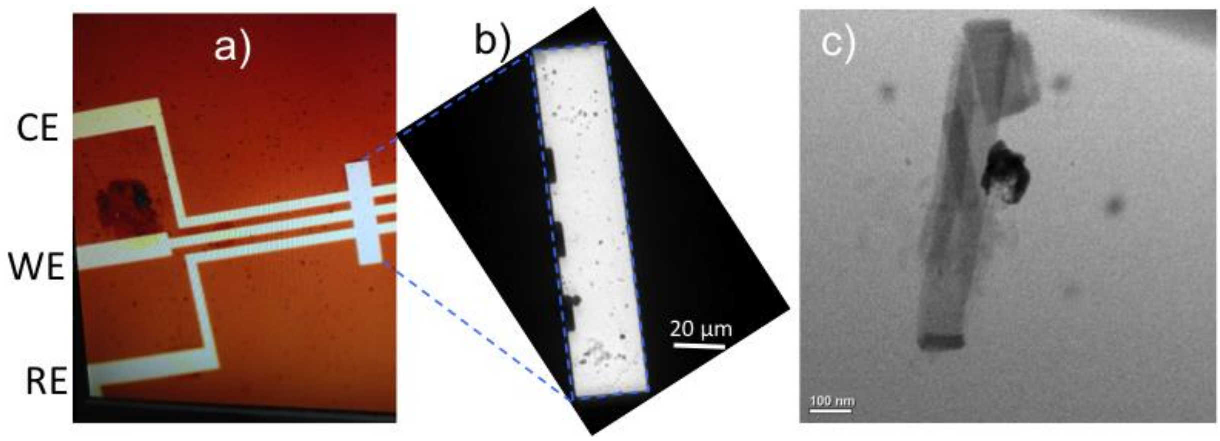


Figure 2. Preliminary tests of electrochemical cells loaded with liquid electrolyte and electrode materials. (a) Optical image of a patterned chip, with integrated working (WE), reference (RE), and counter (CE) electrodes, (b, c) bright-field TEM images of nanoparticles in the presence of liquid electrolyte.

Some preliminary TEM, synchrotron and electrochemical characterization has been made on $LiFePO_4$, one of the model systems selected. Single-crystalline $LiFePO_4$ nanoplates, with well-defined morphology and orientation, will be integrated into liquid and solid electrochemical cells (Fig. 1) for correlative *in situ* TEM and synchrotron x-ray studies, aiming to determine the *non-equilibrium* reaction pathway in $LiFePO_4$, and compare with computational modeling.

The full suite of tools/equipment associated with the developed electrochemical cells will be eventually housed in the new dry room at the Interdisciplinary Science Building (ISB), where electrodes (including lithium) and electrolyte can be installed into the electrochemical cells and tested in a moisture-free environment. Potentially this provides a new platform for battery research using several neighboring facilities (ISB, CFN, NSLS-II).

Milestones: In the 1st year, an electrochemically active liquid cell was tested for *in situ* TEM experiments. Extensive cell assembly and tests will be made in our lab, and some *in situ* TEM measurements will be made at the TEM facilities in the CFN and Condensed Matter Physics Department. In the 2nd year, the whole suite of instruments and *in situ* techniques will be developed and made available for the 1st light experiments at NSLS-II. In the 3rd year, *in situ* studies of single-particle electrochemistry of advanced battery systems will be completed.

References: [1] F. Wang et al., "Tracking of Li Transport and electrochemical reaction in nanoparticles", *Nat. Comm.* 3, 1201 (2012) 1; [2] R. Malik, F. Zhou, and G. Ceder, "Kinetics of non-equilibrium lithium incorporation in $LiFePO_4$", *Nat. Mater.*, *10*, 587 (2011).

Elucidating the Role of Nanostructured Domains in CIGS PV Device Performance

LDRD Project # 13-024

Matthew 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 currently 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 nano-scale 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. Achieving these goals would strengthen BNL's energy strategy by supporting the U.S. CIGS manufacturing industry via improved fundamental understanding that is then leveraged to reduce the cost of thin-film photovoltaic manufacturing.

APPROACH:

Transmission electron microscopy (TEM) studies of CIGS films have shown strong chemical fluctuations at the nanoscale and the presence of Cu-rich and Cu-poor regions, but have not correlated nanoscale measurement to local device performance. A key prediction of this model is the loss of intra-absorber charge separation in CIGS when the overall absorber composition becomes too enriched with gallium.

The approach we are taking is to connect regional device performance (microns) with nano-scale chemical and structural properties of the films. Standard CIGS cells, with peak efficiencies of 17% or more, are being fabricated through co-evaporation at the College of Nanoscale Science & Engineering at the University of Albany (Prof. Harry Efstathiadis and Dr. Daniel Dwyer), with Ga concentrations varying from 0.1 to 0.6, and for different substrate processing temperatures.

Areas of relatively good and poor performance are being identified via micron-scale characterization of CIGS devices using laser-beam induced current (LBIC) measurements, which creates a 2D spatial map of photo-generated current. Such a measurement effectively allows the spatial mapping of photo-generated charge extraction efficiency, yielding insight into the spatial variation of carrier transport and extraction. The 2D charge extraction efficiency maps created with LBIC measurements are being correlated with structural measurements such as micro X-ray fluorescence (X27A at the National Synchrotron Light Source (NSLS)), admittance spectroscopy, micro-Raman spectroscopy, scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX), transmission electron microscopy (TEM – Eric Stach, Center for Functional Nanomaterials (CFN) and Feng Wang, BNL), and grazing incidence X-Ray Scattering (GIWAXS) – Ben Ocko, BNL, NSLS, X9) in order to correlate the micron-scale performance variation with the nano-scale chemical and structural properties. In addition scanning transmission electron microscopy/electron energy loss spectroscopy (STEM-EELS) is being used for detailed studies of grain boundaries and the formation of n-type and p-type percolation networks within the CIGS layer.

