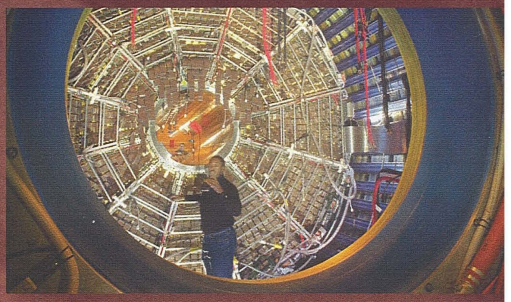
BNL-52351-2010

LDRD 2010 Annual Report

Laboratory Directed Research & Development Program Activities



BROOKHAVEN NATIONAL LABORATORY

BNL-52351-2010

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

March 2011

Acknowledgments

The Laboratory Directed Research and Development (LDRD) Program is managed by J. P. Looney, who serves as the ALD for Policy & Strategic Planning, and by Kevin Fox, Special Assistant to the Assistant Laboratory Director for Business Operations (ALDB). Preparation of the FY 2010 report was coordinated and edited by J. P. Looney and Kevin Fox who wish to thank Kathi Barkigia and Sabrina Parrish for their assistance in organizing, typing, and proofing the document. A special thank you is also extended to the Production Services Group for their help in publishing. Of course, a very special acknowledgement is extended to all of the authors of the project annual reports and to their assistants.

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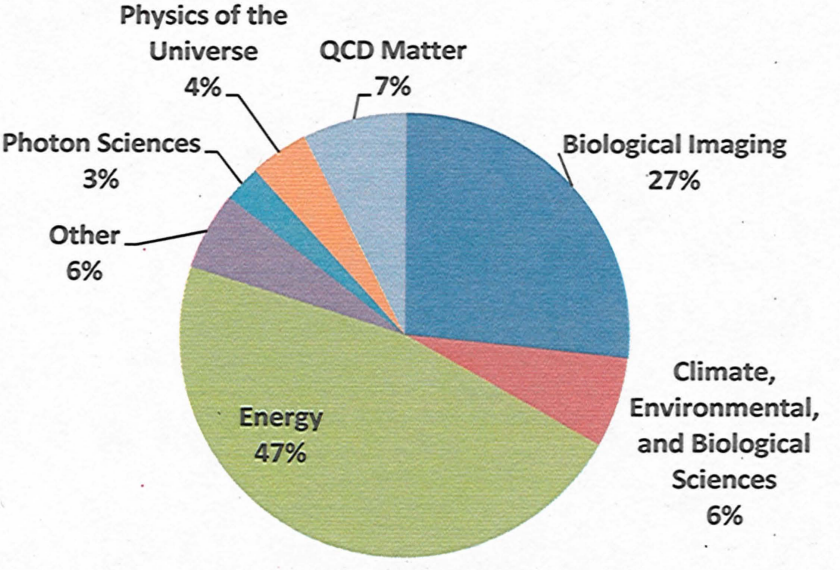
Introduction

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 FY2010, as required. In FY2010, the BNL LDRD Program funded 51 projects, 28 of which were new starts, at a total cost of $11,272,216. Approximately 6% of the total funds was invested in a focused FY2010 LDRD call for proposals and the remaining ~94% was awarded to openly competed LDRD projects.

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 and 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 four smaller initiatives that support growth and program development in targeted areas, i.e. Accelerator Science and Technology, Biological Imaging, Computation, and Detectors for National Security. Approximately 94% of BNL LDRD funds supported one of the major or targeted initiatives, of which about 67% supported the five major initiatives. About 6% was invested in other innovative research and development activities. In total, these LDRD investments supported 72 postdoctoral researchers and graduates students in whole or in part. In FY2010, new LDRD investments supported the BNL initiative in QCD Matter; $6.467M supported projects started in FY2010, of which ~$700k funded the focused call for proposals in the Science and Technology of an Electron Ion Collider (EIC). However, the funding in Figure 1 below for QCD Matter is somewhat larger (7%) due to ongoing EIC-related projects).

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.



Allocation of FY2010 LDRD Funding by BNL Initiative Area

LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

2010 PROJECT SUMMARIES

Sensitive Searches for CP-Violation in Hadronic Systems

LDRD Project 07-005

Yannis Semertzidis

PURPOSE:

This LDRD supported the development of the software program for the needs of the deuteron and proton EDM experiments. The tracking program is used to study beam and spin dynamics of charged particles stored in a ring with arbitrary electric and magnetic field combinations.

APPROACH:

The task of developing an accurate and at the same time efficient beam and spin dynamics software tracking program requires sophisticated levels of understanding of the issues involved. We therefore had to make sure that we could check our results in a reliable way. We decided to first start with a continuous magnetic ring with weak focusing that could be estimated analytically to high precision.

Our post doc Dr. Fanglei Lin worked on this project using an efficient software program already developed for the needs of RHIC to study the effect. She did her Ph.D. thesis using this program analyzing the spin resonances at AGS. Her experience with this program was extensive and her former supervisor Dr. Alfredo Luccio is a member of our collaboration and therefore continued to work with her.

A graduate student from Istanbul Technical University, Mr. Selcuk Haciomeroglu, worked with an entirely different approach using differential equations describing the particle velocity and spin precession in an electromagnetic field region. He then used 4th order Runge-Kutta (RK) predictor-corrector integrator with a very small time step (0.5 ps) to integrate the equations.

The third method used was an actual analytical estimation of the effects to second order. Those estimations were needed in the muon g-2 experiment so that corrections could be applied to the observed muon frequency precession due to finite beam emittance. They have been calculated very early on (several decades earlier) by several authors using different techniques and are in excellent agreement.

The EDM requirements for the storage ring are very strict. In addition, the commonly available programs don't regularly include electric fields since they add a substantial complication. This complication arises from the fact that while magnetic fields conserve the particle kinetic energy, the electric fields conserve only the total mechanical energy (kinetic plus potential energy) and not just the kinetic energy. During last year we have developed a thorough understanding of the issues involved and for the most part we have solved them.

TECHNICAL PROGRESS AND RESULTS:

Since the magnetic field case is easier we developed this one first. After debugging the software programs we were able to estimate the so called pitch effect, i.e. the g-2 spin precession correction in a magnetic field of a particle with non-zero vertical oscillation amplitude. That effect to second order is at the parts per million (ppm) level and the RK integrator gave a result that was in agreement with the analytical estimation to very high accuracy. We were also able to

define the origins of those corrections in both the particle physical motion and to the relativistic effects due to motion along the field direction.

It was found that the efficient program did not estimate the second order effects accurately, giving misleading answers. After determining the origin of those problems, it was possible to estimate the second order effects accurately enough without compromising its calculation speed too much. This program has been benchmarked and is now used to estimate the spin coherence time of the stored beams at COSY/Jülich in Germany.

The next step to track particles in storage rings dominated by strong electric fields proved to be much more challenging. After a few months of debugging the program that used the RK method, we were able to produce a reasonable tracking with accuracy that was acceptable for the needs of the experiment. This program is slow; using a Mac book pro that has 2.7 GHz CPU speed, it can track an equivalent of 10 ms particle storage time in about 10 hours of continuous running. The estimation of particle oscillation tunes for the horizontal and vertical directions as estimated by two different techniques, one of which is analytical, and the results from the RK method agree to very high accuracy. This gives us confidence in the tracking results.

The fast programs need to use a different approach in the presence of E-fields than the one used in magnetic fields only. The issue of changing the particle momentum during horizontal oscillations complicates the equations of motion and the integration method. This development is tedious and requires novel techniques that have not yet been applied in the field of beam and spin dynamics tracking. The concepts have been developed and the application is currently in its final phase.

We are preparing a proposal for the DOE Office of Nuclear Physics that will be submitted by the end of the spring 2011.

Strongly Correlated Systems: From Graphene to Quark-Gluon Plasma

LDRD Project 08-002

D. E. Kharzeev and A. M. Tsvelik

PURPOSE:

The fundamental goal of the project is to study the role played by the chirality describing the state of motion of the relativistic particles in a condensed matter setting, such as mono and multi layer graphene samples. The chirality manifests itself in a qualitatively different way depending on the number of graphene layers. The technical objective of our project is to study the effect of the chiral nature of the particle spectrum on the transport properties of mono and multi layer graphene.

APPROACH:

Graphene samples are unique in their high mobility, controllable properties and most notably the relativistic dispersion relation of carriers. Even though the fractional quantum Hall effect has been reported recently in suspended samples, the observation of effects of electron-electron interaction at low magnetic fields in exfoliated graphene remains a challenge. We have realized that working with multilayered graphene may provide a way to detect interaction effects. Indeed, in a n-layer graphene, the Berry phase associated with the chirality is $n\pi$. This corresponds to an n-th power of momentum in the dispersion of the quasi-particles. It follows that while the effective mass of carriers in mono-layer graphene vanishes at low energies, it is constant in a graphene bi-layer and is divergent in a graphene tri-layer. Experimentally this behavior has been reported in measurements made by our team of collaborators: Liyuan Zhang, Yan Zhang, Jorge Camacho, Igor Zaliznyak, Tonica Valla, and Myron Strongin at Brookhaven National Laboratory. Collaboration with the local group proved to be useful and essential for the project.

To provide our experimentalists with theory support, we developed a transport theory in graphene multi-layers including effects of screening due to the electron-electron interaction.

TECHNICAL PROGRESS AND RESULTS:

It is known that being able to account for an ionized Coulomb impurity is essential for the description of the transport in non-ballistic graphene mono-layers. In fact the constant mobility slightly away from the neutrality point can be explained if the cross-section scales with the inverse energy. As this is a property of Coulomb impurities, it is clear that they are responsible for the mobility being constant at high enough densities. The impurities in bi or tri-layers are similar to those in a mono-layer. Moreover, the density dependence of the mobility is qualitatively similar to the one in a mono-layer. The naïve application of the transport theory to the multi-layers would not produce the correct mobility density dependence. We therefore had to resolve this puzzle. The key to this question is the following observation. The density of states in multi layers is big and even divergent at low energies. It promotes effects of interactions. One of the most obvious such effects is the screening of the external ionized potential. Contrary to a mono-layer, in a multi-layer the impurity is universally screened and becomes proportional to an inverse density of states.

Remarkably, inclusion of interaction effects on the level of screening allows us to understand the major qualitative features of experimental results.

Getting to Know Your Constituents: Studies of Partonic Matter at the EIC

LDRD Project 08-004

Werner Vogelsang

PURPOSE:

The goal of this LDRD was to develop and commission an operational framework for the extraction of the distributions of quarks and gluons, the elementary particles of the strong interactions in nature, from future data taken at an Electron-Ion Collider (EIC). This goal has been fulfilled. The main technical result of the work pursued in this LDRD is an extensive computer (Fortran) code that may be used to carry out sensitivity studies for quark and gluon distributions in future EIC measurements. The code helps determine the optimal choices for the collision energies and detection capabilities at an EIC and could therefore become an essential part of the preparations for this machine.

APPROACH:

The EIC, with its unique assets of high energy and availability of polarized and nuclear beams, will be the ideal place for investigations of the quark and gluon (or, "parton") sub-structure of nucleons and nuclei. Other lepton scattering experiments, as well as RHIC, are presently already providing information and will continue to do so in the pre-EIC era. In making the science case for an EIC, it is therefore important to assess the impact that EIC measurements would have. This is also closely tied to the developments of the optimal design of an EIC. This need for detailed early studies is the background for the present project. The specific implementation of analyses of quark and gluon distributions in polarized nucleons and in nuclei and their application to the needs at an EIC had not been achieved so far.

Our investigations were performed in a staged approach. The first stage was the development of the global analysis technique and its benchmark application to RHIC data. This was completed in 2009 and reported previously. Over the past year, we have further improved the analysis code by implementing a full analysis of the correlated experimental uncertainties. For this, we devised a new analytical method for treating the normalization uncertainties of the data and correlations among uncertainties (K. Boyle, C. Gal). This method significantly speeds up the performance of the analysis code. We also completed the second stage of the project, by adding simulated EIC data to the analysis (S. Taneja). Here the goal was to investigate the impact future EIC data would have on our knowledge about polarized parton distributions. In collaboration with Michael Savastio at Stony Brook University, we have used PYTHIA to simulate deep-inelastic scattering events at the EIC. The generated sample has been used to obtain estimated statistical uncertainties for spin asymmetry measurements at the EIC. We have next used the results of the benchmark analysis discussed above and computed the actual spin asymmetries at the EIC. These asymmetries were then randomly shifted with a Gaussian distribution, making use of the uncertainties previously determined with PYTHIA. The resulting EIC "data" and their "uncertainties" were added to the full global analysis. The analysis was then run with all data sets, including the "EIC data sample", and new sets of parton distributions and their uncertainties were obtained. The main technical analysis method we are using to carry out the work is a mathematical approach known as "Mellin technique". This technique allows us to incorporate all presently available data at "next-to-leading order" of QCD. The actual analysis can then be done in terms of a χ^2 analysis. This also includes a proper treatment of the correlated experimental and theoretical uncertainties and their impact on the extracted quark and gluon distributions.

The co-investigators on this LDRD project were A. Deshpande (Stony Brook) and R. Milner (MIT), D. Kharzeev, and R. Venugopalan (BNL). We decided to choose a somewhat unusual "strategic" approach for realizing the goals of this LDRD: rather than hiring a postdoctoral researcher for the duration of the project, we only did a part-time contract hire and used the remaining funds for attracting more senior visitors for short and/or long-term visits to the laboratory. We hired Dr. Swadhin Taneja on a contract basis from Stony Brook University for the past year. This strategy has worked out exceptionally well. In addition, K. Boyle and C. Gal (Stony Brook) have been collaborators in the project.

We have had visits by M. Stratmann (Würzburg/Regensburg), D. de Florian and R. Sassot (Buenos Aires U.) in FY10, who are experts in analysis techniques for nucleon and nuclear quark and gluon distributions. They also participated in work on the project. LDRD funds have also been used for travel by the PI to workshops and conferences to present the results of our global analysis, among them to two EIC workshops at the INT in Seattle this year.

TECHNICAL PROGRESS AND RESULTS:

FY 2010 was the final year of funding for this project. As mentioned above, we have essentially completed the project. A sample result of a global analysis that includes projected EIC data is presented in the Fig.1, which shows the spin-dependent gluon distribution of the proton, as a function of momentum fraction. As can be seen, EIC measurements would be expected to give a significantly decreased uncertainty of the gluon distribution, compared to the present situation. We are now using these results to identify the requirements for energies and detectors at the EIC.

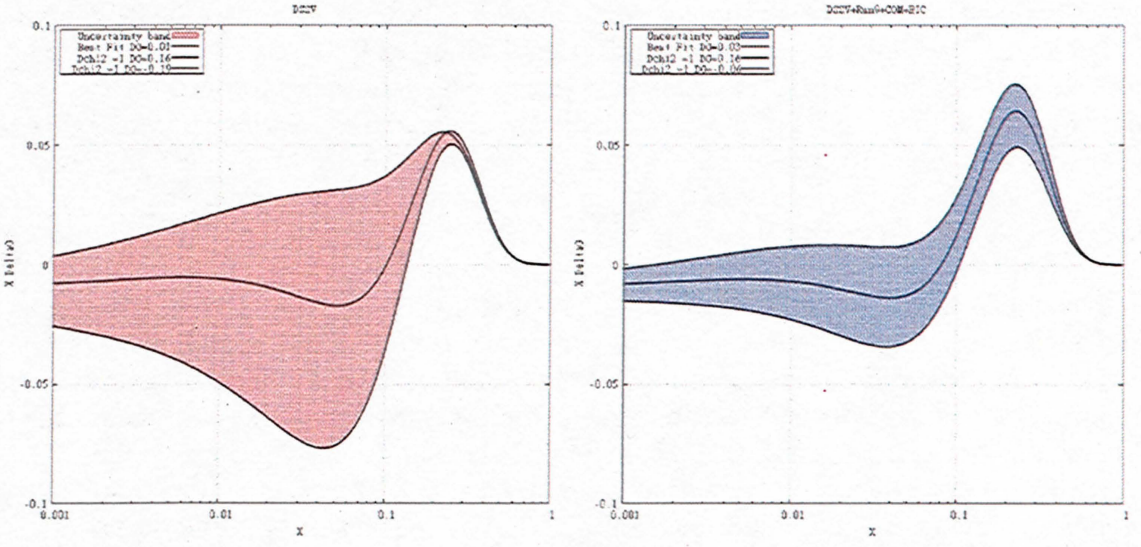


Fig.1: Spin-dependent gluon distribution Δg as function of gluon momentum fraction x, along with its 1-sigma uncertainties. Left: Extracted from previous RHIC and DIS data, as published in ***Phys. Rev. D80 (2009) 034030****. Right: Extracted from latest Run-9 RHIC pion data, COMPASS data, and simulated EIC data for 10 GeV on 250 GeV ep collisions with luminosity 6/fb.*

Development of the Deuteron EDM Proposal

LDRD Project 08-005

Yannis Semertzidis

PURPOSE:

This LDRD supported the study of the maximum Electric (E)-fields that can be applied between two specially prepared metallic plates as a function of the distance between them. The technical goal of the proton EDM experiment is to achieve reliable operation at 10.5 MV/m for a 3 cm plate separation.

APPROACH:

For the E-field development, we have borrowed a high voltage testing system from Cornell University and have installed it on the AGS experimental floor. We also borrowed specially made plates, one made out of stainless steel (SS) and the other of titanium (Ti). After conforming with all the safety requirements, we were able to turn it on and take data. Selcuk Haciomeroglu, a Ph.D. student from Istanbul Technical University working on the development of the EDM proposal is doing his Ph.D. thesis on this work.

The 10.5 MV/m bending electric field is very conservative in comparison with the new methods developed for energy recovery linac (ERL) R&D. However, the ERL R&D was done on plates with area several hundred cm^2, while we need an area three orders of magnitude larger for the EDM storage ring. Depending on the results of this test, we may have to increase the storage ring radius. Decreasing the electric field by 1 MV/m by increasing the ring radius by 10%, for example, increases the total projected cost by less than 10%, since some things, beamline design, etc., are independent of the storage ring radius.

TECHNICAL PROGRESS AND RESULTS:

The electric field testing helped us understand the issues with very high electric fields on metallic surfaces. Usually, the E-field that can be safely applied on metallic surfaces is of the order 5-10 MV/m, but it can go up to 30 MV/m when the surface is treated with high pressure water rinsing (HPR). First we have tested the plates without HPR to set the baseline. We have also caused several sparks to establish the recovery time and have also applied high pressure glow discharge, which helps clean up the plates after a severe spark. These tests determine the recovery time for the plates in case we have a major discharge during the experiment.

During the test we learned the following procedural lessons:

1) Raising the high voltage between the plates needs to be done very slowly, monitoring the dark current very closely. A high voltage breakdown is very hard to recover from by spark conditioning alone. We established certain dark current limits before we could raise the high voltage to the next level.

2) We found that the plates recover to a very high degree when we apply a glow discharge using an Ar-He gas mixture at about 50% level each and a pressure of about 100 Torr. The glow discharge needs to be on for about 20 minutes to clean up any debris, due to high voltage breakdown, from the metallic plates. After glow discharge we were able to mostly recover to the pre-sparking levels.

At the conclusion of this LDRD, the preliminary stage of the tests has been completed. We are now preparing for the next phase using specially treated stainless steel plates. We have now acquired new plates from Cornell University that have been treated with HPR in order to compare their E-field performance. Those plates are currently being installed in the vacuum chamber for bake-out and pump-down. The vacuum chamber interior is being cleaned and will be ready for testing within two months from now.

Another of the outcomes of this LDRD is data for preparation of a proposal for the DOE Office of Nuclear Physics that will be submitted by the end of the spring 2011.

Development of Small Gap Magnets and Vacuum Chamber for eRHIC

LDRD Project 08-008

Vladimir N. Litvinenko

PURPOSE:

The development of small gap magnets, both dipoles and quadrupoles, and a vacuum chamber compatible with a multi-pass energy-recovery linac has a high potential for making the ERL a cost effective solution for eRHIC using the RHIC tunnel for four of its five return loops. Using the RHIC tunnel is the only viable option of operating eRHIC with electron energies at and above 10 GeV. Otherwise - like in the ring-ring option- the power of synchrotron radiation will be too high and energy consumption will be prohibitive. Designing and testing the quality of mini-gap (gaps ~5 mm) dipole and quadrupole magnets with a common vacuum chamber are a critical step for developing this concept. Using results of the magnetic field quality for tracking particles through 4 passes around the RHIC is a critical validation of this approach.

APPROACH:

Using an ERL for eRHIC provides an electron beam with very small emittance and as a result with very small sizes. In return, it allows one to design loop magnets for eRHIC with very small gaps (few millimeters) and install them at a single vacuum chamber. Small gaps and low magnetic fields of the magnets provide for an energy efficient lattice extending for about 16 kilometers. The main research was focused on checking the viability of this concept, including studies of the quality of magnetic fields in prototype dipole and quadrupole magnets, stresses and deformation of thin-wall convolutions of the vacuum chamber. Small gap magnets with low-current coils are low weight and can be inexpensive. The approach was to design such magnets and test various manufacturing techniques (grinding, EDM, etc.) and check the quality of the resulting field. The resulting field errors should be compared with requirements coming from numerical tracking.

Year 1 milestones: a) model, design and manufacture dipole magnet; b) develop tracking code; c) design and simulate vacuum chamber stresses and sagging with ANSYS

Year 2 milestone: a) design and manufacture quadrupole magnet; b) complete magnetic measurements; c) manufacture prototype of vacuum chamber

Year 3 milestone: a) analyze the data and a make decision on the next step

TECHNICAL PROGRESS AND RESULTS:

We had analyzed the results of magnetic measurements for the dipole and quadrupole prototypes made at BNL as well made by high quality manufacturers outside of BNL. For reasons beyond our control, the final quadrupole ordered from outside of BNL is not yet delivered.

We use a Group 3 Hall probe mounted on a 3-axis translation stage to map the field. The probe and its holder have the thickness of 3mm, which will fit even the 5mm gap. This measurement system has the ability to do both longitudinal (z direction) and vertical (y direction) scans. However, due to the limitation of the small gap, the ability of the horizontal (x direction) scan is very limited, even for a 10 mm gap quadrupole. The movement accuracy of the translation stage

can be as low as 1 micron. In a real measurement, the minimum movement step is 25 microns. The relative coordinate of the magnets with respect to the probe home position is measured through the geometric survey. The quadrupole prototype is measured at exactly the same set-up as the dipole.

The quality of the dipole magnetic field is satisfactory and allows considering a more economic combined function magnet for eRHIC. The quality of the quadrupole field is marginal and better manufacturing quality is required. We expected that the outside manufacture would deliver a better product.

Table 1: The high harmonic component of the field at 2mm and 4mm off center. They are measured by units, 0.01% of the quadrupole component at the same location.

Harmonic number	At 2 mm	At 4 mm
2 (Sextupole)	43	88
3 (Octupole)	7.2	19
4	-4.2	-34
5	-2.8	-44
6	0.3	8.2

We also simulated the effect of quadrupole allignment errors of ±100 microns on the eRHIC orbit and found that a traditional SVD orbit correction method is sufficient to control the orbit withing 50 microns RMS.

The LDRD part of these studies is completed.

Novel Methods for Microcrystal Structure Determination at NSLS & NSLS-II

LDRD Project 08-022

Allen M. Orville, Alexei S. Soares, Howard R. Robinson and Annie Héroux

PURPOSE:

Without a doubt structural biology has revolutionized our understanding of biological processes at a molecular level. Macromolecular crystallography (MX) is the predominant method in structural biology and continues to be recognized by Nobel Prize selection committees. For example, the Nobel Prizes in Chemistry in the last decade awarded to MacKinnon (2003), Kornberg (2006), Tsien (2008), and Ramakrishnan, Steitz, and Yonath (2009) all focused on MX and used synchrotron radiation.

These and many other important advances in MX continue to motivate researchers to their attempt to solve increasingly difficult scientific problems, especially crystal structures of large macromolecular assemblies and membrane proteins. Unfortunately, these systems often yield only microcrystals measuring just a few microns in one or all dimensions. Although crystalline, a great difficulty of such microcrystal morphology relates to extracting the highest resolution diffraction data possible from such small samples. To that end, a critical step is mounting microcrystals in such a way as to minimize the amount of solution surrounding the microcrystal. It is absolutely essential to reduce the noise in the data by background scattering from the solution. However, typical methods for mounting microcrystals include scooping them up by hand with 20-300 μm loops and flash cooling them. This approach is especially difficult when working with microcrystals and most often includes a large volume of solution around each crystal. The result is a very weak diffraction signal relative to the large background noise. Consequently, the often observed showers of microcrystals are discarded as frustrated scientists continue to explore other crystallization conditions. Thus, traditional MX methods simply do not work for many of the frontier challenges in structural biology.

APPROACH:

We are very excited to report an alternative mounting and data collection strategy that we developed specifically for use with slurries of microcrystals. Our new methods are better at controlling the amount of solution surrounding microcrystals and consequently provide more signal and less noise in the data. The novel approach is to use acoustic energy to launch 2.5 nanoliter droplets of microcrystal-containing solutions through the air, catching them on standard mounts, cryocooling them, and then using a several micron-sized X-ray beam to raster-scan across the mesh to locate and collect diffraction data serially from several microcrystals. We are the first to report that moving crystals with acoustic energy does not affect their diffraction quality. Moreover, we were able to use the diffraction data from several micron-sized crystals to solve the three-dimensional structure with SAD phasing methods. Therefore, our results are generally applicable and will impact nearly the entire field of macromolecular crystallography. We also envision applications of our methods at the new free electron laser X-ray sources in Europe, Asia and at SLAC in the USA.

Research Plan: Our strategy to collect X-ray diffraction data from microcrystals is illustrated below in Fig. 1: **Acoustic Droplet Ejection (ADE)** and **Raster-Scan.** First we mount the microcrystal slurry with ADE methods. Next we use the X-ray beam to scan across the grid until

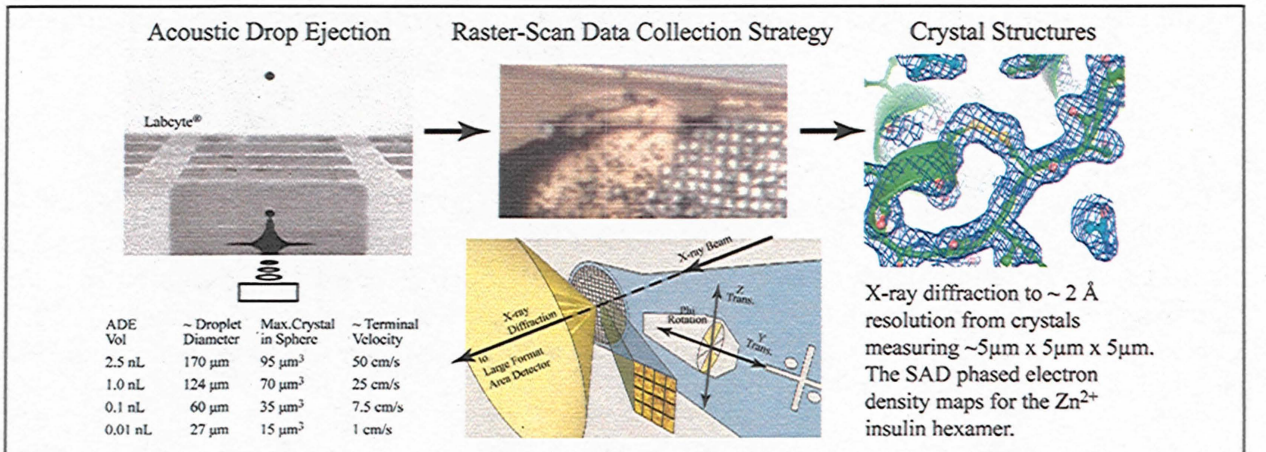


Fig. 1: *Acoustic Droplet Ejection (ADE) methods, with a raster-scan data collection strategy, yield crystal structures. (**Left**) An illustration of ADE launching a 2.5 nL water droplet (~170 µm in diameter) from the surface in a standard 96-well plate. (**Middle, top**) An image from beamline X25 of the actual insulin microcrystal slurry supported on MicroMesh (25µm x 25µm grid pattern) used to solve the structure. (**Middle, bottom**) Our concepts for raster-scanning with a microdiffractometer to support cryo-crystallographic structure determination. (**Right**) The electron density map from a full dataset merged from nine microcrystals with a 20µm x 20µm X-ray beam at X25 within the field of view shown in the middle panel.*

we find a microcrystal via diffraction. A portion of the whole diffraction data is then collected from each microcrystal. The whole dataset is built up from several microcrystals as necessary.

TECHNICAL PROGRESS AND RESULTS:

Funding for this LDRD project ended on September 30, 2010. In the past, it supported partial salaries for Dr. Marc Allaire with his graduate student, Mr. Matthew A. Engel (full salary, enrolled in the Biomedical Engineering Program at SUNY-SB), as well as Drs. Soares and Orville (PI). We routinely produce microcrystal showers of several well-known standard proteins including lysozyme, Zn^{2+} insulin, taumatin, and nitroalkane oxidase. We are currently focusing on the ADE technology and the Raster-Scan strategy at beamline X25.

Dr. Soares and Mr. Engle visited Labcyte (Sunnyvale, CA) from 11/2008-10/2009 to develop ADE methods and test them for suitability with micro-crystallography. Drs. Soares, Allaire and Mr. Engle also traveled to beamline ID23-D at the Advanced Photon Source (APS) from 12/18-21/2009 to use their minibeam facility for data collection from microcrystals mounted with ADE methods (see below). We believe that our most important innovation to date is our plans and development of ADE technology for use in microcrystal structure determination. Consequently, these concepts are the basis of the record of invention and our initiation of the patent process during FY 2009.

ADE is a "touchless" method that focuses ultrasonic acoustic energy into a liquid, which mixes and ejects small droplets from the surface and deposits them to a specified location with micron accuracy. This strategy also has the advantages of precision, speed (up to 200 Hz), ultra-low-volume transfer, and the technology eliminates cross-contamination of samples. The droplet size is controlled over a range of ~10 picoliters to 2.5 nanoliters by selecting different frequencies and harmonic overtones. We have shown that ADE methods can eject 2.5 nanoliter droplets of a suspension of microcrystals in Mother Liquor. We prepared two types of microcrystal slurries,

Zn^{2+} insulin and lysozyme that each contained high concentrations of microcrystals in the 2-20 μm size range. We brought our samples to the Labcyte facility to use ADE methods to transfer 2.5 nanoliter droplets (~170 μm in diameter) through the air to a conventional MiTeGen MicroMesh, which spread to cover about 200 μm region of the grid. We observed numerous microcrystals in the 2-20 μm range in their largest dimension disperse on the grid that transferred with the droplet. These crystals were subsequently rapidly cryo-cooled with liquid nitrogen, a standard procedure in crystallography, and then analyzed for diffraction quality and structure determination. The X-ray diffraction data were collected at two different minibeam-capable synchrotron beamlines: X25 at the NSLS and ID23-D at the Advance Photon Source (APS). Our results indicate that ADE does not alter the crystal quality as deduced from the X-ray diffraction data and refined crystal structures. Both molecular replacement and SAD phasing techniques were used to solve the structures of ADE-transferred microcrystals.

Our *blue-sky* vision for this LDRD project includes the last objective or our proposal submitted to the NIH Roadmap Initiative (RFA-RM-09-022) Transformative Research Projects Program (R01). We still plan to develop a very high throughput, **Optical Goniometer** as illustrated in Fig. 2. We will start with an ADE system that launches ~150 picoliter (~65 micron diameter) droplets into the air from a well or sitting drop containing a microcrystal slurry. In the final development, the transducer frequency and microcrystal slurry concentration will be optimized such that each droplet is ~10 picolilters (~25 microns in diameter), contains approximately one microcrystal each, and maximizes the ratio of crystal volume to droplet volume. We will hold each droplet in the X-ray beam with an optical trap comprised of a single laser beam. Furthermore, linearly polarized laser light will also apply a torque to birefringent crystals, and thus orient and rotate each microcrystal. With laser powers in the 10 – 100s mW range, optical traps can manipulate a range of sizes of aerosol droplets, and generate several hundred pN•nm of torque to rotate micron size particles with angular velocities up to 200 rad/s. Therefore, our optical goniometer will also provide a means to mix and initiate enzyme reactions within ADE droplets, as well as to collect diffraction datasets with a duty cycle that matches the lifetime of each sample used at the NSLS-II, other third generation X-ray sources, or the intense X-ray pulses at the FELs.

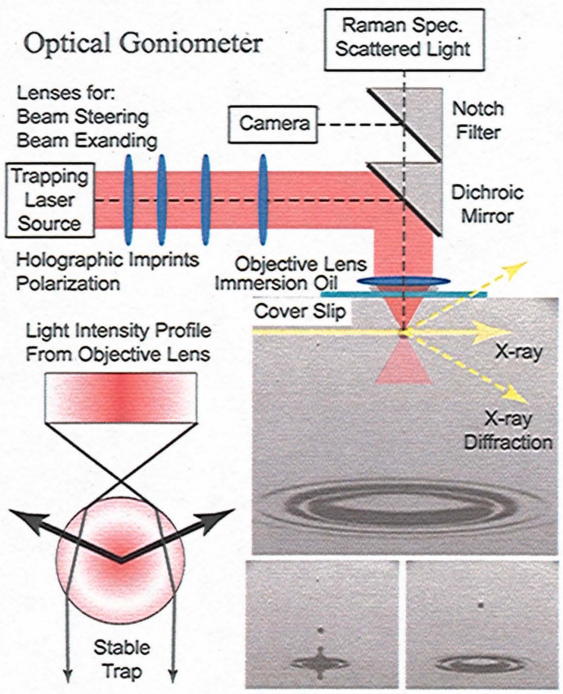


Fig. 2: Coupling ADE methods with laser-based optical tweezers creates an optical goniometer suitable for very high throughput micro-crystallography.

Combined PET/MRI Multimodality Imaging Probe

LDRD Project 08-025

David J Schlyer

PURPOSE:

The goal is to design a multimodal imaging probe for use with our combined MRI-PET animal imaging system which will allow simultaneous PET and MRI measurements. The probe will contain both a positron emitting radionuclide and a superparamagnetic MRI contrast agent in a single iron oxide nanoparticle. There is mounting evidence that most disease processes can be identified by altered molecular profiles and/or cell behavior prior to visual anatomic alterations. Insight into these processes could potentially allow for (1) the early detection of disease, (2) more accurate prognoses and personalized treatments, (3) the ability to monitor the effectiveness of therapeutic treatments, and (4) improvements in our understanding of how cells behave and interact in their intact environment in living subjects. This dual probe concept combines the strengths of both PET and MRI into a powerful new tool for quantitative molecular imaging.

APPROACH:

Molecular imaging with PET has already had a profound effect on our understanding in both preclinical and clinical areas including cancer research and many aspects of neuroscience from cognition to psychiatric diseases. MRI is beginning to move from structural and functional imaging to molecular imaging, but this is in the early stages and requires considerable development. The combined use of PET and MRI with our proposed imaging agents could be a quantum leap forward in synergistically addressing problems of cellular pathophysiology. One key advantage of this approach is that the radionuclide probe is included in the nanoparticles which means that the radionuclide will stay with the nanoparticles as opposed to some other radiolabeled nanoparticles in which the radionuclide is attached to the nanoparticles using a chelating agent which may release the radionuclide under biological conditions.

We will address each of our specific aims in the following ways.

Specific Aim 1 - Incorporate Iron-52 in Nanoparticles: Superparamagnetic iron oxide (SPIO) MR imaging contrast agents consist of an iron oxide nanoparticle core covered with a coating material (such as dextran). A diagram of the probe is shown in Figure 1.

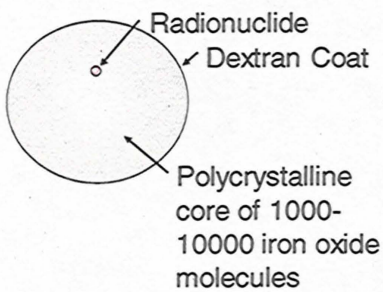


Fig. 1: *Schematic diagram of the radiolabeled nanoparticle molecular probe*

We have prepared magnetic particles doped with the radionuclide Fe-52. They were synthesized by a microemulsion technique in the lab with controllable sizes of 4-150 nm using a method developed by Molday [1]. The nanoparticle is coated with dextrane to reduce agglomeration. The labeling with biologically active molecules will be done in collaboration with the Center for Functional Nanomaterials (CFN) at Brookhaven National Lab (BNL) and the BNL Medical Department radiochemists.