TECHNICAL PROGRESS AND RESULTS:

Figure 1 summarizes our progress during the first 5 months of this project.

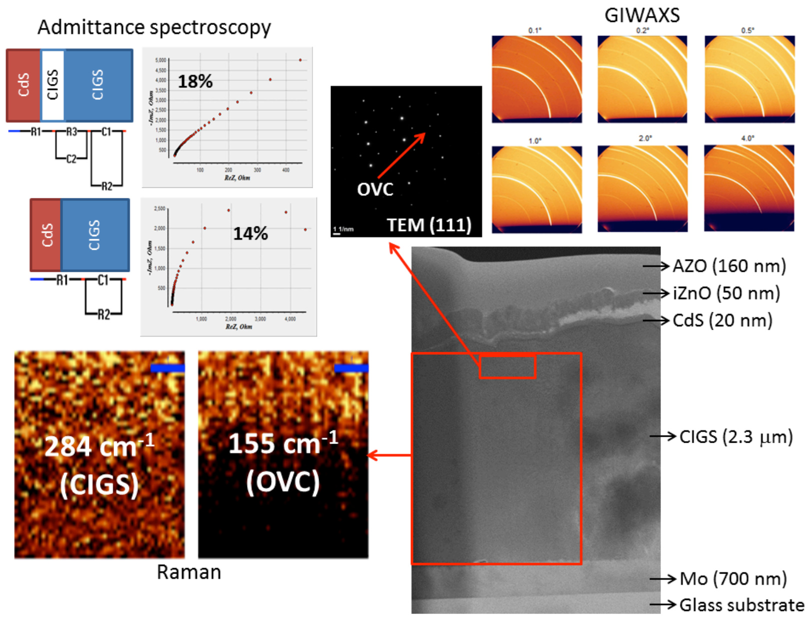


Figure 1: Evidence for the OVC layer at the CIGS/CdS interface of CIGS solar cells. Admittance spectroscopy and GIWAXS suggest that the spatial extent and uniformity of the OVC layer is correlated with power conversion efficiency.

While deep-level defects are known to contribute to bulk recombination in CIGS, it is also hypothesized that a 10nm-100nm thick Cu-poor ordered vacancy compound (OVC) layer within the CIGS layer at the CIGS/CdS interface is essential to high performance by greatly reducing the interface recombination. Recent measurements in our lab have combined Raman spectroscopy and TEM at the CFN, capacitance-voltage measurements in our lab, and GIWAXS measurements at NSLS (X9) to confirm the presence of this OVC layer via proxy measurements such as typical co-existing phases ($CuIn_3Se_5$) and Cu-deficiency (see Fig. 1). Importantly, we observe that the structure of this OVC layer appears to be fundamentally different for high performance (18.5% power conversion efficiency) cells compared to lower performance (14.5%) cells.

FY14 milestone: STEM-EELS (or/and EDX), will be used to map the spatial distribution of different phases (α or β) at the nanometer scale, including a comparison between the nanoscale variation in the bulk compared to the OVC layer near the CdS interface.

FY15 milestone: Information learned during FY13 and FY14 will be used to adjust process conditions to produce optimum stoichiometry for device performance, leading to efficiencies greater than 20% and more uniform efficiencies over large areas.

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

LDRD Project # 13-025

Xiaoyu (Shawn) Wang

PURPOSE:

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

APPROACH:

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

TECHNICAL PROGRESS AND RESULTS:
Work completed from Jan. to Dec. 2013 produced the following technical progress: 1) procured PSS/E software from Siemens PTI and attended training courses for performing dynamic simulations; gained hands-on experience on how to run the software, which facilitated development of customer-written dynamic models for photovoltaic (PV) generation and BESS within PSS/E; 2) developed a virtual machine based control system to provide inertial response; integrated this control system into a two-machine power system to investigate its effectiveness for provision of inertial response. The simulated system was implemented using PSCAD software for integration of a BESS with the PV generation system; 3) collected and statistically analyzed solar transient data from the Long Island Solar Farm (LISF) and failures of grid components; developed and implemented in MATLAB an algorithm for generating statistical samples representing variability of solar generation and random failures of grid components; 4) implemented an automated process of performing the simulations assessing grid frequency responses in MATLAB; 5) investigated literature concerning failure modes, degradation effects and data for PV systems; 6) analyzed BNL weather conditions to establish patterns and define probabilities and distributions to use in the development of the probabilistic risk assessment analysis for evaluation of production-oriented risk; conducted FMEA analysis to identify failure modes, effects and causes for PV systems; results obtained from this analysis were incorporated into the studies in 3; 7) contacted external PV experts (such as SunEdison) to validate results and approach. Some highlights of the results are briefly elaborated below.

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

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

The control systems and methodologies developed in FY13 will be migrated to the commercial software PSS/E in FY14. The FMEA analysis and PSA approaches will also be further fine-tuned as additional irradiance data and PV plant failure data become available.

In situ Studies of Interfaces Under Extreme Environments

LDRD Project # 13-027

Simerjeet K. Gill

PURPOSE:

Currently there is lack of fundamental understanding of kinetics and reaction mechanisms that occur at Zirconium alloys-Steam interface under extreme environments in the nuclear reactors. Such understanding is vital to design and develop advanced cladding materials for more economical and safer nuclear power. This project is aimed at addressing this lack of understanding. The proposed approach is to develop a reaction cell for *in situ* investigation of interfacial interactions under high-temperature and pressure conditions to investigate corrosion and hydriding mechanisms in zirconium alloys samples using X-Ray diffraction and X-Ray fluorescence techniques at National Synchrotron Light Source II (NSLS-II). Such studies will help in elucidating the phase and structural changes associated with corrosion conditions for various zirconium alloy systems which will aid in design and development of corrosion-resistant next generation cladding materials.