Specific Aim 2 - Use Simultaneous PET/MRI: We have developed a scanner that will allow the simultaneous acquisition of quantitative physiological data using PET, and high resolution anatomical or even complementary functional data using MRI.

TECHNICAL PROGRESS AND RESULTS:

The iron oxide nanoparticles synthesized by the Molday method gave a good magnetic signal as shown in Figure 2. The darker the circle, the better the contrast agent.

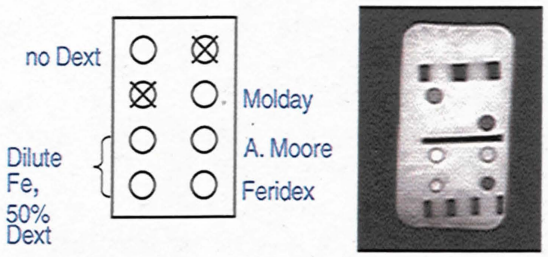


Figure 2 Comparison of magnetic characteristics with different methods of synthesis (Molday [1] and Moore [2]) with commercial iron oxide nanoparticles (Feridex).

As can be seen, the preparation using the Molday approach gave a signal that was very similar to the signal from the commercial Feridex paricles. These particles were used in PET experiments and the whole body distribution in the rat is shown in Figure 3.

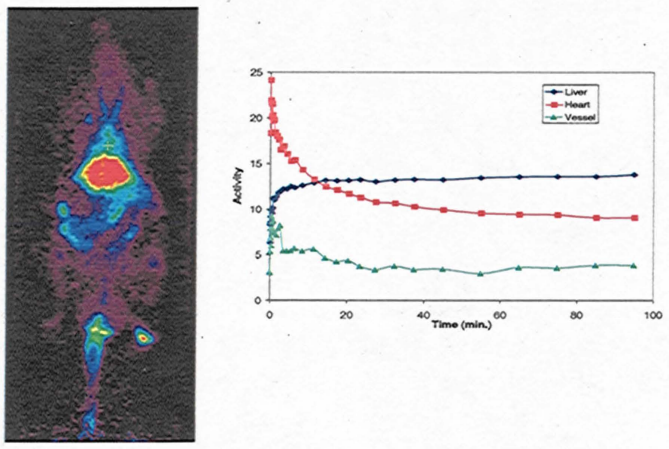


Fig. 3: Iron-52 labeled iron oxide nanoparticle biodistribution in a rat over 95 minutes.

The iron oxide nanoparticles were also imaged in a mouse using MRI. The same pattern of accumulation is shown, with a high accumulation in the liver (Figure 4).

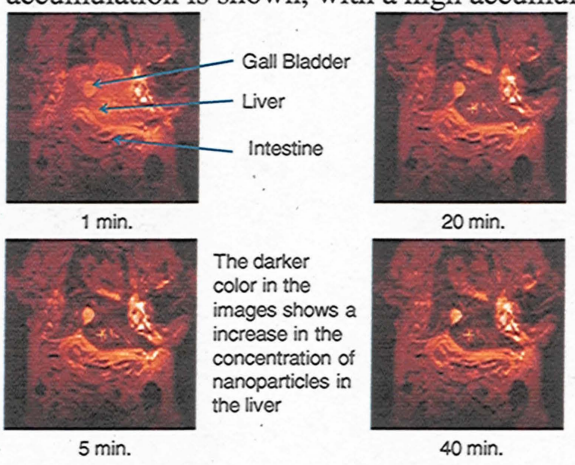


Fig. 4: Iron oxide nanoparticle biodistribution in a mouse liver over 40 minutes.

The final step in these experiments will be to carry out the simultaneous imaging. This can happen as soon as we have access to iron-52 again at the BLIP.

Follow on Funding: A grant of 300K over 2 years was obtained from Battelle as part of a Multi-scale Toxicology Initiative. The grant is to use these multimodality probes to investigate the biodistribution of these nanoparticles and to assess the toxicity.

References:
1. R. S. Molday, D. Mackenze, *Journal of Immunological Methods,* 1982(52): 353-367.
2. A. Moore, E. Marecos, A. Bogdanov, R. Weissleder, *Radiology*, 2000(214): 568-574

Genomic DNA Methylation: The Epigenetic Response of *Arabidopsis Thaliana* Genome to the Long-Term Elevated Atmospheric Temperature and CO_2 in Global Warming

LDRD Project 08-028

Qiong (Alison) Liu

PURPOSE:

The goal of this project is to determine the changes of DNA cytosine methylation in the genome of *Arabidopsis* plants in response to elevated ambient temperature and CO_2 concentrations such as would occur during global warming. This epigenetic information will help us identify genomic and genetic loci that are regulated by elevated temperature and CO_2 that can impact on plant development, flowering time, grain and biomass production, and to understand how regulation of DNA methylation in the plant genome can help plant's adaptation to environment.

APPROACH:

Exponential emission of CO_2 into the atmosphere resulting from human activities has led to an enhanced greenhouse effect or global warming. Prolonged increase of temperature has been shown to increase the growth rate and to induce early flowering of plants in laboratory experiments (Balasubramanian S. et al. PLoS genetics. *2006* 2(7): 980-9), and is correlated to biomass and grain reduction in crops (Peng S. et al. Proc Natl Acad Sci U S A. 2004 101(27): 9971-5). Palebotanical evidence has linked a fourfold increase in atmospheric carbon dioxide and an associated 3° to 4°C greenhouse warming to a well-documented major faunal mass extinction during the period of the Triassic-Jurassic boundary (McElwain JC et al. Science 1999 285: 1386-90). Some prior evidence suggests that plants may respond to altered temperature and CO_2 level via an epigenetic response. For example, microarray studies have identified many gene expression changes in *Arabidopsis* when the plant is grown at a few degrees higher temperature (Balasubramanian S. et al. PLoS Genetics, 2006, 2(7); 980-9). A few small RNAs are also generated or altered in *Arabidopsis* growing at a lowered temperature (Oh M. et al. Journal of Plant Biology, 2007, 50(5); 562-67).

We have taken several approaches to understand how elevated ambient temperature can function to affect the epigenome. We have used HPLC and LUMA assays to analyze the overall genomic DNA methylation and the bisulfite sequencing method to identify altered methylation in cytosine in the single nucleotide resolution. We have also analyzed the deep sequencing results of small RNAs libraries to identify the miRNAs that are altered in their expression by elevated temperature and CO_2. The altered siRNAs expression indicates regulation of genomic DNA methylation. We have completed analysis of 4 bisulfite sequencing libraries and 8 small RNA libraries in these plants.

For this progress, Alison Liu has collaborated with (1) Dr. Michael Zhang at Cold Spring Harbor Lab for bioinformatics work, (2) Cold Spring Harbor Laboratory Genome Research Center for sequencing small RNA libraries, and (3) Dr. Ecker's lab at Salk Institute.

TECHNICAL PROGRESS AND RESULTS:

This LDRD project started in March, 2008. The summarized results to date are as follow:

(1) The phenotypic characterization and the paper: *Arabidopsis* plants were grown in our newly purchased growth chambers at 23°C and 26°C. We have completed the characterization of the newly identified phenotypes and demonstrated that elevated ambient temperature can reduce seed production significantly and biomass production moderately, and promote root development in *Arabidopsis* plants. A paper is being written for publication.

(2) The small RNA expression and genomic DNA methylation changes induced by elevated ambient temperature and CO_2, and the Nature paper:
Small RNA libraries were generated using *Arabidopsis* plants grown at 22°C and 28°C, and 400ppm and 800ppm CO_2 concentrations, by following the Illumina small RNA preparation instruction manual. We have obtained duplicate libraries making 8 libraries in total. We have also found novel miRNAs and siRNAs with differentiated expression rates at different temperatures and CO_2 concentrations.

We have also sequenced bisulfite libraries to identify the genomic DNA methylation changes induced by elevated temperature and CO_2 concentration and analyzed the results using bioinformatics methods. These results also revealed the interaction between CO_2 and temperature. These results suggest that small RNA and genomic DNA methylation might play an important role in plant adaptation to elevated temperature and CO_2 concentration in global warming conditions.

A presubmission enquiry has been submitted to the journal Nature, and the Nature editor asked us to submit the complete manuscript. It's entitled "Elevated ambient CO2 concentration and temperature alter small RNA expression and DNA methylation in *Arabidopsis.*"

Fabry-Perot Interferometer & Hard X-ray Photoemission

LDRD Project 08-034

Elio Vescovo

PURPOSE:

The purpose of this LDRD is to manufacture a Fabry-Perot (FP) etalon by micro-etching techniques on a single crystal Si wafer. The etalon design has the advantage of easy construction and robust alignment, and could perform with energy resolution below 0.1 meV. The etalon is characterized by two resonators in series. The optical output of the system can be measured as a function of the temperature gradient between the two resonators.

APPROACH:

Recently the feasibility of high-resolution FP resonators working in the hard x-ray region (~14 keV) has been demonstrated [1]. The resonator consisted of two single crystals of α-Al_2O_3 separated by 50 mm. However, the two crystals must be aligned to nanometer precision. We proposed to manufacture the etalon by micro-etching techniques on a single crystal Si wafer. The critical alignment between the two diffracting Si planes is therefore automatically guaranteed with atomic level precision. The single piece interferometers will be produced using the facilities of the CFN and will be tested at beam line X13B at NSLS.

TECHNICAL PROGRESS AND RESULTS:

During the first year of this LDRD, we prepared and characterized at X13B a few high-resolution FP monolithic structures. The results were encouraging but in order to carry out real tests, we needed to use beamlines with higher energy resolution than available at NSLS. We started applying for beam time at the SPRING8 synchrotron source, where similar studies have been carried on in the past. However, obtaining beamtime proved too long a process for this LDRD. So we decided to use the remaining part of the LDRD within the available resources at NSLS and to modify our design of the interferometer accordingly. Our objective was first of all to prove the interference mechanism of the device in the hard X-ray regime. This can be done irrespectively of the high-resolution. We designed a new structure with lower resolution (about 10 meV), which however can be tested at the X13B beamline at NSLS (see Fig.1).

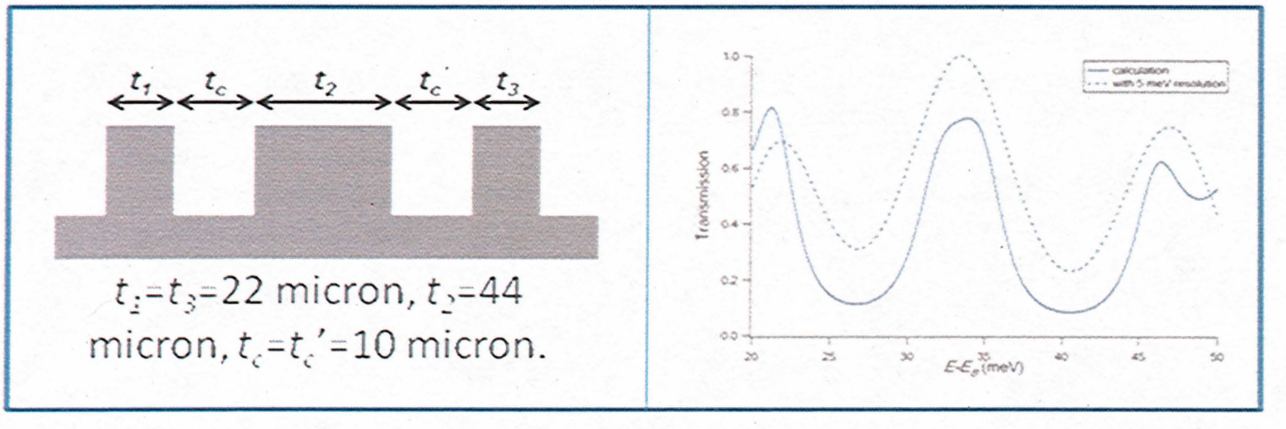


Fig.1: Left panel: modified FP interferometer geometry. The height is 100 micron. Right panel: calculated transmission spectrum (solid line) and its convolution with a 5meV Gaussian (dashed line) for the FP structure shown on the left.

In this new geometry, the gaps between the Si walls are narrower than before (10 micron compared with 60 micron). This creates new challenges for the etching process due to the larger depth to gap ratio. New photolithography masks were therefore made through an outside vendor, and new structures were fabricated at the CFN clean-room facility. A new etching recipe had to be implemented and tested. Figure 2 shows the best cross section of the etched structure that we were able to obtain. The much reduced gap of 10 microns makes this structure much more difficult to obtain. However calculations indicate that the main factor is the gaps inter-distance and variations of the wall thickness are less important. The structure of Fig 2 should be therefore adequate to display the interference affect.

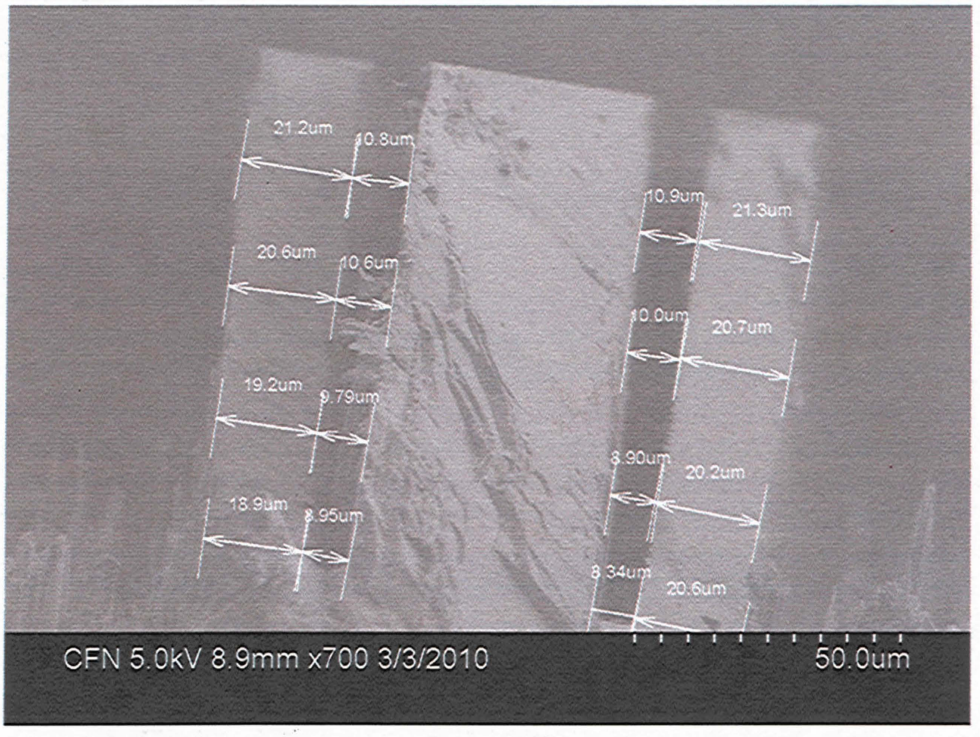


Fig.2: *FP interferometer structure has been fabricated at the CFN. The etching process was optimized to maintain minimum gap width variation*

At present we are working on setting up an adequate monochromator at X13B to allow testing of this structure. The present monochromator provides already the necessary energy resolution of 5 meV at 14.4 keV but does not allow for reliable energy scans because it uses two motors. A new nested monochromator, making use of a single movement for energy scans, has been built and characterized. According to our simulation, it should provide enough energy resolution to detect the interference fringes from the two-resonator structure. However up to now, we could not detect them in the experiment. Possibly the device geometry has to be further improved.

[1] Y. Shvydko, X-Ray Optics, Springer Series in Optical Sciences (2004)

Ultrafast Electron Diffraction for Transient Structure and Phase Transition Studies at the NSLS SDL

LDRD Project 08-037

X.J. Wang, I. Bozovic, Y. Hidaka, C.C. Kao and J.B. Murphy

PURPOSE:

Ultrafast electron diffraction (UED) is a promising technique that allows us to observe a molecular structure transition on the time scale less than 100 femtoseconds (fs). Great progress was made in developing a MeV-UED system at the Source Development Laboratory (SDL) this year: assembly of the UED electron beamline completed; a new design of the UED klystron developed, and testing is in progress. The SDL UED system will be a unique tool for ultrafast science and beam physics at BNL.

APPROACH:

The time resolution of a conventional UED has been limited to ~ 1 picosecond (ps) the system operating at the energy of 10 to 100 keV. It can be reduced to the order of 100 fs by decreasing the number of electrons in a bunch at the cost of reduced signal-to-noise ratio (SNR), which requires multiple shots to obtain resolvable diffraction patterns. One of the main causes for this limitation of UED is the space charge effect that prohibits a further compression of the electron beam bunch length. To overcome the space charge effects, we pioneered the idea of using a photocathode RF gun for the UED application. The photocathode RF gun is capable of producing MeV electron beam, which will significantly reduce the space charge effect, and lead to short electron bunches. Figure 1 the MeV-UED electron beamline assembled at the SDL.

Fig. 1: *The MeV UED system installed at the NSLS SDL*

TECHNICAL PROGRESS AND RESULTS:

Great progress was made in both MeV-UED construction and further optimization of its performance. The complete MeV-UED electron beamline was assembled at the SDL (figure 1).

Other important progress in UED hardware construction is:

- Completion of the design and installation of laser safety interlock for the UED experiment.
- Retrofit a Toshiba klystron onto the old UED klystron tank.
- Low-level RF system constructed.
- All utilities for the UED operation are operational.
- 3 different samples for UED experiment installed inside the sample chamber (figure 2).

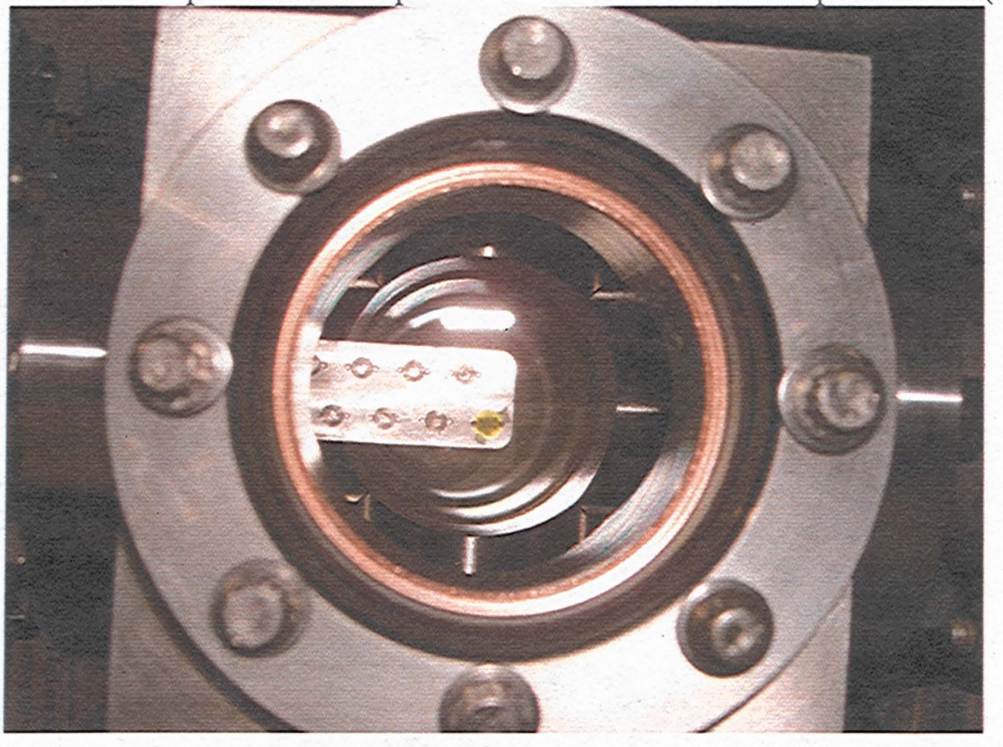


Fig. 2: *Samples installed in the vacuum chamber*

One of the most important accomplishments is experimental studies of surface photoemission from a magnesium (Mg) cathode at the SDL [1]. We experimentally demonstrated the Mg cathode could have smaller thermal emittance than copper. This result will be explored in our MeV-UED operation in the future.

1. H.J. Qian, J.B. Murphy, Y. Shen, C.X. Tang, X.J. Wang, "Surface photoemission in a high-brightness electron beam radio frequency gun", APPLIED PHYSICS LETTERS **97**, 253504 (2010).

The Development of a Laser Based Photoemission Facility for Studies of Strongly Correlated Electron Systems

LDRD Project 08-039

P.D. Johnson

PURPOSE:

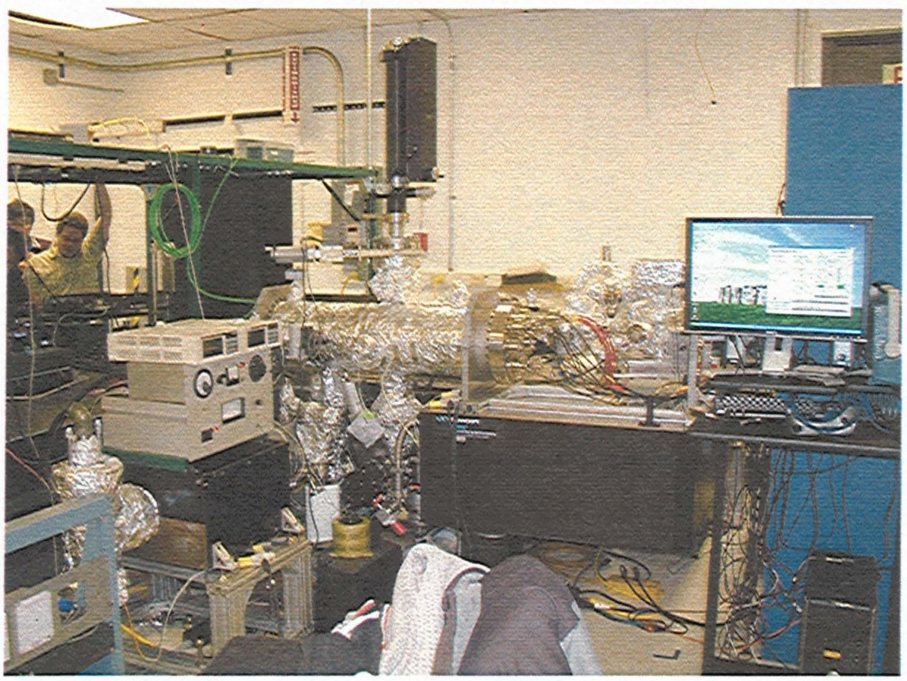
The objective of this research program is to establish a photoemission facility based on the use of a laser as a source. The use of such a source has two objectives. Firstly, it is widely believed that the use of the lower photon energies available from a laser based source will result in a more bulk sensitive PES experiment. This has never really been confirmed and needs to be investigated. Secondly the laser source is a high rep rate 75Mhz source that represents an ideal source for investigating the properties of a new high resolution time of flight (TOF) electron spectrometer developed at BNL. The latter represents a new type of electron spectrometer that may well see application at a variety of FEL type light sources.

APPROACH:

A laser based source that produces UV radiation by frequency doubling and quadrupling will be commissioned in the new laser laboratory in building 480. A new time of flight electron spectrometer, designed at BNL has been constructed and commissioned. The two separate components are currently being brought together to establish the laser based PES facility, which is intended for studies using both direct photoemission and two-photon-photoemission.

TECHNICAL PROGRESS AND RESULTS:

The new TOF electron involves the coupling of a parabolic collection mirror to a "velocity filter" that employs oscillating electrostatic fields to select electrons of particular energies. The



The TOF spectrometer being installed and commissioned in building 480

spectrometer was initially assembled in building 510 and tested by firing a beam from an electron gun directly into the velocity filter. Those tests, which were very successful allowed us to reduce the effects of stray magnetic fields in the experimental chamber and as noted in the previous report reduce the effects associated with the electrostatic coupling of the high frequency fields within the filter.

The next stage in the commissioning has been to remove the entire experimental facility including vacuum vessel and associated electronics from building 510 to building 480. This stage has been successfully completed and the entire facility has been brought to high vacuum again. However the entire program was brought to a halt when the synchrolock associated with the laser system failed. The synchrolock is an important component because the experiment requires the laser source and the electron spectrometer to be locked together in phase. Unfortunately it has taken the manufacturers, Coherent, several months to repair the synchrolock. However at the time of this reporting the device has finally been returned to BNL and shown to be operational again. The engineers from Coherent will visit BNL and recalibrate the lasers so that the experimental program can be resumed.

While waiting for the repairs to be completed, the Labview based data acquisition system required to drive the experiment has been modified and hopefully improved.

Theory of Electronic Excited States in Heterogeneous Nanosystems

LDRD Project 08-042

Mark S Hybertsen

PURPOSE:

Understanding and predicting the energy level alignments in heterogeneous nanosystems is both important and very challenging for theory and computation. Predictive theories of electronic excitation energies are well established, but they are severely limited in the scale of systems that can be treated with present day computational capabilities. We plan to explore physically motivated approximations that may result in a significant improvement in the efficiency of these calculations for nanosystems and to implement these improved methods exploiting large scale parallel computing. If successful, this research could enable excited state calculations for systems comparable in size to those treated with conventional Density Functional Theory, a significant technical breakthrough. For BNL and the CFN specifically, this project will nucleate a new computational electronic structure research effort, attract external users to the CFN, and enable partnerships with key external groups.

APPROACH:

Prediction and understanding of the excited electronic states of nanomaterials are frequently essential to explain and modify their function. Examples include electron transfer through a molecular bridge, the active electronic states in novel photocatalytic nanocrystals, and resonant energy transfer in light harvesting structures. Large scale applications of Density Functional Theory (DFT) based computations enable theoretical understanding of chemical bonding and other important properties in such systems. However, the orbital energies from DFT calculations do not accurately model electronic excitation energies. For example, they are empirically found to poorly approximate key quantities such as the band gap in semiconductors or the ionization potential of molecules, although overall trends may well be useful. So-called hybrid functionals (e.g. B3LYP) give more accurate bond energies and are now widely used in quantum chemistry. A recent modification of this approach for solids resulted in improved band gaps for semiconductors [1]. However, this approach still misses essential physical processes, particularly the image potential effect that plays a critical role in heterogeneous nanosystems. Predictive theories of electronic excitation energies are well established, but entail substantially more complex calculations. As a consequence, while ground state calculations are now done for systems of order 1000 atoms, excited state calculations are limited to systems of order 100 atoms.

In our recent research in collaboration with Neaton and Louie (Molecular Foundry, LBNL), the well-established, full GW approach was applied to benzene on graphite, an example of a molecule coupled to a metal electrode [2]. The GW approach includes the image potential effects and we demonstrated the strong influence that the environment has on the benzene excitation energies [2]. However, the GW approach is computationally very demanding. Our treatment of the benzene on graphite was among the largest systems that can be treated today, of order 100 atoms. Many applications to interesting nanosystems are presently out of reach. Analysis of the benzene calculations showed that the change in electron correlation energy on the molecule due to interaction with the surface was largely due to static polarization effects [2]. This result suggests to me that a static approximation in the GW framework can be developed that will be broadly applicable to heterogeneous nanosystems. We envision an approximate treatment based on the GW framework for electronic excitation energies that can be applied

broadly. In addition to the non-locality of exchange, it will account for polarization and screening explicitly. The latter is required to capture image potential effects. The feasibility and potential accuracy needs to be analyzed and the computational complexity must be explored.

TECHNICAL PROGRESS AND RESULTS:

Research Associate, Wei Kang, who started in July, 2008, has been supported by the LDRD funding to carry out the research under my direction. His research work has been divided into two parts. First, he has implemented the several existing codes with the conventional GW methodology, together with the Bethe-Salpeter methodology and he investigated electronic and optical excitations in titanates and oxynitrides. These materials are of fundamental interest for photocatalytic water splitting. The titanates proved to be a very challenging system so he has devoted significant time porting the codes to the NY Blue facility, as well as implementing a full frequency approach that proved essential for quantitative results. His work focused on rutile and anatase was published this year [3]. Work on oxynitrides, in collaboration with the Khalifah group (Stony Brook and BNL Chemistry), is on-going.

In the second part of his work, he has developed a new approximate treatment of the self energy operator in the GW framework, along the lines planned above. In particular, he devised an approach to include the local fields in a new static approximation. He then tested this approach for a diverse set of crystals, atoms and molecules. Although relatively simple, the new approach is surprisingly accurate, giving energy band gaps within 10% or better of the more exact theory. These results were published this year [4]. The next step in developing approximate methods will focus on efficient models for the screening response, as part of the CFN group research plans.

IMPACTS:

The LDRD support for this project lasted through July, 2010. Dr. Kang has continued in the CFN Theory and Computation Group for an additional year. His work has laid the ground work for new research that was written into the research plans for the group and presented during the Sept. 1-3, 2010 CFN Peer Review. Dr. Kang gave a poster on his results at the review.

With Dr. Kang, we are also exploring collaboration with a group in Trieste to take advantage of the latest advances in GW methodology [5]. Dr. P. Umari visited the CFN in April 2010 to introduce us to the new approaches. While at the present time these new approaches do not appear well adapted for the materials of interest to us for water splitting, we believe this collaboration will be useful for molecular systems of interest for certain CFN user projects. The code implementations and progress Dr. Kang has made will fold directly into the research program of the newest staff member in my group, Dr. Deyu Lu. Finally the work on photocatalytic materials for water splitting will be part of the basis for my participation in a CMCSN proposal (Lead PI, J. Muckerman; whitepaper accepted for a full proposal).

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2. J.B. Neaton, M.S. Hybertsen and S.G. Louie, *Phys. Rev. Lett.* **97**, 216405 (2006).
3. W. Kang and M.S. Hybertsen, *Phys. Rev. B* **82**, 085203 (2010).
4. W. Kang and M.S. Hybertsen, *Phys. Rev. B* **82**, 195108 (2010).
5. P. Umari, G. Stenuit, and S. Baroni, *Phys. Rev. B* **81**, 115104 (2010).

Nanofabrication Methods Using Solution-Phase Nanomaterials

LDRD Project 08-043

C. T. Black and J. E. Allen

PURPOSE:

The project has implemented a new thin-film nanofabrication method for uniform large-area assembly of materials from solution, leveraging self assembly of porous aluminum oxide templates. We have successfully used this technique to fabricate and study solar cells composed of organic semiconductors, discovering enhanced device performance when the organic materials are confined to nanometer-scale volumes. We have also combined this self-assembly approach with both inorganic nanocrystal deposition and inorganic thin-film growth by atomic layer deposition to lay groundwork for more complex device architectures that we are pursuing either internally or through external collaborations.

APPROACH:

Processing materials from solution is a straightforward and efficient means for thin film device fabrication. Building *nanostructured* devices from solution is complicated by a lack of control of nanomaterial assembly over large-areas. This challenge is common to many areas of nanotechnology –the need for accurately positioning *nm-scale* elements across *cm-scale* areas.

The primary project objective has been to develop capabilities for building complex solid-state electronic structures from solution-phase nanomaterials. The research has involved three specific directions: (1) refining the fabrication approach; (2) demonstrating its utility in studying photogenerated charge transport in *organic semiconductor* solar devices; and (3) incorporating additional *inorganic* elements in pursuit of more complex device architectures.

Dr. Jonathan Allen, a Research Associate funded by this project, primarily carried out this experimental research under the guidance of C. T. Black. Project collaborators have included Dr. Chang-Yong Nam (CFN), Dr. Dan Johnston (CFN), Dr. Kevin Yager (CFN), Dr. Ben Ocko (CMPMS), Prof. Vladimir Bulovic (MIT), Prof. Joseph DeSimone (UNC), and Dr. Alec Talin (NIST).

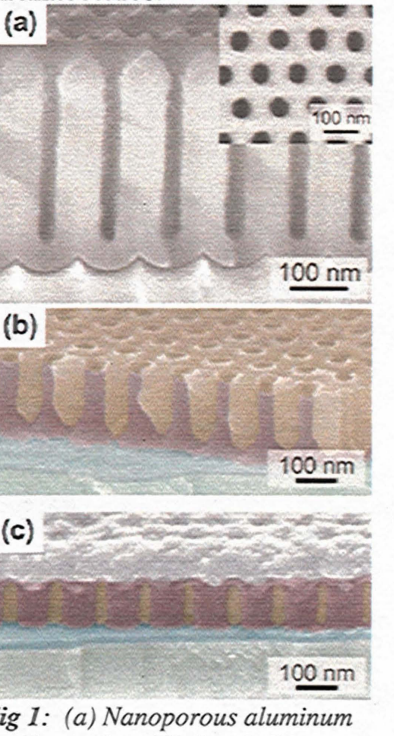


Fig 1: (a) Nanoporous aluminum oxide template filled with (b) organic semiconductor and (c) as an organic solar cell element.

TECHNICAL PROGRESS AND RESULTS:

In FY2009, we established procedures for fabrication of highly ordered porous aluminum oxide templates — a capability not present at BNL previously. The technique generates large area samples of highly ordered nanoporous templates, with close control over all dimensions (Fig. 1a). Our first target device demonstrations (FY2010) have templated solution-processed organic semiconductors suitable for solar device applications (Figs. 1b, c). Confining blended polymer:fullerene organic solar cell materials within nanometer-scale cylindrical volumes nearly doubles the supported photocurrent density compared to equivalent unconfined volumes of the same blend, and increases the polymer hole mobility by over 1000 times. Grazing incidence x-ray diffraction shows that the confinement disrupts polymer ordering and reduces grain size,

and also changes the orientational distribution. Similar confined volumes of the single-component polymer show an almost 400 times enhancement in hole mobility, while the electron conductivity of confined fullerenes decreases by 50 times. A manuscript detailing these experimental results is currently under peer review by the journal *Nano Letters*.

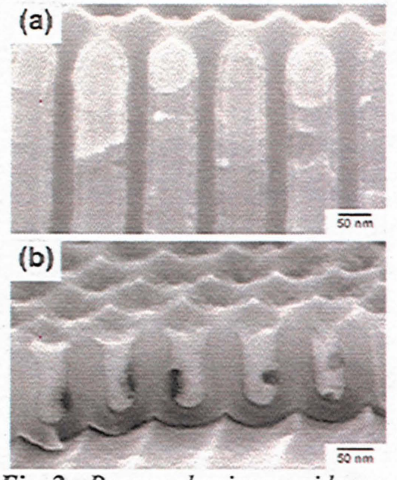


Fig. 2: Porous aluminum oxide template (a) lined with ~10nm TiO_2, and (b) filled with inorganic semiconductor nanocrystals.

We are now exploring further improvements in organic solar cell performance by including inorganic materials in the device architecture. One approach involves lining the self-assembled porous alumina template with titanium dioxide (TiO_2) prior to infiltrating with the organic semiconductor blend. We grow TiO_2 thin films using atomic layer deposition – a new capability within CFN that can coat extremely high aspect ratio structures (e.g., Fig. 2a). TiO_2 acts as an electron transporter in this structure, providing an alternative pathway for electrons to traverse the device active layer (rather than through the poorer performing PCBM). Templated organic solar cells having a TiO_2 transport layer perform with an overall power conversion efficiency of greater than 2%, roughly equal to the performance of untemplated devices despite containing only a small fraction (~30%) of the photoactive material. Templated devices having a conformal TiO_2 layer outperform identical devices without a TiO_2 layer by about 2:1, consistent with improvements in electron collection.

In FY2009 we also developed an efficient method for infiltrating nanoporous AlOx templates with *inorganic* nanocrystal materials, and we have begun to leverage this capability in a collaborative project with Dr. Vladimir Bulovic (MIT), as part of the Center for Excitonics Energy Frontier Research Center. We are investigating templated structures for alternating current quantum-dot light emitting diodes (AC-LEDs). In this case, we apply a solution containing highly concentrated CdSe quantum dots to a template before physically cleaning the surface using an elastomeric squeegee. This process both removes excess material from the top surface and also forces additional material into the template pores. Under appropriate conditions, quantum dots enter the template pores and self assemble in the pore bottoms in a densely packed arrangement (Fig. 2b). Our MIT colleagues have previously demonstrated that similar unconfined quantum dot films emit light under AC voltage bias, and we will explore the possible benefits of quantum dot confinement on the device light-emitting efficiency.

We are pleased with our progress during the two years of LDRD funding (FY2009 and FY2010). The ultimate project output will be at least two high quality publications detailing use of our technique in understanding improved electronic properties of organic semiconductor solar materials. We will continue to actively pursue this research using CFN programmatic funds. Importantly, our development of this self-assembly based fabrication approach has spawned collaborative interactions in areas outside our primary research interest, including: (1) Professor Vladimir Bulovic, MIT, Confined quantum-dot light-emitting diodes; (2) Professor Joseph DeSimone, University of North Carolina, Fabrication of nano-biomaterials for nanomedicine; (3) Dr. Alex Talin, NIST, Nanostructured cathodes for lithium-ion batteries. We will continue to support and pursuer these collaborative projects, likely through the CFN User program.