Successful demonstration of the proposed *in situ* capability will make high impact science opportunities available at NSLS-II and pave the path for BNL towards the development of advanced synchrotron-based X-Ray methods for *in situ* studies of materials under extreme environments. In addition, development of such a capability will fulfill BNL's mission of transitioning to new and more efficient energy sources to meet the world's current and future energy needs.

APPROACH:

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

The proposed new approach to address understanding of corrosion of zirconium alloys for design of next generation cladding materials is to perform *in situ* corrosion studies using large grain samples. We are developing and utilizing a reaction cell to study single crystal zirconium alloy samples with a few large grains and polycrystalline bulk zirconium alloys treated with saturated steam at 400°C and 1500 psi for 3-4 days. Such *in situ* investigation of large grain zirconium alloy samples will help understand the changes in grain and oxide structure that occur during the stress produced by corrosion conditions, which will further help optimize the design of corrosion resistant next generation cladding materials. This work was done in collaboration with Eric Dooryhee and the X-ray powder diffraction (XPD) team, Vincent DeAndrade and the Submicron Resolution X-ray Spectroscopy (SRX) team, and Arthur Motta at Penn State University.

TECHNICAL PROGRESS AND RESULTS:

In FY13 and FY14, two main scientific efforts under the LDRD project were:

1. Development of a safe cell design optimized for *in situ* data collection: A reaction cell for *in situ* studies (Figure 1) which can work under ambient conditions to high temperature (up to

450 °C) and pressure (2000 psi) conditions was designed. To provide corrosion resistance, a Hastelloy reaction cell was chosen.

The cell dimensions were engineered so that the available sample surface area to reaction medium ratio complied with the industrial ASTM standards for investigating corrosion reactions. Finite Element Analysis was done to ensure safe operation and absence of high stress zones and design recommendations were incorporated into the computer-aided design (CAD) drawings for the cell. A few key features of cell design set-up are:

- Pressurizer: so that small changes in temperatures do not lead to large changes in pressure.
- LabVIEW based data collection platform for complete T and P remote monitoring.
- Built-in safety mechanisms: Safety burst disc on pressurizer and alarm set-up in electronics.

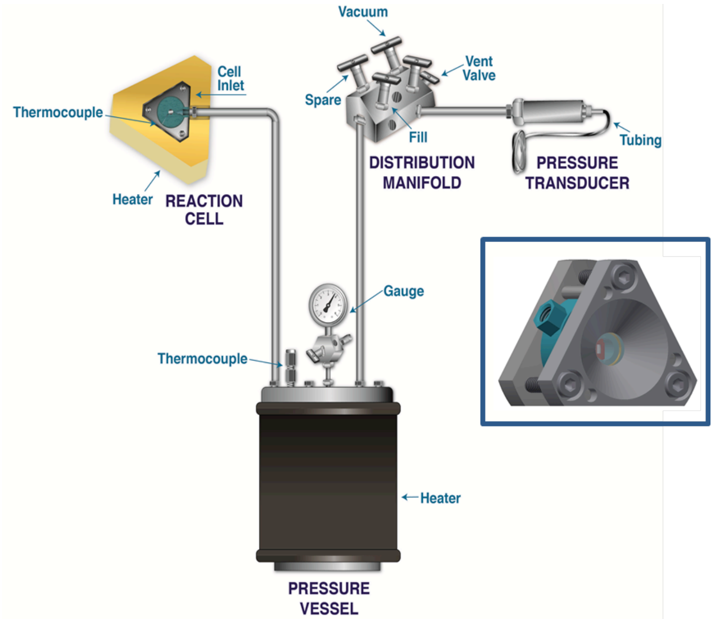


Figure 1: Schematic showing the reaction cell and fluid delivery system. Insert shows the CAD drawing of reaction cell developed at BNL

2. **Data collection for Zircaloy-4 system:** To establish proof of concept and optimize beamline set-up, XRD data (Figure 2) on Zircaloy-4 unexposed and samples exposed to 360 °C water in an autoclave at Penn State for 45 and 270 days was collected. Along with standard α-Zr peaks, ZrO_2 peaks corresponding to monoclinic ZrO_2 were observed in exposed samples and enhancement of oxide peaks (Figure 2A) was seen after 270 days of exposure. Further to elucidate the texture of Zircaloy oxide, we used a rotation stage in FY13 and collected the data for both exposed and control Zircaloy-4 samples. The samples were rotated in steps of one degree and a total of 120 data measurements were taken on every sample. As seen in Figure 2B, the Zircaloy-4 sample exposed for 270 days showed new oxide peaks on rotation confirming the presence of texture and preferred orientation in the monoclinic oxide.

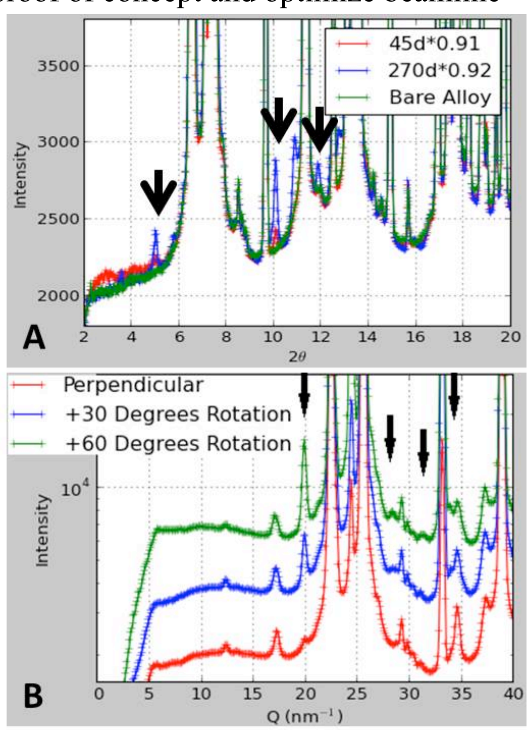


Figure 2: X-Ray Diffraction data collected for Zircaloy-4

SUMMARY: The milestones of FY13 and 14: design of reaction cell and collection of proof of concept *ex situ* data were achieved. The milestone for FY 15 is to commission the cell on XPD and SRX beamlines and collect the *in situ* data.