Identification of Organic Aerosols and Their Effects on Radiative Forcing

LDRD Project 08-051

Yin-Nan Lee

PURPOSE:

The purpose of this research is to develop a new methodology for identifying organic components present in ambient aerosol particles formed in the atmosphere known as secondary organic aerosol (SOA) to improve understanding of their sources, formation, distributions, and contributions to radiative forcing. Specifically, we focus on a class of compounds which is difficult to characterize at the molecular level but exhibits moderately high molecular weight (MW~300 to 500 Da) containing possibly phenolic and carboxyl moieties similar to humic material, referred to as humic-like substances (HULIS). The sources and formation of the purported HULIS, which can account for up to 20% of the organics, are largely unknown. This work attempts to identify their presence and the conditions favoring their occurrence using a new sampling technique. The high-risk explorative nature of this work stems from the fact that HULIS are ill-defined and do not lend themselves to positive identification and method improvement with "standards", and are not consistently present in the atmosphere.

APPROACH:

Traditional techniques for sampling organic aerosols involve high-volume filter sampling (without size selection) over extended periods (days to weeks) followed by extraction using organic solvents. The sample is then concentrated by purging using inert gases to reduce the eluate volume from tens of milliliters to a fraction of a milliliter. Although this approach has the advantage of producing sufficient sample for multiple analyses, potential artifacts can result from on-filter interactions of aerosols and gases leading to further reactions as well as from contamination from super-micron size primary biological and soil particles which can overwhelm the aerosol mass concentration. Further, possible reactions of the myriad organic compounds during extraction and concentration stages can result in altered chemical forms.

We employ a novel sampling technique which is on-line, continuous, and without concentration in organic solvents. This technique, developed at BNL, referred to as Particle-into-Liquid Sampler (PILS), grows aerosol particles into droplets with water steam, which are collected using an inertial impactor. The liquid sample collected on the impactor is continuously washed off with a stream of purified water and passed through a suitable sorbent to retain the organic compounds. These compounds are eluted off the sorbent using a small portion of methanol or acetonitrile after sampling is finished. This technique is free from potential reactions that can take place either on the filter medium or during the concentration step. In addition, aerosol size cut to < 2.5 μm is achieved with a cyclone to remove large primary particles.

To speciate and characterize the MW of the organics in the sample, we employ the High Performance Liquid Chromatography-Electrospray Ionization-Mass Spectrometry (HPLC-ESI-MS) technique capable of producing molecular ions. A reverse-phase column is used to separate the analytes in an elution order roughly corresponding to the MW. Since the ESI ionization efficiency varies with the properties of the analyte (functional groups, acidities, etc), the ion signal is typically not a quantitative measure of the analytes. Without having standards for the unidentified organic components, we employ in parallel an Evaporative Light Scattering Detector (ELSD), which atomizes the eluate, evaporates the solvent, and forms aerosol particles of the

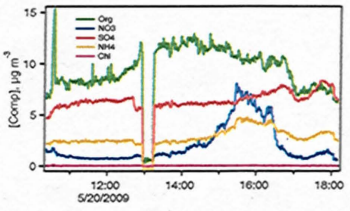
eluant for light scattering detection to provide an independent measure of mass loadings of the analytes against which the ion signals can be compared. To aid data interpretation, we make simultaneous independent determinations of aerosol chemical composition, i.e., SO_4^{2-}, NO_3^-, NH_4^+, and total organics (Org), using an Aerodyne Aerosol Mass Spectrometer (AMS) to provide the context for aerosol properties such as acidity and total organic mass loading. The primary disadvantage of the PILS technique is its small sampling rate (i.e., 10 L/min for hours vs >1000 L/min for weeks with the filter technique), therefore requiring a high ambient organic aerosol loading (i.e., >15 μg m^{-3}) which was rarely met during the summer of 2009 at BNL.

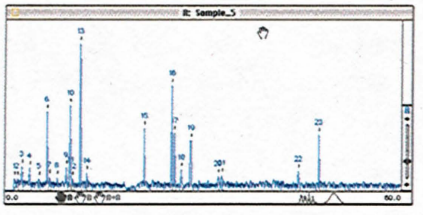
Dr. L. Bowerman was a collaborator during the first year. She helped with the since abandoned filter sampling approach. Dr. C. Dodge replaced Dr. Bowerman after she left the Division, and helped with the operation of an HPLC-ESI-MS belonging to Environmental Research and Technology Division. Delays were experienced due to these changes.

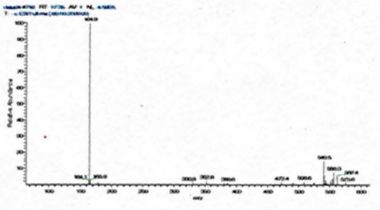
TECHNICAL PROGRESS AND RESULTS:

A complete sampling strategy and the arrangement/acquisition of necessary instruments and apparatus were in place after year and a quarter into the program. These included the setup of an existing Thermo-Finnigan HPLC-ESI-MS (Model LCQ) system, acquiring and setup of an Agilent ELSD, and method development for the Solid Phase Extraction technique, as well as bringing the PILS and AMS instruments on line.

Aerosol sampling and analysis were performed during the second year of this project. In an experiment, an aqueous aerosol sample collected using the PILS was passed through a sorbent (Strata-X-AW, Phenomenex) appropriate for collecting carboxylic acid containing molecules. Simultaneous AMS data are shown in left figure. After 6-8 hours collection, the organics were eluted off the sorbent using 1 mL CH_3OH, and the sample was analyzed. Although the ELSD chromatograms (center figure) showed well separated peaks, the ESI-MS however did not exhibit corresponding ion chromatograms. Indeed, no dominating ion peaks were observed. On the other hand, analysis of model compounds (phthalic, hydroxylphenylacetic, protocatechuic acids, all containing an aromatic and carboxylic group) showed a reasonable detection (mass spectrum of phthalic acid, retention time 17.5 min, shown in the right figure). However, we were unable to see a distinctive mass spectrum for fulvic acid (the soluble fraction of humic acid) at a similar sample loading.







Several possible explanations for the low response of the ESI-MS can be offered. The first is that none of the eluted organics were ionized because they don't mimic the model compounds. With that we may state that HULIS were absent in these samples. However, it is also conceivable that the concentrations of organics eluted from the HPLC are too low for the ESI-MS. Although the injected amounts of the model compounds and the aerosol organics sample were comparable, ~100 ng, the organics in the sample are distributed across many species, each being present in a much smaller amount.

While the approach and the techniques established in this research are in principle sound, we need to have either improved instrument sensitivity or an increased sample material to remove the ambiguity described above. Considering the variability in SOA properties and loading, it is evident that only a long term continuous analysis can provide meaningful data needed for gaining improved understanding of organic aerosol, in particular the HULIS, regarding their sources and formation mechanisms.

Computational Climate Science

LDRD Project 08-060

Andrew Vogelmann

PURPOSE:

Assessments of the potential impacts of pollution on climate are hampered by an incomplete understanding of the atmospheric physical processes needed in climate models. Our objective is to assess and improve these physical processes via model simulations that will be run on the New York Blue (NYB) supercomputer by a team of researchers from BNL and the Institute for Terrestrial and Planetary Atmospheres at Stony Brook University (SBU). The follow-on implications of this research, in terms of new programs and BNL institutional strategy, are: (a) establish a climate science modeling institutional capability on NYB; (b) foster cross disciplinary collaborations within BNL, and between BNL and SBU; (c) support the ELS Strategic Initiative in Climate Research; and (d) support the FY08 Laboratory Strategic Initiative in Computational Science by expanding the range of scientific applications that would run on NYB.

APPROACH:

Accurate simulation of convection is an ongoing challenge that affects climate model transports of water vapor, cloud, and aerosol. We endeavor to improve our understanding by using the tropics as a convection testbed to determine whether explicit convection treatments are needed in global climate models to accurately simulate convection and aerosol transport. Simulations are run on the NYB supercomputer with successively high resolutions, and will be validated using newly available satellite observations and observational techniques developed at BNL.

- NYB atmospheric simulations use the Weather Research and Forecasting (WRF) Model, and its chemistry module extension WRF/Chem. WRF is a next-generation mesoscale model designed for atmospheric research that is ported to NYB as part of this project.

- WRF simulations are evaluated using new cloud and aerosol observations that provide constraints and insights into the model behavior that include: (a) a cloud identification and tracking algorithm; (b) an artificial neural network (ANN) being developed by BNL researchers that uses satellite data to characterize tropical cloud fields and their behavior; (c) new aerosol observations from the CALIPSO space-borne lidar that provides the first routine, global observations of aerosol vertical profiles and particle size.

- We can target the most deficient physical processes by exploiting NYB computational power to perform ensemble runs to map the variances of the model solutions in a phase space that considers the uncertainties in the model parameters associated with convection.

The team is an interdisciplinary group of computer scientists and researchers at BNL and SBU that capitalizes on existing expertise. BNL units involved include the Atmospheric Sciences Division (Vogelmann, Lin, Luke, Daum, Jensen, Johnson, Liu, McGraw, Troyan), the Scientific Information Systems Group (Wagener, Cialella, Behrens, Gregory), and the Computational Science Center (Davenport, Efstathiadis, Slatest, Cortijo). The primary SBU faculty involved in this effort are Drs. Zhang, Colle, He, Jiao, Khairoutdinov, and Chang.

The novelty of this work is in the modeling approach that requires NYB computational power, and the use of newly available satellite observations. The risks are: (a) this level of WRF modeling (long simulations at high resolution for a large domain) has not been attempted before and could trigger instabilities, and (b) the core observational and modeling capabilities exist at BNL and SBU, but they have not worked together before on such a comprehensive study.

TECHNICAL PROGRESS AND RESULTS:

In the prior fiscal year, after the successful porting and testing of WRF on NY Blue, simulations for the Tropical Western Pacific had been initiated. These simulations exploited the computational power available from NYB by treating a broad swath across the Tropical Warm Pool (22°S-17°N, 100-162°E) at high resolution (4 km). These simulations were assessed using a procedure that we developed to analyze the modeled cloud lifecycle. A cloud tracking algorithm was applied to satellite observations and to WRF simulations to assess the fidelity of the model via statistical comparisons of the size and longevity of tropical mesoscale convective systems (MCSs). Initial results indicated a paradox, where the simulated MCSs were smaller than those observed (by half) yet had similar longevities. The explanation for this paradox was the primary technical focus of this year's research.

Simulations were conducted using four other microphysics schemes, which provide different representations of how cloud water and ice particles form and precipitate from the cloud systems. We found that the choice of the scheme caused striking differences in the simulated cloud behavior, while enhancing the model resolution had little effect. Generally, the fidelity of the simulations (in terms of cloud-tracking statistics) improved with enhanced sophistication in the treatment of ice and its partitioning between hail and graupel hydrometeor classes. Interestingly, while some schemes could simulate the size distribution of MCSs properly and other schemes could simulate the number of MCSs properly, no scheme could properly simulate both metrics. This result suggests the value of diagnostic procedure that we had developed.

A new procedure was developed to analyze the internal workings of the storms, by following the simulated MCSs and examining the concentration profiles of the different hydrometeor classes, as well as the associated distribution of updrafts and downdrafts. These results indicated that the microphysics scheme that produced the narrowest vertical velocity distributions produced the best agreement with the observed MCS size distributions, but the broadest distributions produced the best agreement with the observed number of MCSs. From the point of view of additional radar observational capabilities that might shed light on these diagnostics, we determined that observations of graupel and snow profiles are most likely to provide the needed information. These results were presented at the First Annual Atmospheric System Research Science Team Meeting, and at the AMS 13th Conference on Cloud Physics and Atmospheric Radiation. A manuscript is in preparation.

In recognition of the importance of microphysics treatments to MCS simulations, in addition to the soon-to-be-available enhanced observational capabilities via new radar systems, we hired a new postdoc (K. Van Weverberg) to help advance this line of research. He has an excellent background in the requisite modeling and observation disciplines, and has initiated research to improve cloud microphysics parameterizations within deep convective systems.

Programmatically, we advanced joint research activities of the BNL-SBU climate science virtual institute. The 4th NY Blue Climate Science Workshop was held in November, where we updated each other on NY Blue research activities and troubleshot bottlenecks. Excellent progress was made on a joint SBU-BNL project (lead Wuyin Lin, BNL) to develop on NY Blue a high-resolution climate modeling capability for regional climate change studies by interactively nesting WRF within a global climate model. A prototype has already been constructed, is numerically stable, and is undergoing refinements and testing.

In summary, this LDRD helped spawn research that will continue into the future via the FAst-*physics* System TEstbed and Research (FASTER) Project (lead Y. Liu, BNL), a $15M project catalyzed by this LDRD, as well as through new research components in our division's Science Focus Area proposal.

A Novel Spintronic Room-Temperature High Purity Germanium X- and Gamma-Ray Spectrometer

LDRD Project 08-062
Giuseppe Camarda and Aleksey Bolotnikov

PURPOSE:

This proposal addresses the serious need for high-resolution, room-temperature X-ray and gamma radiation spectrometers for nuclear non-proliferation, homeland security, and synchrotron applications. High-Purity Germanium (HPGe) is the world's preeminent radiation detector material, because of its unique combination of material perfection, excellent charge transport properties and unsurpassed spectroscopic performance. However, the room-temperature band-gap of germanium is only 0.74 eV, and thermal charge generation must be suppressed by cooling the material to near liquid nitrogen temperatures, otherwise, the noise in the device is too large to provide spectral information. The necessity of cooling HPGe radiation detectors is both costly and cumbersome, and it has limited the utility of these devices. The energy resolution of HPGe detectors operated at liquid nitrogen temperatures is below 0.5%, and there has been an enormous push to develop a room-temperature detector that can provide the same energy resolution. The search has proven difficult and has recently focused on wide band-gap compound semiconductors, such as CZT, CdTe and HgI_2. These detectors currently can provide room-temperature energy resolution near 1-2% @ 662keV, but the material imperfections have limited the size and corresponding detection efficiency of these devices. Therefore, none of the existing room-temperature radiation detectors have provided the combination of cost and performance necessary for security and synchrotron uses. A new spintronic high-purity germanium gamma-ray detector concept is proposed. Spintronic devices are based on the manipulation of an electron's spin state in addition to its charge, and have the potential to result in order-of-magnitude scale improvements in the performance of various semiconductor devices. In this project we are investigating the feasibility of applying spintronic principles to the production of a gamma-ray spectrometer based on HPGe that operates at elevated temperature.

APPROACH:

Semiconductor spin electronic devices offer great promise as a revolutionary technology for detecting radiation. Despite significant effort and investment worldwide, commercial semiconductor spintronic devices have not been realized. This fact highlights the challenge inherent in any semiconductor spintronics project.

We are undertaking initial steps towards constructing a spintronic gamma-ray detector using semiconductor material, such as High-Purity Germanium (HPGe) and Si.

We will test devices for unambiguous spin-transport signatures via nonlocal magnetoresistance measurements.

We anticipate realizing a measurable enhancement in resistance in the device structure compared to a non-magnetic-contacts reference one.

The success of our work under this project will afford proof-of-principle for the world's first spintronic gamma-ray spectrometer. Our development of the proposed spintronic detector could

revolutionize the field of gamma-radiation detection and provide a room-temperature energy resolution far surpassing any existing instrument.

TECHNICAL PROGRESS AND RESULTS:

In FY08 the team acquired the raw material needed for the structure fabrication and then sliced and polished it into wafers of 0.5mm, 1mm and 1.5mm thickness. The surface preparation/cleaning procedures were developed.

For FY09, we designed the photo-masks to fabricate a device structure with Ge to observe spin-transport. We anticipated realizing a measurable enhancement in resistance in the device structure compared to a non-magnetic-contacts reference one.

Hall Effect measurements were successful at elevated (>130 K) temperatures, but some contacts problems were encountered at lower temperatures. New measurements are planned in that range.

Biofuels and Nanotech for Improvement of Oil Heat Combustion Systems

LDRD Project 08-082

T. Butcher and M. Rafailovich

PURPOSE:

Condensing boilers achieve very high efficiency levels by recovering heat from the flue gas before it is discarded. The recovery of latent heat from the water vapor in the humid gas is a very important part of the total heat recovery but the condensate formed is corrosive – leading to the need for expensive alloys in the heat exchanger. This project is focused on the potential replacement of these alloys in the condensing section of home heating boilers with polymeric materials. The requirements for selecting the polymer are fairly rigorous and cannot be satisfied by any polymer alone; the polymer must withstand relatively high temperatures (T~250C) and be resistant to degradation in the presence of the sulfuric acid environment found in condensates produced from conventional oil combustion. Furthermore, even though the polymer is not in contact with fire, its proximity to an open flame and to the ignition electronics found in boilers, OSHA and other building code regulations are expected to require that the materials must be flame retardant, and conform to UL94-V0 requirements. Since no single polymeric material can satisfy these criteria, the focus of this research was to develop organic-inorganic polymer blend nanocomposites, where the mechanical, chemical, and thermal properties could be tailored to meet the specific requirements for optimal boiler construction.

APPROACH:

Specific classes of polymers are known to be resistant to acid corrosion. These polymers include polypropylene, polycarbonate, Teflon, and other fluoro-polymers. The major drawback of these materials is their high degree of immiscibility, which makes it difficult to tailor their properties

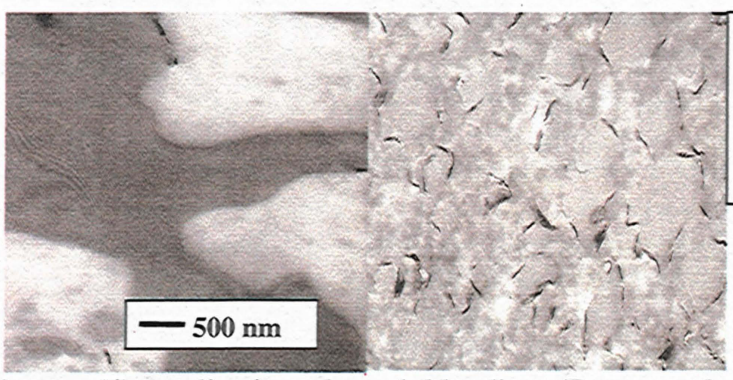


Fig. 1: *Effect of clay on flame retardant PC/SAN polymer blend. Compatibilization is achieved by forming in situ grafts on the clay and localizing the platelets at the interfaces.*

for specific applications through blending. For example, polycarbonate, which has good thermal and corrosion resistance is too brittle, while polypropylene (PP), polyvinylchloride (PVC), and Teflon, which have the desirable impact toughness, deform easily when heated and therefore do not satisfy the UL-94 flame retardant criteria without further modification. We had previously demonstrated that it was possible to achieve compatibilizaion of a large group of polymers using exfoliated nano-clays [Compatibilizing bulk polymer blends by using organoclays Si M, Araki T, Ade H, Kilcoyne ALD, Fisher R, Sokolov JC, Rafailovich MH. *Macromolecules* 2006 39 (14): 4793-4801]. This enabled us to adopt an approach where different polymers are blended together, with specific flame retardant formulations to achieve the proper mechanical and thermal properties.