Modulation Enhanced Diffraction (MED): A New Tool For Powder Diffraction and Total Scattering Studies

LDRD Project # 13-031

E. Dooryhee

PURPOSE:

The objective is to develop a new method which introduces structural and quantitative selectivity into time-dependent diffraction measurements in a comprehensive range of catalytic, physical chemical processes. MED will extend the capability of the diffraction and scattering techniques at National Synchrotron Light Source II (NSLS-II). MED consists in applying a periodic external stimulus (partial pressure of reactants, T, P, electrical field, dopant concentration) to enhance the structural features responsible for key properties in functional and engineering materials. The project is in line with the *in operando* strategy that BNL is deploying for discovering, optimizing the synthesis and processing novel functional materials. The LDRD grant is helping to establish BNL/NSLS-II as a major actor and a U.S. leader in using this potentially powerful tool for *in situ* and *in operando* x-ray diffraction. MED opens research opportunities in at least four BNL mission areas: solid state physics and chemistry, energy and materials research, catalysis and transformation of materials, and the operation of NSLS-II. As MED has the potential to enable a many fold leap in x-ray diffraction sensitivity, it clearly is of interest to a large community within BNL and worldwide.

APPROACH:

Recent work has demonstrated the usefulness of MED for Powder Diffraction (van Beek 2011) and in Pair Distribution Function analysis. Applications are: adsorption/desorption in framework materials, reversible ion intercalation in organic/inorganic matrices for batteries and fuel cells, polarization- or magnetization-induced displacements by electric or magnetic fields in multiferroics, structural properties and surface intermediates in catalysts under changing pressures of the reactants. First applications prove that MED is selective and sensitive to structural changes resulting from a periodic stimulus without the need to vary the wavelength as in other techniques, like anomalous diffraction. MED is quite distinguishable from previous steady state measurements, ultimately revealing the active transient or non-equilibrium states that typically occur during a process. Our experimental work over the past 6 months includes:

Location/ Beamline	Start Date	Finish Data	Compounds
APS/11-ID-B	April 20, 2013	April 24, 2013	Cu/CuO; CeO_2/CuO
NSLS/X17A	August 8, 2013	August 15, 2013	Cu/CuO; MOFs
NSLS/X7B	August 20, 2013	August 26, 2013	CeO_2/Cu; $CuFe_2O_4$
APS/11-ID-B	October 24, 2013	October 28, 2013	IR & PDF on CeO_2/CuO
APS/17-BM	November 21, 2013	November 25, 2013	MOFs

The main collaborators have been: J. Hanson (Chemistry), J. Parise (Stony Brook University (SBU)/Photon Sciences (PS)), J. Rodriguez (Chemistry), S. Ghose (PS), S. Senanayake (Chemistry), Anna Plonka (SBU). During these measurements, we worked on mixtures of Cu-Fe oxides used for numerous industrial catalytic processes including the Water-Gas Shift reaction ($CO+H_2O \rightarrow CO_2+H_2$) (Hanson et al. Catalysis Today 205 (2013) 41–48). The reversible nature of the Cu migration preserves the activity of the catalyst and protects Cu from deactivation. The migration of Cu was accurately monitored using MED. We also worked on selective gas sorption in Metal Organic Frameworks (MOFs). MOFs are highly promising materials for various large-scale gas separation processes including carbon dioxide over N_2. MED is measured while the stream flows through the MOF in order to determine the origin of the remarkable selectivity toward CO_2, in an attempt to develop strategies for stabilizing the amount of atmospheric CO_2.

TECHNICAL PROGRESS AND RESULTS:

Andrey Yakovenko was appointed as a Postdoctoral Research Associate on 6/3/13. He left BNL on 12/6/13 to join the Advanced Photon Source. He continues to collaborate on the MED project. Here is the status with respect to the work plan submitted in the LDRD original proposal:

Task	Description	Duration	Status
Sample screening and tests	1. Select high-impact science cases XRD and PDF measurements (NSLS X7B, NSLS X17A and APS 11ID) 2. Visit ESRF BM01 and ID15 where MED was first tested	6 months	1. Done, MED will be extended to more application studies. 2. Done (based on approved peer-reviewed proposals) 3. Scientist met at the ACA conf (2012) and scientist invited at BNL (2013).
Setting-up and experiment controls	1. Develop appropriate instrumentation and set-up at NSLS for later implementation at NSLS-II XPD 2. Design the dedicated sample environment (HP, HT flow cell with RGA and DSC to monitor the cycles). 3. Interface a system for pulsing gas	16 months	1. Done, implementation for NSLS-II to be started. 2. Customization of an existing cell is started. 3. Done. Equipment has been purchased, including a fast switching valve, a Residual Gas Analysis system, and a PCI data acquisition card.
Experiment	1. Measure diffraction intensities 2. Benchmark MED in real-case studies and test domain of applicability		1. Done at odd and even frequencies 2. Done
Data analysis	1. Develop the kinematical theory and algorithms to model the different structural parameters 2. Compute the frequency filtering (demodulation and correlation) algorithms and phasing of the demodulated diffraction signal	6 months	1. Done: theories of Phase-Sensitive-Detection and MED are explored. 2. Done: the program "2DMED" has been developed in Python. 2DMED was successfully benchmarked and tested. Data can now readily be analyzed using this software.

Next actions/milestones:

Tasks or milestones	FY14	FY15
Recruit another postdoctoral research associate in replacement of Andrey Yakovenko. The candidate is identified; an offer is in preparation	X	
Continue experiments (2 proposals submitted). Extend MED to other important systems	X	X
Extend MED to PDF (PDF gives some insight into the disordered/amorphous part)		
Publish our results (2 papers currently in preparation)	X	X
Release the software package to the community	X	
Organize a MED workshop at the CFN/NSLS users meeting		X
Continue to develop the MED hardware/software for early science work at the NSLS-II	X	X
Upgrade the CMOS detector	X	
Complete gas system with new flow controller and a pumping unit for special gases	X	
Develop the reaction cell	X	X

Development of At-Wavelength Metrology Tools

LDRD Project # 13-032

Mourad Idir and Konstantine Kaznatcheev

PURPOSE:

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

APPROACH:

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

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

TECHNICAL PROGRESS AND RESULTS:

Most of the work for the LDRD project will start in FY14. A new post doc, Lei Huang will join the team mid December 2013.

Some hardware has already been purchased to start the construction of our high resolution detectors and a contract has been approved to start the development of dedicated software for At Wavelength Metrology with the University of Arizona.

Multidimensional Imaging Data Analysis: From Images to Science

LDRD Project # 13-033

Wah-Keat Lee

PURPOSE:

Data from synchrotrons such as the National Synchrotron Light Source II (NSLS-II) are increasingly multidimensional in nature. In imaging, synchrotron measurements provide *local* (spatial/temporal/spectral) information on a particular property of the sample (e.g., absorption coefficient, or fluorescence). However, in most cases, the desired information depends on the relationships between the local values of these properties or in linking information from different modalities. Extracting such information is a major challenge. The goal of this LDRD is to develop two tools that are broadly applicable to multidimensional data: (1) registration of 3D images from different techniques and (2) extraction of relevant scientific information from 3D images of heterogeneous porous media. These tools are aimed at Early Science Experiments at NSLS-II, and will be applicable across a wide range of samples.

APPROACH:

The approach here is to develop and test these two tools with x-ray imaging data from composite electrodes for solid oxide fuel cells (SOFC) and lithium-ion batteries. Composite electrodes in energy devices (e.g., batteries and fuel cells) are highly heterogeneous, consisting of several phases: ion conductors, electron conductors, pores for electrolyte/fuel/by-products transport, and in the case of batteries, an energy storage component, such as lithium-metal-oxide. While the chemistry occurs at the interfaces at the nm or sub-nm scales, the actual performance of the devices is also dependent on the macroscopic morphological properties such as the porosity, tortuosity, continuity and throats of the different phases in the electrodes. The scientific goal of this research is to be able to link device performance with measurable changes in the electrodes (e.g., cracks, coarsening, or surface degradations). In addition, knowing the complete morphology will enable comparison and validation of performance simulation codes. The NSLS-II will provide outstanding tools to measure these systems. The transmission x-ray microscope (TXM), at the Full-field X-ray imaging (FXI) beamline is capable of measuring 3D density (~1% sensitivity) at 30 nm resolution in under 20 s. Scanning micro/nano fluorescence probes (XRF), such as the Hard-X-ray Nanoprobe (HXN) and Submicron Resolution X-ray Spectroscopy (SRX) beamlines are capable of measuring 3D elemental distributions with better than parts-per-million sensitivity, but are much slower than the TXM. One suspected cause of performance degradation in a SOFC Ni-YSZ (Yttrium stabilized ZrO_2) anode is due to nickel surface poisoning from contaminants such as sulfur. The TXM does not have the sensitivity to detect such contaminants, but XRF does. On the other hand, another cause of deteriorating performance is the structural damage (cracks and changes to transport channels), which is much better tracked by TXM. Thus, in order to fully characterize the electrode, it is necessary to combine TXM measurements that look at gross morphological changes, with XRF to look at subtle poisoning/diffusion effects at the nickel particle surfaces, on the *same* sample. The TXM data will be taken at the NSLS using the instrument at X8C, while the XRF data will be taken using a Hard X-ray Nanoprobe (HXN) prototype instrument at the Advanced Photon Source. The tools developed here will not only benefit the energy storage research, but also other BNL/DOE core-mission areas, such as oil extraction, environmental contamination and material science.

We also plan to work very closely with Dantong Yu and Yong Chu who are PIs in a related LDRD that deals with the development of a workflow system.

TECHNICAL PROGRESS AND RESULTS:

The main task in FY13 was the recruitment of the postdoctoral candidates. The positions were posted in December 2012, shortly after notification of approval of the LDRD. We held multiple phone interviews and officially interviewed 5 candidates. We successfully recruited two candidates in FY13. Gabriel Iltis, from Professor Dorthe Wildenschild's group at Oregon State University, started at BNL on September 23, 2013 and Thomas Caswell, from Professor Sidney Nagel's group at the University of Chicago, is expected to start on January 20, 2014. In the meantime, we have worked closely with Dantong Yu and Yong Chu who are PIs in a related LDRD that deals with development of a workflow system. We hold a common weekly meeting for both LDRDs. We plan to incorporate the tools we develop into their workflow system.

	FY13	FY14	FY15
Milestones	Recruitment of research associates.	Survey of available software. Acquire data for use in project. Implement basic image manipulation tools into workflow prototype system developed by Dantong Yu.	Acquire data for use in project (as needed). Implement image analysis tools into workflow system. Document tools.