TECHNICAL PROGRESS AND RESULTS:

In the first phase we used polycarbonate, styrene, and acrylate polymers in order to establish proof of concept. We were able to demonstrate; (a) the addition of clays was able to stabilize the blends against further decomposition in the presence of heat or flame. Scanning Transmission X-ray Microscopy was performed at the Berkeley ALS in collaboration with Harald Ade (University of North Carolina) and electron microscopy was performed at Stony Brook University on thin films obtained from cross sections of samples that were exposed to flame or high temperatures. The images clearly showed that the clays stabilized the phases, improved dispersion of the flame retardant formulation, and catalyzed conversion of the flame retardant component, increasing its efficiency in extinguishing the flame. (b) Cone calorimetry measurements performed in collaboration with Dr. Takeshi Kashiwage, from NIST confirmed that the addition of the clays greatly decreased the heat and mass loss rates of the nanocomposites. Simulations of the UL-94 testing at Stony Brook University showed that the nanocomposites were able to pass the stringent V0 requirements for self-extinction within seconds after exposure to open flame.

Summary of accomplishments during the current phase of the granting period:

Even though the addition of clays improves the flame retardant behavior, the time to ignition is shortened. This was explained in terms of the lower heat capacity of the nanoparticles which can accelerate local combustion. This problem was addressed using nanoparticle mixtures.

We have shown that the addition of certain nanoparticles mixtures can enhance flame retardancy to a greater degree than the addition of either of the nanoparticles alone (Role of Surface Interactions in the Synergizing Polymer/Clay Flame Retardant Properties Seongchan Pack, Takashi Kashiwagi, Changhong Cao, Chad S. Korach, Menachem Lewin, and Miriam H. Rafailovich, *Macromolecules* 2010, **43**, 5338–5351). The effect is particularly efficient in polymer blends, where more variables need to be considered in the flame behavior. We studied PS/PMMA blends and the respective homopolymers. We focused on the combination of multiwall carbon nanotubes (MWCNTs) with clays. We found that the flame retardant (FR) particles segregated preferentially to the MWCNTs thereby allowing the clays to segregate to the blend interfaces. In this manner both phase stabilization and good dispersion can be achieved. Both long – "l" (0.5-40 μm) and short – "s" (1-2 μm) MWCNTs were studied and the results indicated that the s-MWCNTs produced superior flame retardant properties. On the other hand, the combination of s-MWCNTs and clay significantly reduced the heat release rate (HRR) and mass loss rate (MLR) relative to compounds with only one type of nanoparticles. Electron microscopy images of the nanocomposites and the chars showed that after heating, the s-MWCNTs were able to diffuse and form a distinct phase in the nanocomposite. Exclusion of the clays allowed the s-MWCNTs to achieve better physical contacts, thereby improving the thermal conductivity. In contrast, the l-MWCNTs were entangled and therefore unable to move. The clays formed a barrier between the tube contacts, resulting in an increase of the specific heat and the HRR and MLR relative to the unfilled or the compound with only clays. *We therefore concluded that one must consider the organization of nanoparticles, as well as their chemical nature when designing flame retardant nanocomposites, since specific synergies may be established which can reduce the overall concentration of fillers.*

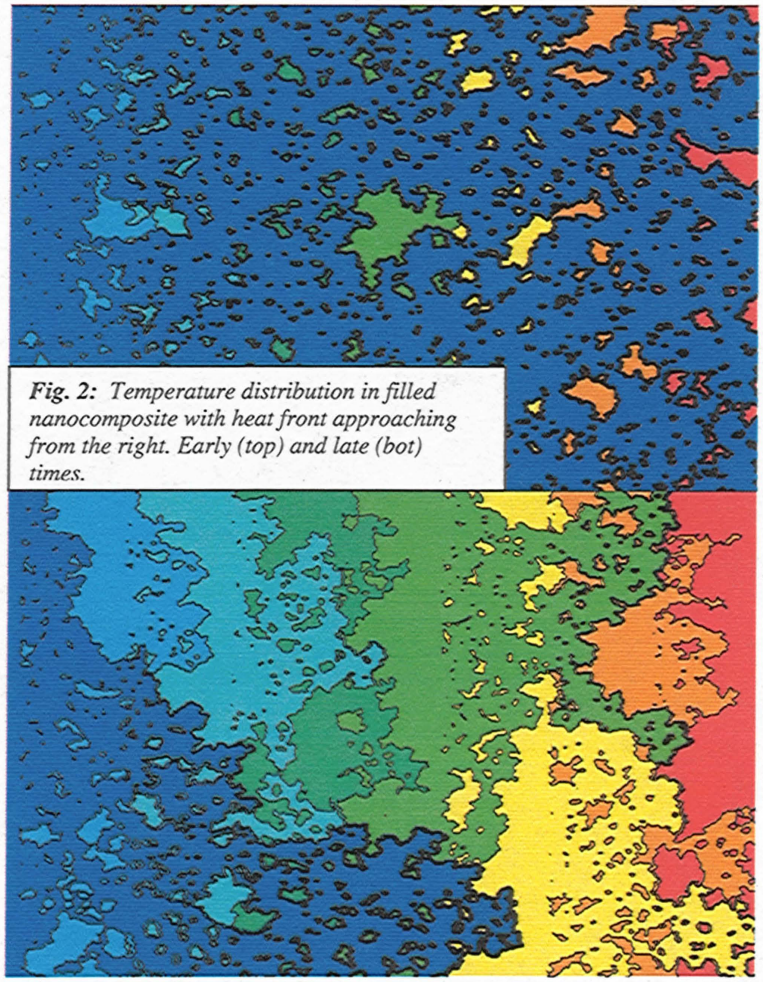


Fig. 2: Temperature distribution in filled nanocomposite with heat front approaching from the right. Early (top) and late (bot) times.

Another significant finding in the work from the previous period is our observation that the addition of most types of nanoparticles, including the standard FR formulations, even if they improved the overall flame behavior, i.e. heat and mass release rates, they *decreased* the time to ignition. In collaboration with Prof. Dillip Gersappe, we proposed a model where the propagation of heat in a heterogeneous nano structured polymer medium could be studied, using the conduction properties of the different materials and the structure of the nanoparticles, as inputs. A typical result is shown in Figure 2 where we can see isolated hot (red) spots initially forming in advance of the heat front where nanoparticles are present. We can show that these form due to the lower specific heat of the particles, which allows them to heat up faster than the surrounding matrix, and the relatively poor conductivity of the matrix to dissipate the heat (top image). When the local temperature exceeds the combustion temperature of the material, early ignition occurs and spreads (bottom image). If a thermally conducting nanoparticle is added, which also has a large aspect ratio, it is possible to achieve a state where the particles percolate and dissipate the heat of the approaching front, thereby significantly *increasing* the time to ignition.

Proposed work for the next period: During the next phase of this LDRD, we propose to focus on nanoparticle combinations which will decrease the time to ignition, as predicted by the simulation, while at the same time increase the thermal conduction of the materials. These nanocomposites should have improved heat exchange properties, while at the same time satisfy more stringent requirements for flame retardancy. We propose to use combinations of nanoclays, for compatibilization, together with s-MWCNTs in concentrations where percolation occurs and enhances the thermal conductivity.

More recently it has been shown that graphene can easily be exfoliated within a nanocomposite and achieve superior thermal and electrical conductivity properties. We are now experimenting with new methods to produce large quantities of graphene and graphene oxides, which will be incorporated within nanocomposites. Together with Prof. Gersappe, we propose to simulate the properties of these nanocomposites and see if they can be enhanced with the addition of nanotubes which will increase their conductivity and decrease the concentration of the graphene required to achieve percolation and uniform conduction properties within the nanocomposite.

Solar Water Splitting: Quantum Theory of Photocatalytic Processes at the Water/Semiconductor Interface

LDRD Project 08-083

Philip B. Allen

PURPOSE:

Artificial photosynthesis is the dream of inventing inorganic systems whose efficiency in harvesting sunlight and making fuel exceeds that of natural photosynthesis. The alloy of GaN and ZnO is currently a very good candidate for absorbing sunlight and catalyzing oxidation reactions at the water interface.

APPROACH:

We have worked with James T. Muckerman and Mark S. Hybertsen on theoretical modeling of the alloy. The method is electronic structure computations based on density functional theory (DFT).

TECHNICAL PROGRESS AND RESULTS:

Based on computations completed in the previous fiscal year, we constructed an accurate cluster expansion (CE) for the $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ solid solution. The subsequent Monte Carlo (MC) simulation revealed a phase diagram, with a wide miscibility gap and an x=0.5 ordered compound. The disordered phase displays strong short range order (SRO) at synthesis temperatures. To study the influences of SRO on the lattice and electronic properties, we conducted DFT calculations on snapshots from the MC simulation. Consistent with previous theoretical and experimental findings, lattice parameters were found to deviate from Vegard's law with a small upward bowing. Bond lengths depend strongly on the local environment, with a variation much larger than the difference of the bond length between ZnO and GaN. The downward band gap bowing deviates from parabolic by having a more rapid onset of bowing at low and high concentrations. An overall bowing parameter of 3.3 eV is predicted from a quadratic fit to the compositional dependence of the calculated band gap. Our results indicate that SRO has significant influence over both structural and electronic properties.

Nanoscale Electrode Materials for Lithium Batteries

LDRD Project 09-001

Jason Graetz, Yimei Zhu, Xiao-Qing Yang and Weiqiang Han

PURPOSE:

The objective is to develop a fundamental understanding of how electrode nanostructure and morphology affect electrochemical performance (e.g. capacity, cycle life, rate capability) and how morphology and nanostructure are affected by lithiation and repeated cycling.

APPROACH:

In this effort we will synthesize and characterize nano-scale electrodes (anodes and cathodes). We expect these electrodes will exhibit improved reversibility as a result of their nanoscale dimensions, which circumvent conventional mechanisms of mechanical deterioration. In addition, the shorter lithium diffusion paths will promote high cycling rates.

TECHNICAL PROGRESS AND RESULTS:

Anodes: Silicon has received much attention due to its high theoretical capacity; however, slow kinetics and poor long-term capacity retention remain key barriers for its application as an anode. Over the past year we investigated the process of lithiation in nano and bulk silicon using synchrotron *in-situ* x-ray diffraction (XRD) and electron energy-loss spectroscopy in the transmission electron microscope (TEM-EELS). We found that nano silicon undergoes a non-linear amorphization process upon lithiation, which is in stark contrast to the linear process occurring in bulk Si. Also the Si nanoparticles remain amorphous and there is no evidence of crystalline $Li_{15}Si_4$ at deep discharge (<50 mV).

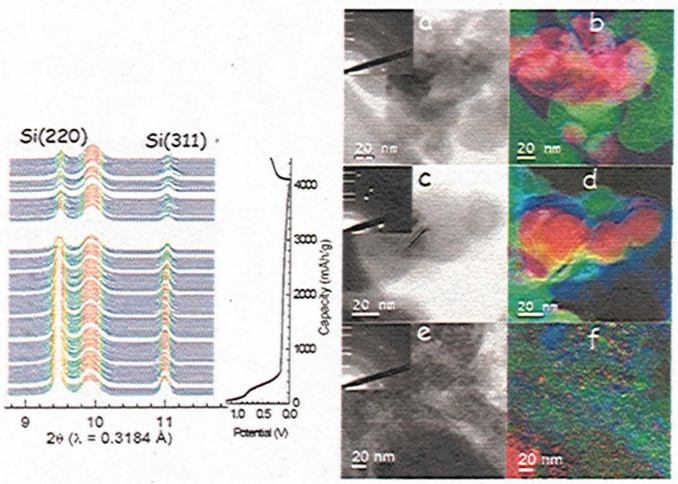


Fig. 1: *Structural/chemical changes in silicon using in-situ XRD (left) and ex-situ TEM-EELS (right)*

New silicon/carbon composite anode materials were synthesized and their structures and electrochemical performance were investigated. Three commercial Si-C samples were studied: Si nano powder from Shenyang (China) with particle sizes between 30-50 nm; Si powder from Yuantong (China) with average particle size of ~10 μm; and Si powder from Yuantong after mechanical milling (16 hrs) with average particle size of 1 μm. The reversible capacity and efficiency of the Yuantong sample increased from 1058 mAh/g and 40.8% to 1811mAh/g and 59.7% respectively after ball milling. The Shenyang nano-scale silicon sample showed the best performance among the three with 2465 mAh/g reversible capacity and a 64.0% first cycle efficiency. The Shenyang nano Si powder sample was selected for further studies using TEM.

In 2010 we demonstrated that graphene significantly enhances the reversible capacity of porous silicon nanowires achieving a charge capacity of 2470 mAh g^{-1} (6.6× greater than the capacity of

commercial graphite). This relatively high capacity could originate from the favorable charge transport characteristics of the combination of graphene with the porous Si 1D nanostructure.

We developed a novel synthesis route for preparing carbon-coated Magnéli Ti_nO_{2n-1} nanowires and demonstrated a reversible capacity of 182 mAh/g for Ti_9O_{17} nanobelts, greater than the theoretical capacity of a-TiO_2 (167 mAh g^{-1}) (Figure 2). Furthermore, the Magnéli nanobelts exhibit high power density along with excellent cycling stability when used in hybrid electrochemical cells.

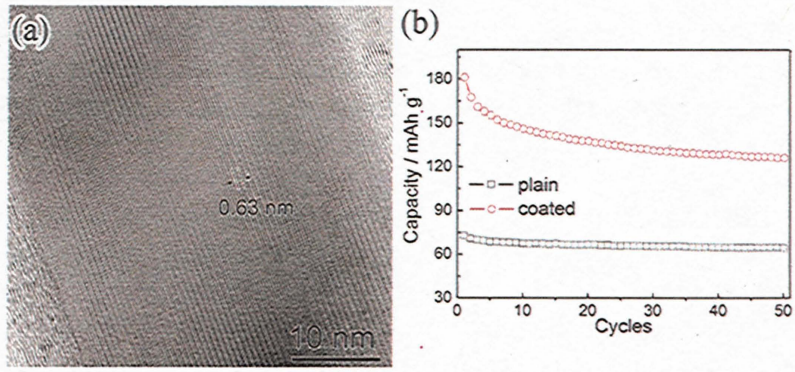


Fig. 2: (a) HRTEM image of carbon coated Ti_9O_{17} nanobelts; (b) Reversible (Li+ removal) capacities.

Cathodes: We investigated the concentration of anti-site defects in hydrothermally prepared $LiFePO_4$ as a function of temperature by high-resolution, *in situ* x-ray powder diffraction. We found that the concentration of anti-site defects (initially around 5 to 6 %) decreased slowly with temperature and rapidly dropped to 0% at ~500°C, significantly lower than expected. This suggests that a mild, post-synthesis heat treatment in an inert atmosphere (i.e. helium) is effective at eliminating the Fe and Li exchange and can be used to enhance electrochemical performance. Importantly, our results also demonstrate that intrinsic structural defects in cathode materials can be monitored by *in situ* high-resolution synchrotron x-ray diffraction.

Nanoporous $LiFe_xMn_{1-x}PO_4$ (with x = 0, 0.05, 0.1 0.15, and 0.2) was synthesized using an inexpensive solid-state reaction. $LiMnPO_4$ has a redox potential (~4.0 V), but slow kinetics limit its utility. We found that introducing iron into crystalline $LiMnPO_4$ generates a solid solution of $LiFe_xMn_{1-x}PO_4$ and increases kinetics. $LiFe_xMn_{1-x}PO_4$ electrodes were characterized using x-ray diffraction and energy-dispersive spectroscopy to examine their crystal structure and elemental distribution and electron microscopy was employed to characterize the micromorphology. We demonstrate that the electrochemical performance of $LiFe_xMn_{1-x}PO_4$ rises continuously with increasing iron content while the average potential decreases. The highest energy density and best electrochemical performance was achieved with $LiFe_{0.2}Mn_{0.8}PO_4$. *In situ* synchrotron studies during cycling revealed a reversible structural change during lithium insertion/extraction.

Large single crystals (~1 mm) of $Fe_5(PO_4)_2(HPO_4)_2{\cdot}4H_2O$ and $Mn_5(HPO_4)_2(PO_4)_2{\cdot}4H_2O$ were prepared by hydrothermal synthesis and their crystal structures were solved by direct single crystal analysis. These compounds and their derivatives have high theoretical capacities and will be investigated further in FY11.

Year	**Milestone**
FY11	Synthesis and electrochemical characterization of nanoscale silicon and novel olivine cathodes; *in-situ* synchrotron studies (XRD, XAS, small angle) and *in-situ* electron microscopy of cycling lithium electrode.

Bioconversion of Lignocellulose to Ethanol and Butanol Facilitated by Ionic Liquid Preprocessing

LDRD Project 09-002

A.J. Francis, J. F. Wishart and J. Dunn

PURPOSE:

Lignocellulosic biomass is a potential source of biofuels and biochemicals. Lignocellulose is naturally recalcitrant to enzymatic hydrolysis and microbial fermentation and therefore pretreatment is necessary to improve its digestibility and to obtain simple sugars for fermentation. Current pretreatment methods such as the dilute acid method are corrosive, energy intensive and produce inhibitory compounds for fermentation. A greener and better approach of pretreatment is to use ionic liquids (ILs). The overall goal is to develop a comprehensive process for bioconversion of lignocelluloses to ethanol and butanol using ILs as a pretreatment step followed by fermentation by *Clostridia*.