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, 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 photoelectrons' current. A few attempts yielded sub 100 nm spatial resolution limited mainly by a high background photoelectron current. We propose to develop novel 'smart tips' based on carbon nanotubes (CNT) to reduce photoelectron currents and drastically improve spatial resolution. We will evaluate the performance of the CNT based tips using well defined samples and will conduct elemental mapping in topological insulators $Bi_{2-x}Mn_xTe_3$ crystals. By locating the position of substitutional Mn, X-ray assisted STM provides a direct visual method for examining the tendency to form clusters from the atomic to submicron scale, elucidating the effects of magnetic impurities and ferromagnetism on the topological surface states. Moreover, Bi_2Te_3 has long been studied as a parent compound for a family of excellent ambient-temperature thermoelectric materials, in line with energy research supported by DOE. Upon completion, this project will culminate in the development of a unique capability available for chemically specific elemental mapping with a potential to be integrated into Hard X-ray Nanoprobe (HXN) beamline at the National Synchrotron Light Source II (NSLS-II) and enabling start-of-the-art materials science research.

APPROACH:

We propose a novel approach to development and fabrication of 'smart tips' suitable for X-ray assisted STM measurements at the NSLS-II. Multi-walled CNTs have been successfully used for scanning probe microscopy applications and demonstrated excellent (sub-nm) resolution of topographic features when operated in tapping mode. We will utilize nanofabrication capabilities available at BNL (Center for Functional Nanomaterials (CFN)) and Argonne National Laboratory (Center for Nanoscale Materials) to fabricate CNT based STM tips. The procedure is schematically shown and described in Fig. 1. Typical STM tunneling currents I_{tunnel}^{STM} are equal to a few tens of pA. We estimate the I_{tunnel}^{X-ray} to be a fraction of I_{tunnel}^{STM}, thus reducing photoelectron current to a few pA will enable observation of X-ray induced tunneling. We will evaluate performance of CNT tips using well defined, reference samples. As a real test, we propose to perform measurements on $Bi_{2-x}Mn_xTe_3$ crystals. These materials attract a lot of attention due to their ambient temperature thermoelectric properties, and at the same time, exhibit bulk topological insulator behavior, hosting Dirac-like conducting surface states. Of

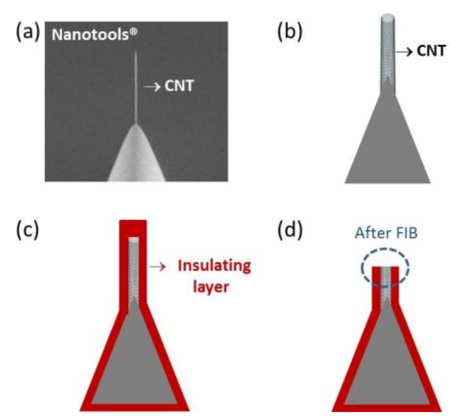


Fig. 1. Schematic representation of a process to fabricate CNT based tips for X-ray assisted STM measurements. The tip equipped with the CNT probe a), b) is coated with SiO2 layer using DC magnetron sputtering technique c). Focused ion milling (FIB) is used to remove part of CNT and expose the uncoated apex of the tip d).

particular interest is the effect of magnetic impurities and ferromagnetism on the topological surface introduced by Mn doping. $Bi_{2-x}Mn_xTe_3$ is a complex system and elemental mapping with atomic resolution will allow us to correlate macroscopic properties with the crystalline structure.

This work benefits from extensive collaboration within BNL and other groups involved in X-ray assisted STM studies. The NSLS-II team includes Dr. Hui Yan, a recently hired postdoc for this project, and Dr. Y. S. Chu and Dr. Hanfei Yan, HXN beamline staff. We also collaborate with CFN staff at BNL; this includes Dr. Ming Lu, who is involved in sputtering and deposition of the protective layer on top of the CNT tips (see Fig. 1). Dr. X. Tong and Dr. P. Sutter are STM experts at CFN who help us with the evaluation of the tips prior to synchrotron measurements. External collaboration involves the group of Dr. V. Rose at the Advanced Photon Source (APS) at Argonne National Laboratory. As a first step they provide beamtime for testing of CNT tips (while no beam is available at NSLS-II) and will also enable measurements on various material systems.

TECHNICAL PROGRESS AND RESULTS:
This project is still in its early phase. It had a delayed starting date and funds became available in April 2013. After extensive search and interviewing a number of postdoctoral candidates, Dr. Hui Yan accepted an offer and started working on the project. Her hiring date was October 21st 2013. During a very short period of time, a very significant amount of work has been accomplished. The initial visit to Dr. Rose's group at APS took place; a schedule for the beamtime and measurements has been outlined. A number of discussions at BNL were held, these involved CFN staff scientists (Drs. X. Tong and P. Sutter) to ensure access to STM systems for tips characterization prior to synchrotron measurements. Discussions with Dr. Ming Lu at CFN resulted in defining a strategy for coating of CNT tips with a protective SiO_2 layer. At this point, rapid access and full scale CFN user proposals are in preparation to grant access to instruments needed for CNT tips fabrication and characterization. An initial interaction with Carbon Design Innovations, Inc. took place and characteristics for bare CNTs attached to Pt-Ir and W tips were defined. We are on the way to procure the initial 10 tips equipped with CNTs and desired specifications Once received, they will be treated and coated at the CFN with subsequent testing in STM systems. Once proven that nanoscale resolution can be achieved, CNT tips will be transferred to the APS and initial tests will be performed in the synchrotron environment. This is a milestone for the first year of the proposal.

During the second year of funding, we will install 'smart tips' at the Nanoprobe beamline ID-26 (APS) through an established collaboration with Dr. V. Rose. We will perform proof-of-principle experiments on well-defined test samples and will investigate various materials systems. Upon successful outcome of the test measurements at the APS, we will propose a module for the HXN nanoprobe at NSLS-II to enable state-of-the art science experiments; this work will potentially enable development of a new capability available for users at NSLS-II.

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

LDRD Project # 13-036

O. Chubar (Tchoubar) and C. Kitegi

PURPOSE:

During the initial stage of the project execution, we first concentrated on structuring our project into several logical parts with separate partial objectives. This would allow for reaching the final goal - development and construction of a novel type of insertion device, Segmented Adaptive-Gap In-Vacuum Undulator (SAGIVU) for great benefits, in terms of spectral flux and brightness, at the National Synchrotron Light Source II (NSLS-II) and other low-emittance storage ring sources. The parts of our project relate to the development of the main technical sub-systems of the SAGIVU, in particular: mechanical carriages of individual segments and entire undulator (1); magnet systems of individual segments and junctions between them (2); impedance-reduction liner foil system (3); and the vacuum system (4). We believe that if given the chance to implement our ideas and planned developments in each of these sub-systems, which are also present in standard In-Vacuum Undulators (IVU), this will significantly improve the current position of BNL in the area of development and construction of innovative insertion devices for Light Sources not only among other U.S. National Laboratories, but also worldwide.

APPROACH:

The first IVU, that were proposed and realized at BNL in 1990s, exploited the possibility of focusing the electron beam in a second-generation Light Source down to very small size in the vertical direction. Due to this, it was possible to use the undulators at a very small (several millimeter) magnetic gap and small (1-2 centimeter) period to produce hard X-ray undulator radiation at a medium-energy storage ring. However, because of the large electron beam emittance (and therefore large divergence of the focused beam) and short straight intervals available for insertion devices in second generation rings, it was not possible to make the first IVU long: the typical length of such devices varied from several tens of centimeters to one meter. In modern low-emittance Light Sources, such as NSLS-II, the straight sections are much longer: there is ~5 - 7 m of continuous space available for an insertion device. Our calculations showed that the most efficient use of this space for producing high X-ray flux and brightness is to "fill" it with a number of adjustable short undulator segments similar to the short IVU, operating at different magnetic gaps, "tailoring" the electron beam "envelope" in the straight section and having different periods to allow for producing the radiation at the same resonant photon energy.

The mechanical design of the SAGIVU can greatly benefit from the developments made at BNL for the short IVU in 1990s. As a "starting point" for the design of the carriage for one SAGIVU segment, we decided to use the compact "single-tower" type design of the 30 cm long X9 undulator of the NSLS X-ray ring, revise it fully, and improve known weak points.

For realizing our project, we invited experienced physicists and engineers of BNL's Photon Sciences Directorate to work with us. However, the selected candidate did not start work because our project was placed into "delayed start" in FY14. We also try to use the services of mechanical companies located in the proximity of BNL, such as Advanced Energy Systems (AES) Inc.

TECHNICAL PROGRESS AND RESULTS:

In FY13, we started R&D work on two (out of four) main sub-systems of SAGIVU – the mechanical carriages and magnet system. The progress of these developments is illustrated in Figures 1 & 2.

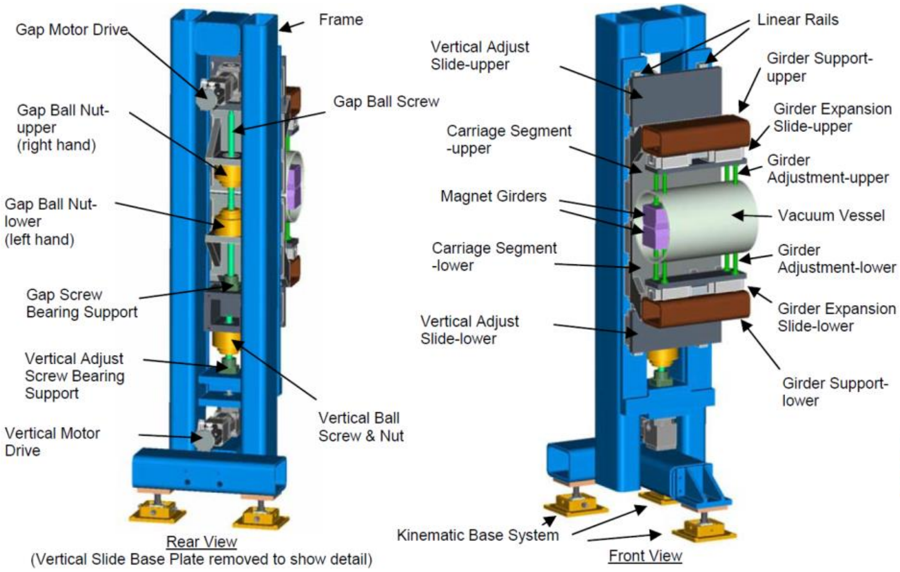
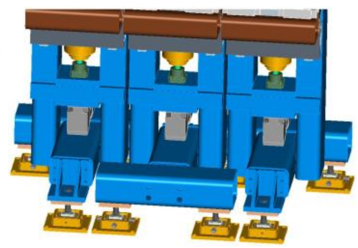


Figure 1. Computer-assisted design model of the SAGIVU mechanical carriage (pre-conceptual design): rear and front views of the individual segment carriage and possible adjacent installation of multiple carriages.



The preliminary design of the SAGIVU segment carriage (made in collaboration with AES) has a number of unique features and improvements compared to the X9 design. For example, the vertical offset mechanism has been completely changed (simplified and made more reliable), and the rigidity of the linear rail system was greatly increased.