APPROACH:

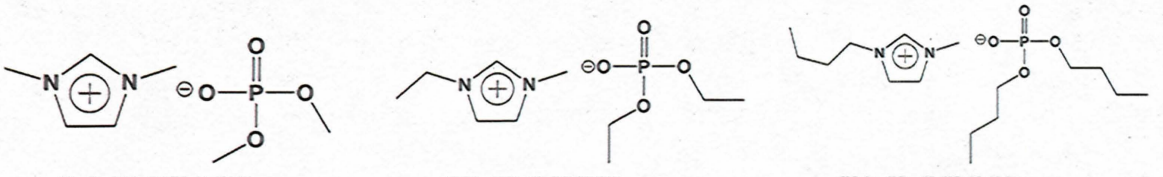
The specific objectives of this project are to (i) develop a simple and low cost pretreatment process using physical-, chemical- and biochemical- based methods to convert lignocellulose to fermentable substrates by the anaerobic fermentative bacteria *Clostridia*, and (ii) select *Clostridia* strains capable of fermenting a variety of simple and complex sugars, and modify their metabolic regulatory pathways to enhance the production of ethanol, butanol, and hydrogen as major end products. This project will advance the fundamental knowledge of potential application and development of environmentally benign new materials for biofuel production.

The specific outcomes of this research are: (i) synthesis of new ILs with valuable properties for cellulose processing; (ii) correlations between structure and characteristics for the design of new ILs for biocatalysis; (iii) metabolically modified *Clostridia* strains suitable for effective production of ethanol and butanol; and (iv) development of a process for the conversion of biomass into ethanol, an important energy source, in keeping with the aims of the BNL bioenergy initiative.

This is a multidisciplinary collaborative project involving microbiologists, molecular biologists, and physical, organic and analytical chemists. Other members of the group include M. Thomas, A. Gupta, and Y.V. Nancharaiah.

TECHNICAL PROGRESS AND RESULTS:

Ionic Liquid (IL) Pretreatment of Lignocellulosic Biomass. Dialkylphosphate ionic liquids 1,3-dimethylimidazolium dimethylphosphate [MMIM][DMP], 1-ethyl-3-methylimidazolium diethylphosphate [EMIM][DEP], and 1-butyl-3-methylimidazolium dibutylphosphate [BMIM][DBP] (Fig 1) were investigated for pre-processing of biomass. These ILs can be easily



[MMIM][DMP] [EMIM][DEP] [BMIM][DBP]

Fig. 1: *Dialkylphosphate ILs for processing of lignocelluloses*

prepared in one step using efficient microwave synthesis techniques. They are cheaper and more stable than 1-ethyl-3-methylimidazolium acetate [EMIM][Ac], which has been frequently used in cellulose dissolution studies. [EMIM][Ac] and [MMIM][DMP] were found to dissolve the most hardwood flour by weight, however the longer alkyl chain congeners [EMIM][DMP] and [BMIM][DBP] were shown to work best when small quantities of anti-solvent water were present. The cellulose was recovered by water addition and the disruption of its recalcitrant form was confirmed by FTIR. The ionic liquids were recovered with yields of 95 to greater than 99%.

Effect of electron shuttles on modulation of ethanol and butanol production by Clostridium sp. Addition of exogenous electron shuttles ferrihydrite ($Fe(OH)_3$), anthraquinone disulfonate (AQDS), and nicotinamide adenine dinucleotide (NADH), with bicarbonate showed no significant effect on fermentative metabolism of glucose by *Clostridium* sp. and production of ethanol and butanol. Bicarbonate addition to a growing culture accelerated growth and glucose fermentation which shifted from acidogenesis (acetic and butyric acids) towards solventogenesis (ethanol and butanol). In contrast, methyl viologen (MV), enhanced ethanol - and butanol - production by 28- and 12-fold, respectively with concomitant decrease in hydrogen, acetic and butyric acids compared to the control. The results show that MV addition affects hydrogenase activity with a significant reduction in hydrogen production and a shift in the direction of electron flow towards enhanced production of reduced products ethanol and butanol.

Enhanced growth of Clostridium sp. in modified medium. We were able to grow the *Clostridium sp.* in phosphate-buffered medium after repeated sub culturing. This change in media composition had two positive effects: (i) controlled the reduction in culture pH because of the production of acids and (ii) significantly reduced the fermentation time from 96 h to 36 h. This improvement is important as rapid consumption of substrates and production of ethanol and butanol for commercial viability of the process.

Effect of ILs on Clostridum sp. and Fermentation. The three ILs [EMIM][Ac], [EMIM][DEP]), and [MMIM][DMP] relevant in biomass pretreatment showed that the growth and metabolism of *Clostridium* sp. is not impacted by ILs at levels (<2.5 g/l) that are likely to be retained in lignocellulosic biomass pretreatment.

Effect of ILs on Cellulase and β-glucosidase activity. We tested the effect of [EMIM][Ac], [EMIM][DEP], and [EMIM][Cl] on cellulase, β-glucosidase, and recombinant enzymes (BgLA, CelC, CelO) activities. The IL concentrations tested ranged from 1-40%. Higher concentrations of ILs affected all the enzymes tested significantly, while the lower concentrations had little effect.

MILESTONE - FY 2011:

(i) Complete studies with the DNA carrying a recombinant β-glucosidase gene from the straw mushroom, *Volvariella volvacea* V1-1. This fungus grows faster at a higher temperature than other mesophilic fungi when using straw as a substrate, suggesting that it encodes enzymes that might be intrinsically useful for industrial production of glucose from cellulosic materials. The β-glucosidase gene has been cloned and the recombinant protein was expressed in *E. coli* using a non-T7 bacterial expression plasmid, pTrc99A. One of our current goals is to recover and reuse the attached enzyme from the matrix after cellulose digestion in the presence of ILs.

(ii) Determine the fermentability of IL-pretreated hardwood flour, switch grass, and poplar biomass by *Clostridium* sp.

(iii) Optimize fermentation of IL-pretreated biomass by manipulation of process parameters, including IL pretreatment.

(iv) Examine membrane micro- and nano-filtration methods for separating ionic liquids from oligosaccharides, sugars, enzymes and fermentation products (collaboration with U. of Rostock).

Organic Photovoltaics: Nanostructure, Solvent Annealing and Performance

LDRD Project 09-003

B. Ocko, C.T. Black and R Grubbs

PURPOSE:

Organic photovoltaic devices (OPV) hold great promise as active elements in next-generation solar cells because of their low costs, environmental considerations and mechanical flexibility. Two significant factors - both largely structural in origin – limit the efficiency of organic photovoltaic devices, insufficient interfacial surface area between the donor and acceptor within the thin absorption region of the thin film and low charge mobility and high recombination rate. Understanding these issues may lead to improved OPV devices with higher efficiency, currently 8.3% (Konarka, 2010), a several percent increase over the last few years.

APPROACH:

Our approach to improving the performance of OPV devices involves (1) developing new materials with enhanced electronic and structural characteristics, (2) providing increased control of the nanoscale phase separation between donor and acceptor components, and (3) improving the internal microstructural characteristics of the material, including the molecular orientations and crystallinity. The synthesis effort is led by Barney Grubbs (CFN/SBU), the electronic device characterization is led by Chuck Black (CFN), and the x-ray scattering effort is led by Ben Ocko (CMPMS). Many team members are involved with device fabrication such as tests of OPV cells, nanostructures, and nanopatterning.

TECHNICAL PROGRESS AND RESULTS:

We have hired a team of talented post-docs, all with very different backgrounds and skill sets, who are now working closely on several projects. Two post-docs have moved on and have been replaced with strong scientists. Progress is being made on multiple fronts, as detailed below.

Nano-structured architectures: We are investigating the use of nano-structured architectures to better understand and improve the performance of Bulk Heterojunction (BHJ) organic photovoltaic devices. We are carrying out parallel approaches, as detailed below, to control the nansocale architectures.

(1) We are working to control the chain packing orientation of semiconducting P3HT by confining the material within large-area nanostructured surfaces patterned using electron-beam lithography. P3HT(poly-3(hexylthiophene)) and PCBM(Phenyl-C61-butyric acid methyl ester) BHJ films, formed on nanostructured grating patterns with sub-50nm dimensions, exhibit preferential parallel lamellar stacking, with pi-pi stacking rotated 90 degrees out of the substrate plane. We have characterized the degree of chain re-orientation using grazing incidence x-ray diffraction (GIXRD) in order to measure the influence of the confining geometry dimensions. In the next year, we will understand the relationship between chain orientation and electronic function of pure P3HT and P3HT:PCBM blends by measuring the transverse current—voltage characteristics of the confined materials. A detailed understanding of the correlation between device electrical and optical properties and the material internal structure will inform design of higher performing solar cell architectures.

(2) We are investigating the use of nanoimprinting in fabricating BHJ devices. This process has advantages over conventional BHJ including larger Donor/Acceptor (D/A) interfacial areas,

fewer shunt paths, and preferred orientation. We have now optimized the temperature and pressure for the imprinting process and successfully fabricated large area nano-grating structures of pure P3HT and PCBM. Using GIXRD we have obtained detailed structural information including the periodicity, pattern height and side-wall slope angle of P3HT nano-gratings. These show faithful pattern transfer from the master. Our results also revealed the re-orientation of the P3HT crystalline domains from edge-on to face-on conformation. We have also been imprinting P3HT/PCBM blends. The idea is to use the imprinting to reorient molecular structure to improve device performance. GISAXS and GIWAXS measurements have shown that imprinting is able to induce face-on structure to blends as to pure P3HT. In the future, we plan to investigate the role of the pattern size, different materials and how stamping modifies device efficiency. Also, our supplier of the nanostamps has not been able to provide the new substrates, as required. We are investigating alternatives including the use of E-beam or the use of self-assembled co-polymers as etch masks for making stamps.

(3) We have recently started to investigate the use of chemically nano-patterned substrates to control the phase-separation of OPV thin-films on a sub-100 nm lengthscale. The chemical patterns with feature sizes ranging from 50 to 500 nm are fabricated by oxidation nanolithography of organic monolayers. These patterns can direct the phase-separation of OPV blends owing to the different affinity of the two blend components towards the methyl and carboxylic-terminated surface. We have initiated systematic studies on the effect of pattern feature size and shape on the morphology of the phase-separated blend. A serious limitation of the AFM-based lithography is the considerable time required to pattern areas larger than $\sim 10^4$ mm^2, too small to be relevant to the fabrication of highly efficient OPV devices. For this reason, we are also exploring methods of large-area chemical patterning of organic monolayers using conductive stamps.

Chemical Synthesis: We have developed a method for the preparation of P3HT functionalized with a low percentage of azide functional groups that allow photo-cross-linking of the polythiophene domains of OPV devices. Our initial structural and device studies suggest that functionalizing 5 mol% of the polymer repeat units does not significantly affect polythiophene structure or device performance in BHJ devices. Photo-cross-linking enables us to stabilize the polymer layer so that we can introduce nanometer-scale features in the polymer layer that will persist. We are working to better characterize these cross-linked polymers in OPV devices and focusing upon the preparation and characterization of imprinted devices in order to better understand the effects of nanometer-scale structure on the performance of OPV devices. We are also beginning work to try to develop general strategies for functionalizing semi-conducting copolymers to enable extension of this cross-linking chemistry to other polymer systems.

Push-Pull Polymers: These "third generation conducting plastics" contain alternating electron donor and acceptor co-polymers segments. OPV devices with these materials have improved control of the band gap and they have achieved efficiencies as high as 8.3% (Konarka Inc.). Very little is known about the structure of these materials. We are investigating the morphology and molecular orientation of a series of pull-push co-polymer thin-films using GIWAXS. Our preliminary measurements on these push-pull materials, provided by Konarka Inc., indicate a face-on lamellar stacking, in contrast to the edge-on stacking which is observed in conventional conducting plastics such as P3HT. We are also performing comprehensive investigations on the temperature-evolution of the morphology of these materials. We also intend to try nano-stamping with these materials.

Surface Chemistry and Electrochemistry of Ethanol

LDRD Project 09-004

R. Adzic, J. Hanson, P. Liu, J. Muckerman, J. Rodriguez and M. White

PURPOSE:

The goals of this project are to understand the fundamental surface chemistry and catalysis of ethanol associated with its use as a source of renewable hydrogen (reforming), its direct synthesis as a liquid fuel from renewable sources of "syn gas" ($CO/CO_2/H_2$) and its use as a fuel for direct electrooxidation in fuel cells. This effort is a response to the global need for an alternative fuel which can be generated from renewable sources and that can also serve as a chemical source of stored energy for transportation or electrical power. This interdisciplinary program involves the close collaboration of scientists in surface science, catalysis electrochemistry, and theory and is well-positioned to provide new approaches to alternative fuels that support BNL's energy mission and respond to expected DOE-BES initiatives in catalysis for energy applications.

APPROACH:

Ethanol has been spotlighted as a source of clean, sustainable and readily used transportable fuel and it currently constitutes 99% of the biofuels produced in the United States. In addition to its use as a direct replacement for gasoline, ethanol holds significant potential for use in fuel cells for generating electrical power. Direct production of ethanol from fermentation of biomass, however, suffers from poor efficiency such that bio-ethanol could at best only supplement current needs for liquid fuels. Moreover, the direct electrooxidation of ethanol ($C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$) suffers from slow kinetics even with the best available catalysts in current fuel cell designs. To address these issues, we propose to develop new catalysts for (1) the synthesis of ethanol from renewable sources of "syn gas" that are more readily scalable for industrial production, (2) the low temperature reforming of ethanol as an on-board source of hydrogen for powering fuel cells, and (3) improving the performance of the DEFC. In addition to identifying new catalytic materials, we need to understand the surface reaction mechanisms which could tell us how to selectively make or break the C-C bond in ethanol in order to avoid intermediates or products that act as catalyst poisons, rate-limiting traps or unwanted products.

The work is being accomplished through the coordinated efforts of several groups with expertise in the surface science of model nanocatalysts (Rodriguez White), *in situ* catalyst characterization (Rodriguez, Hanson, Adzic, Zhou), electrochemical methods (Adzic, Zhou) and ab initio theory (Liu, Muckerman). Catalyst materials to be studied will generally consist of nanoparticles of a metal (e.g., Rh, Pd, Pt) or metal alloy (e.g., Pt/Rh, Pt_3Sn, PtMo) deposited on a metal oxide support (e.g., CeO_2) or onto a metal electrode (Pt, Rh). Our work will address the exact role of the metals and oxide in the catalytic processes and investigate the importance of nanoparticle size, and redox ability of the metal oxide components (CeO_x or SnO_x). This work builds on recent successes in the use of metal-ceria nanocatalysts for hydrogen production and the development of a novel ternary catalyst ($Rh/Pt\text{-}SnO_2$) for the electrooxidation of ethanol.

Characterization of the catalysts under reaction conditions will make extensive use of unique *in situ* x-ray probes at the NSLS (AP-XPS, XRD, XAS) and atomic imaging probes at the CFN (e.g., HRTEM). In addition, a new instrument is being built as part of this project that will be able to link well-defined model nanocatalysts prepared under controlled UHV conditions with their performance under realistic reaction conditions.

TECHNICAL PROGRESS AND RESULTS (FY10):

- Theoretical calculations were carried out to gain a better understanding of the ethanol decomposition reaction on Rh metal, which is one of the best known catalysts for the electrooxidation and steam reforming of ethanol. Our results show that the most probable reaction pathway is through an oxametallacycle species, which is the precursor for breaking the C-C bond in ethanol. The complete reaction leads to the production of carbon monoxide (CO) and surface carbon (C) which can deactivate the Rh surface. Additional calculations show that alloying Rh with other metals (Pt and Pd) weakens the carbon-Rh bond which aids in the removal of surface carbon and facilitates ethanol combustion.

- A highly active nickel-doped ceria ($Ce_{0.8}Ni_{0.2}O_{2-y}$) catalyst has been discovered for the production of H_2 through ethanol steam reforming. The results of *in situ* x-ray absorption and diffraction experiments at the NSLS indicate that the catalyst exposes small particles of metallic nickel whose electronic properties are perturbed by interactions with ceria. Moreover, the nickel atoms induce the formation of oxygen vacancies that facilitate the cleavage of the O-H bonds in ethanol and water. In addition to finding a highly efficient, inexpensive catalyst, these studies show the importance of both the metal and the oxide phase in catalysts for ethanol steam reforming.

- The newly constructed instrument funded by this program was used for initial studies aimed at establishing the role of the metal oxide (SnO_x) component in the ternary $Rh/SnO_x/Pt$ electrocatalyst recently discovered by Adzic and co-workers. Surface science techniques were used to prepare and characterize model catalysts composed of SnO_x nano-islands deposited on a Pt surface. Their activity for ethanol oxidation was tested in an electrochemical reaction cell without exposure to air contamination. The catalytic activity of the Pt surface is significantly enhanced with addition of SnO_x nanoislands, with the highest activity occurring for the smallest nanoislands. The latter is attributed to unique surface sites on the SnO_x nanoislands, which activate water dissociation and the removal of CO (formed by ethanol oxidation) which poisons the Pt surface.

- A combined experimental and theoretical effort showed that the rate of methanol synthesis via CO_2 hydrogenation ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$) is significantly higher on Cu nanoparticle surfaces than on planar Cu(111) surfaces. The superior activity of the Cu nanoparticle is associated with its fluxionality and the presence of low-coordinated Cu sites, which stabilize the key intermediates and lower the barrier for the rate-limiting hydrogenation process. Our calculated results also suggest that the methanol yield over Cu-based catalysts could be improved by adding dopants or promoters which facilitate the hydrogenation of key intermediates.

Milestones (FY11)

- Perform experimental and theoretical studies on model nanocatalysts (e.g., Pd/Ga_2O_3) for the synthesis of ethanol from "syn gas" mixtures ($CO/CO_2/H_2$) and the electrooxidation of ethanol.

- Establish the nature of active sites on novel $Ce_{1-x}Ni_xO_2$ catalysts for ethanol steam reforming through surface science investigations on model Ni/CeO_2 surfaces.

- Correlate the physical and chemical properties of SnO_x nanoislands, e.g., particle size and Sn oxidation state, with ethanol electrooxidation activity.

Synergistic Interactions Between Poplar and Endophytic Bacteria to Improve Plant Establishment and Feedstock Production on Marginal Soils

LDRD Project 09-005

Daniel van der Lelie, Safiyh Taghavi, Lisa Miller, Richard Ferrieri, Alistair Rogers and Wei Zhu

PURPOSE:

To use a systems biology approach to understand, model and improve the growth of bioenergy feedstock plants on marginal soils without competition for agricultural resources. The project is characterized by the following elements:

- Understanding the plant growth promoting effects that endophytic bacteria have on their poplar host plant, with special emphasis on root formation and its effect on nutrient acquisition and growth on marginal soil.
- Explore plant-endophyte interactions to make biomass production (feedstock and food) on marginal soils economically feasible.