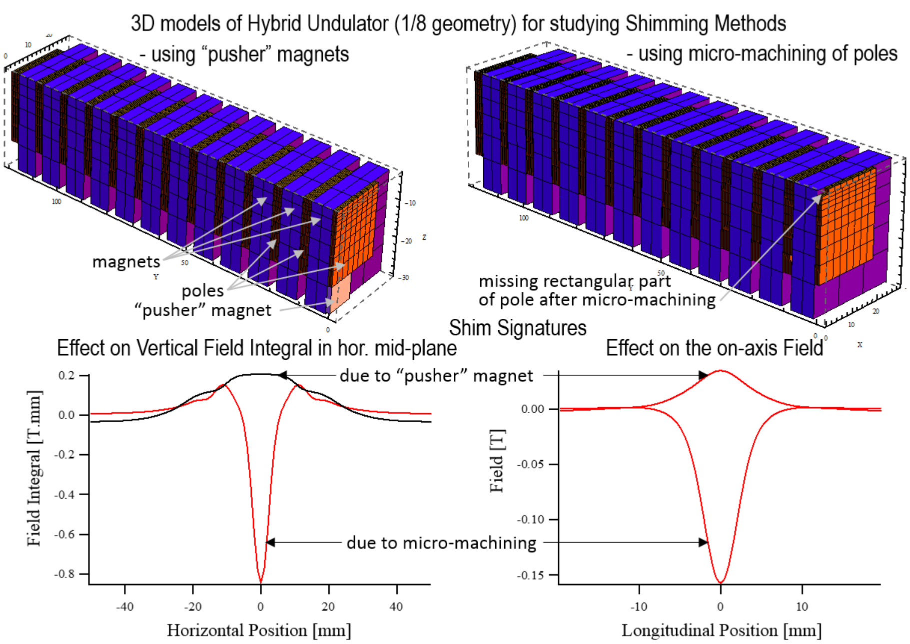


Figure 2. 3D magnetostatics models of IVU set up to explore efficiencies of two new shimming methods: installing "pusher" magnets under (or on top of) the poles (model on the left), and micro-machining of poles (model on the right). The graphs illustrate the calculated "shim signatures", i.e., the variations of the field integral (on the left) and on-axis field (on the right) as a result of these perturbations.

Two new shimming methods were studied using Radia code. The "pusher" magnets method was found to work well for trajectory alignment and radiation phase error compensation, and pole micro-machining for the compensation of multipole errors of field integrals within each segment. The work on detailed design of these two systems and the liner system will continue in FY14.

Catalysis Program in Sustainable Fuels

LDRD # 13-038

Jingguang Chen

PURPOSE:

This LDRD project establishes a research program led by Jingguang Chen, who has started a new position as a Joint Appointee between BNL and Columbia University as of FY2013. Under this project, Dr. Chen will establish a new program in catalysis science at BNL and Columbia University. The LDRD program will provide initial research funding to start research at both BNL and Columbia. At BNL, Dr. Chen will initiate laboratory research, including hiring research staff, and will collaborate with the existing BNL catalysis and electrocatalysis research groups. At Columbia, a subcontract to Dr. Chen will provide startup funding for his laboratory research, including initial graduate student costs. The research efforts will be linked under a common Catalysis Program in Sustainable Fuels. The overall impact of this project will be to strengthen the BNL catalysis science program through new linked research thrusts and the addition of an internationally distinguished catalysis scientist.

APPROACH:

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. A leading energy challenge in the 21st century is to find alternative means to power our transportation infrastructure.

Among energy alternatives, renewable liquid fuels are very promising. Liquid fuels based on organic compounds have advantages in energy density, transportability, and compatibility with the existing fuel and engine infrastructure. Routes to renewable fuels - from biomass, conversion of CO_2 combustion products, or renewable electrical energy sources – involve activation of stable small molecules such as CO_2 and H_2O to synthesize larger hydrocarbon or oxygenate (alcohol, ether, ester) molecules. Dr. Chen's research will focus on fundamental research to improve catalysts and processes for fuels synthesis from small molecule starting materials such as syngas (CO and H_2), CO_2 and H_2O.

Dr. Chen's research is closely linked to the existing catalysis program in the chemistry department. Through co-advised postdoctoral fellows (Xiaofang Yang and Sergei Rykov), Dr. Chen has collaborated with Dr. Jose Rodriguez, Dr. Ping Liu, Dr. Dario Stacchiola, and Dr. Sanjaya Senanayake. Dr. Chen's research also includes collaborations with the co-Principal Investigators of the Synchrotron Catalysis Consortium.

TECHNICAL PROGRESS AND RESULTS:

During the first year of LDRD funding Dr. Chen's group focused primarily on setting up equipment at Columbia and BNL. At Columbia the Chen Group finished the assembly of several ultrahigh vacuum systems for surface science studies, a batch reactor for reaction kinetics and surfaces intermediates, and a flow reactor for steady-state evaluation of catalysts. All the systems were calibrated and became operational by May 2013. Results from using these techniques led to several publications. These preliminary results were also instrumental in receiving an FWP grant for Dr. Chen's efforts at BNL.

At BNL the Chen group members were involved in the design of two laboratories located in the newly renovated lab space in the Chemistry building (555). Several techniques, including an ultrahigh vacuum system for temperature programmed desorption, a CO Chemisorption piece of equipment for measuring surface areas of catalysts, and an electrochemical system for electrocatalysis, were assembled and are currently being calibrated. The Chen Group members started working with the Chemistry and BNL facility personnel to obtain the certification and approval for performing experiments in these two laboratories.

Future milestones at BNL:

Oct. 2013 – Sept. 2014: Finish lab certification and start performing experiments at BNL.

Oct. 2014 – Sept. 2015: Start publishing results from BNL laboratories.