APPROACH:

We are following an integrated research plan to understand at the level of the genome, transcriptome and metabolome the interactions between poplar and two well-characterized endophytic bacteria, *Enterobacter sp.* 638 and *Pseudomonas putida* W619. These two endophytes were chosen, as preliminary genome analysis reveals the existence of distinct mechanisms by which these bacteria can affect the growth of their host plant: IAA production by *P. putida* W619 and production of acetoin and 2,3-butanediol by *Enterobacter* sp. 638. Our hypothesis is that both strains will affect the expression of different regulatory pathways in poplar, but that their altered expression will ultimately result in the same beneficial effects on plant growth and development, and nutrient acquisition. The involvement of different regulatory pathways also opens the possibilities for synergistic effects.

TECHNICAL PROGRESS AND RESULTS:

The following approaches were used:

- **Comparative genomics** (Year 1): *Our hypothesis is that endophytic bacteria have acquired specific functions, which are absent in closely related, non-endophytic bacteria, and that help them thrive in a plant environment.* Annotation and manual curation of the genomes of *Enterobacter* sp. 638, *P. putida* W619, *Stenotrophomonas maltophilia* and *Serratia proteamaculans* 568 was completed and showed the presence of several genomic islands that play a unique role in plant-endophyte interactions.
- **Metabolite analysis** (Years 1-2): *Our hypothesis is that the growth of Enterobacter sp. 638 and P. putida W619 in the presence or absence of poplar will result in changes in metabolite profiles, both for bacteria and plant, especially for compounds involved in plant-microbe signaling and plant growth promoting compounds.* The production of the plant growth promoting compounds acetoin and 2,3-butanediol was specifically induced by the presence of plant sugars in the medium. For instance, metabolome analysis showed the production of acetoin and 2,3-butanediol by *Enterobacter* sp. 638 in the presence of sucrose, while these phytohormones were not produced when lactate was used as a carbon source. On the other hand, the production of the antimicrobial compound 2-phenylethanol by *Enterobacter* sp. 638 was only detected when the strain was grown on rich medium.

- **Transcriptome analysis** (Years 1-3): *We expect changes in gene expression to be directly linked to changes in the plant's nutrient status, metabolite production, and altered plant growth and development.* As an alternative to microarray studies, that gave questionable results, comparative whole transcriptome sequencing was performed on cultures of *Enterobacter* sp. 638 grown on sucrose and lactate. Transcriptome analysis confirmed that growth in the presence of sucrose triggers a response in *Enterobacter* sp. 638 that seems to mimic its plant associated life style. This response seems to be controlled via quorum sensing and causes a change from planktonic growth to biofilm formation. It also affects the expression of pathways involved in plant colonization and nutrient acquisition.
- **Plant growth promoting effects** of various endophytes were tested for other bioenergy feedstocks and food crops, including tomato, tobacco, peppers and sunflower. For all plant types, beneficial effects of plant growth and development were observed after inoculation with *Enterobacter* sp. 638.
- **Effects of endophytic colonization on the carbon and nitrogen status** of their poplar host. *Many of the signals for the plant's C and N status are well know regulators of gene expression (sugars, nitrate, amino acids). We expected to see changes in gene expression that are directly linked to changes in the plant's nutrient status, resulting from improved plant growth and development.* Using a high-throughput enzyme screening platform we found that *Enterobacter* sp. 638 is impacting central C and N metabolism and increasing the availability of amino acids for protein synthesis. These results were confirmed in year 2.
- **Data integration and modeling** (Years 1-3). Transcriptome data are currently being analyzed via cluster analysis in order to identify common trends in expression profiles. This analysis will serve as the basis to develop comprehensive models.

Milestones from the start date of project:

Month 6: List of candidate genes for *Enterobacter* sp. 638 and *P. putida* W619 that are involved in endophytic colonization of poplar, including biosynthetic pathways for plant growth promoting compounds – completed.

Month 12: Microarrays to study the transcriptome of *Enterobacter* sp. 638 and *P. putida* W619 – completed.

Month 18: Identify growth regulating compounds and other secondary metabolites that play a role in plant-microbe communication and plant growth regulation – completed.

Month 18: Identify genes and pathways that are potentially involved in the regulation of plant growth and endophytic colonization – completed.

Month 24: Description of the effects of endophytic colonization on the carbon and nitrogen status of their host plant – ongoing.

Month 30: Collection of endophytic strains mutated in genes involved in the synthesis of plant growth promoting compounds – targets for mutagenesis have been identified.

Month 30: Confirm the involvement of previously identified genes and pathways (based on transcriptome and metabolome data) in the regulation of plant growth and endophytic colonization.

Month 30: A series of comprehensive models that describe the genetic networks necessary for the successful symbiotic interaction between endophytic bacteria and their poplar host plant.

Petascale Data Mining for BNL's Data Intensive Sciences

LDRD Project 10-001

Dantong Yu

PURPOSE:

Our goal is to research and develop techniques of data management and data mining to support BNL's data-intensive science applications, such as climate modeling and computational biology, and to extend the outcomes to other multidisciplinary data modeling and processing programs. Particularly, the foci of our work are to assure the availability of suitable data-mining techniques for identifying patterns and structures in massive datasets from these exemplary applications, along with high-performance tools for particular applications that will allow scientists to gather, organize, analyze, and model large heterogeneous datasets. The research outcome will strengthen BNL's expertise over a broad spectrum, from domain knowledge in data-intensive sciences to the commensurate data modeling and analysis. The success of the project will help BNL to establish a scientific data-management program based on a strong partnership between science and computational research groups. These science groups include the Atmospheric Science Division and the Biology Department.

APPROACH:

Data-intensive applications, such as high energy and nuclear physics, astrophysics (LSST), computational biology, and climate science will generate exabytes of data in the next five years. This prospective explosive growth in storing and processing data poses new critical requirements for data mining technologies and automated tools. New capabilities sorely are needed to intelligently assist scientists in transforming such large volumes of data into useful knowledge, and to expedite scientific discoveries. Accordingly, we propose to develop a new generation of tools and techniques for mining data and acquiring knowledge using computational biology and climate modeling as example applications in a multidisciplinary, heterogeneous data-modeling and data-processing setting.

The fundamental challenge for data mining in today's data-intensive science environment is not in moving small subsets of homogeneous data into a computing cluster to run individual analyses and knowledge derivation routines. Rather, we face a system-level challenge to deal with complex mining processes simultaneously for thousands of scientists on their heterogeneous peta/exabyte datasets, with each of the data mining processes having different requirements in time and accuracy. The following four items summarize the proposed project's scope and milestones.

1. Devise real-time and offline scalable data-analysis methods enabling researchers to identify and select critical features from multiple features,
2. Improve existing methods, and devise new ones for statistical sampling and clustering that effectively extract known and unknown patterns, and support complex searches,
3. Enhance overall performance in data management, and parallelize the proposed data- mining processes to ensure better performance, and,
4. Transform the mined data-products into statistical models so to best represent knowledge in the presence of data uncertainties, inconsistencies, and incompleteness.

Our technical approach is to extend the successful Google MapReduce computing paradigm to solve complex mining problems. We will develop the proposed items in MapReduce's open-source version, viz. Hadoop. The data mining and visualization techniques generated in this project will be deployed, evaluated, and vetted in close collaboration with scientists from two representative projects, viz., BNL's Climate Studies and the DOE's system biology knowledge base project to manage large datasets, build data models, and to compare models with observations. We hired a post-doctoral research associate (Shinjae Yoo) to conduct his research in petascale data-modeling at the New York Center for Computational Science. We also are sponsoring and co-advising graduate students in data modeling and mining.

TECHNICAL PROGRESS AND RESULTS:

We collaborated with BNL's Atmospheric Science Division to investigate data-assimilation methods and modeling evaluation techniques. We planned to form a virtual climate visualization center integrating complementary areas of expertise, including remote sensing, climate modeling, computer science, and statistics. We collaborated closely with the FASTER team (Fast physics system testbed and research) to establish, test, and assess techniques for comparing the climate models and observational data. The collaboration resulted in two proposals in applying data mining techniques in climate modeling. Furthermore, we initiated collaborative work in data-intensive system biology with research groups in BNL's Biology Department and the Cold Spring Harbor Laboratory. The itemized contributions are as follows:

1. Doppler RADAR clustering: We successfully finished the first two iterations of preliminary data-analysis. We identified the preprocessing problems associated with our algorithms and worked on them.

2. Climate Modeling with data clustering: We completed the pilot analysis of Doppler radar data. Based on the findings from this analysis, we continued to implement a distributed clustering algorithm for the whole set of data.

3. Knowledge base for system biology: We submitted a knowledge base pre-proposal. We developed software of Google Map/Reduce based distributed data analysis to process plant gene-sequence data. We observed that the speed of processing data from Sorghum bicolor (a grass) increased linearly with the number of computing cores.

4. Two inter-disciplinary research investigations were initiated in the last year. The first is a joint proposal to the DOE to create a computing platform useable by both experimental and computational scientists to identify the emergent properties arising from integration of multiple 'omics' datasets and data relevant to the genotype to phenotype relationships. We also started to design and implement a solar power forecasting system to collect environmental data, to model the impact of weather on solar output via data mining techniques, to monitor and predict solar output, and to enable smart grid to schedule electricity in real-time in the power-grid system.

The following paper and proposal were submitted within the last six months, and are under review:

1. Shinjae Yoo, Yiming Yang, Jaime Carbonell, "Modeling Personalized Email Prioritization: Classification-based and Regression-based Approaches", Submitted to WWW 2011.

2. Macromolecular Structures, Interactions, and Networks Knowledgebase Center (MSIN Kbase Center), PI: Sergei Maslov, Date of Submission: December/20/2010, DOE, Status: Pre-proposal Pending, Proposed budget: $4,200,000/per year, 2011-2016.

Solar Energy Source Evaluation for Smart Grid Development

LDRD Project 10-006

Meng Yue, Mike Villaran and Robert Bari

PURPOSE:

The purpose of the proposed study is to evaluate the stability, reliability, and power quality of the electrical grid when it is supplied by an increasingly significant contribution from intermittent solar energy generation. The study will also take advantage of a planned BNL solar facility. Systematic approaches featuring stability assessment, coordinated control design, and dynamic inclusion of communication infrastructure will be developed. An existing integrated power system analysis tool, EPTOOL, previously developed at BNL, will be expanded and enhanced to facilitate the study of future Smart Grid development.

APPROACH:

The proposed approaches and tasks are discussed for the individual objectives of this study below. The novel features of the proposed approaches include (1) a stability assessment of the grid using a model of a PV system that accounts for its variability; (2) an advanced coordinated wide-area controller design; and (3) an incorporation of communication links into the power system dynamics. In addition, the integrated tool EPTOOL will be expanded and enhanced to facilitate the study of issues related to the Smart Grid development. The plan is to use the BNL solar energy system to provide parameters and data needed for developing and validating models for the PV system. Hypothetical data can also be used to demonstrate the proposed approach.

TECHNICAL PROGRESS AND RESULTS:

In the first year of this project, a generic solar generation model was developed based on manufacturers' data to analytically relate the irradiance and temperature to the solar generation output. A popular two-staged dc-ac power conversion scheme consisting of a dc-dc converter and a grid-connected inverter was adopted. The first function of the dc-dc converter is to step-up the solar dc output voltage to a level that is higher than the voltage value of the point of interconnection (POI) of the grid such that a step-up transformer is not needed for a voltage-source inverter to inject power into the grid. In addition, the dc-dc converter continuously tracks the maximum power point (MPP) of the solar plant. The grid-connected inverter should be able to maintain its dc input voltage nearly constant under a transient condition and is modeled as a controlled current source in this study. The detailed current-loop control of the inverter is omitted here because it is very fast and the sub-cycle dynamics are not of interest when studying the transient stability of the grid.

The major achievements of this study include (1) development of a modified incremental conductance (IncCond) maximum power point tracking (MPPT) algorithm than can effectively improve the MPPT performance of a solar module/array; (2) development of an interface between solar power plants and the transmission grid including both active and reactive power injection control such that the impact of intermittence of the solar generation, due to, e.g., the cloud transient, on the grid transient can be evaluated; and (3) development of an electrical circuit model for the battery energy storage system (BESS), the interface between the BESS and the grid, and the frequency control. A Matlab-implementation of the developed models and algorithms was performed to provide a flexible integrated tool for studying the impact of

increasing penetration of solar generation and developing better control to compensate for the introduced intermittence.

A cloud transient scenario is considered in this study by assuming the same irradiance variation pattern but with a time delay of, e.g., 0.3 seconds, at each string. This scenario actually simulates a cloud movement at a constant speed in the direction perpendicular to the 8 parallel strings of the solar array, which is a simplified case because it assumes the same string sees the same irradiance despite the different physical locations and cloud movement directions in practice (e.g., the moving direction of the cloud may not be perpendicular to the string).

In addition to the cloud transient caused change of the irradiance, faulted conditions consisting of multiple faults, e.g., transmission line faults, can also be evaluated by using the developed simulation tool.

The milestones for FY2011 include the following:

- Extend the solar generation model to the distribution network and model the detailed grid-connected inverters that can be used to analyze power quality and harmonics;
- Integrate short-term, i.e., 5 minutes, solar generation forecasting algorithms in the model;
- Incorporate the battery energy storage system and develop control strategies for coordination of solar generation and battery charge and discharge;
- Develop dynamic var/voltage compensation;
- Provide a software test-bed for exploiting the real-time PMU measurements in the distribution network;
- Address communication issues in terms of measurement and control of the grid-connected inverters in the model.

High Throughput Quantitative Biochemical Phenotyping

LDRD Project 10-007

Alistair Rogers

PURPOSE:

This LDRD will establish a platform for high throughput biochemical phenotyping. There are only three labs world-wide using robots to conduct automated biochemical and enzymatic assays, Dr. Rogers' lab is one of them. If successful this LDRD will establish Brookhaven as a major player in large scale phenotyping projects. Planned publications will demonstrate the capability of the platform to address critical questions in global change plant biology. The current focus of the research is central C and N metabolism in plants. Therefore, the platform is focused on measuring parameters associated with C and N metabolism. This complements existing analytical assets in plant systems biology at Brookhaven and can be readily adapted to address other challenges in plant biology at the intersection of climate, energy & environment.

APPROACH:

Plant biology is emerging from the genomic revolution and understanding of the interaction between the genotype and the environment is now seen as the major barrier to progress. In order to understand the genetic controls on complex traits such as biomass and yield, it is necessary to grow plants in their production environment which requires extensive sampling of plant tissue throughout development and across seasons. When multiplied by the hundreds to thousands of individual accessions in germplasm collections or breading populations, it is clear that any effort to understand the genotype to phenotype link will require a high throughput solution. This is why Dr. Rogers' lab is pursuing the development of a high throughput phenotyping platform.

The project has three components (1) Set up a robot that is capable of conducting high throughput biochemical phenotyping, (2) identify and develop assays for diagnostic parameters of interest and adapt them to a 96-well format, and (3) use the platform to address science questions that will demonstrate the utility of the platform. In support of components (1) and (2), Dr. Rogers' is collaborating with Dr. Gibon (INRA-Bordeaux) who pioneered the use of robots to conduct biochemical assays in plant tissue. In support of component (3) Dr. Rogers is collaborating with Dr. Leakey and Dr. Ainsworth (SoyFACE-UIUC) on a projects where soybean has been grown at elevated [CO_2] with and without water stress and at high ozone concentration. At Brookhaven Dr. Rogers is collaborating with Dr. Schwender (Biology). He is also leveraging sampling conducted as part of his research into carbohydrate profiles in loblolly pines grown at the Duke Forest FACE experiment. He recently established collaboration with Dr. Zhu (PICB, Shanghai, China) to understand metabolic controls on yield in rice.

TECHNICAL PROGRESS AND RESULTS:

Component 1: During the first year Dr. Rogers hired a post-doc, defined the technical specifications of the robot and purchased it. He also renovated his laboratory to accommodate the new equipment. This included removal of two old plant growth chambers, repairs to the flooring, and upgrades to the electrical supply and purchase of a second -80°C freezer. In the first quarter of the second year, the robot was installed and is currently being commissioned.

Component 2: At the onset of the LDRD project Dr. Rogers' lab had 96-well assays for c. 25 parameters of interest in central C & N metabolism. In the first fifteen months of the project, his

laboratory has expanded this to include nine parameters associated with oxidative stress, five associated with the PEP branch point in central metabolism, four associated with the C4 pathway, and three additional parameters associated with N metabolism.

Component 3: The assays for oxidative stress were developed in collaboration with a graduate student at UIUC and were used to understand the impact of elevated [CO_2] and chronic ozone exposure to acute oxidative stress. This work has resulted in a paper that is currently in press (Gillespie et al. 2011). Samples from the Duke Forest FACE, SoyFACE, a pilot study in rice, and the *Brassica napus* project have been taken and are now at BNL. Dr. Rogers and Dr. Ainsworth are currently preparing a response to a recent DOE-NIFA call to address the genotype-phenotype link in biofuel species.

PROJECT MILESTONES

	FY11			**FY12**			
Activity	**March**	**June**	**Sept.**	**Dec.**	**March**	**June**	**Sept.**
Complete Commissioning of Robot and remaining upgrades to the laboratory	X						
Hold an "open day" for BNL scientists and interested parties to see the robot	X						
Complete analysis of *Brassica napus* tissue pilot study	X						
Complete analysis for the rice project pilot study	X						
Complete analysis of two seasons of samples from the SoyFACE CO_2 x drought experiment		X					
Complete analysis of needle samples from the Duke Forest FACE experiment			X				
Present data at national meeting (TBD)		X				X	
Submit manuscript on technical development of enzyme assays		X					
Submit manuscript on data from SoyFACE experiment			X				
Complete analysis of fine root samples from Duke Forest FACE experiment				X			
Complete analysis for the main *Brassica napus* experiment				X			
Complete analysis for follow up rice experiment					X		
Submit manuscripts on FY12 experiments					X	X	
Present technical and experimental progress to BER	X				X		

Characterization of Materials in Extreme Environments for Advanced Energy Systems Using the National Synchrotron Light Source

LDRD Project 10-008

Lynne Ecker and Lars Ehm

PURPOSE:

Improved material performance under extreme conditions is crucial to every energy technology. The goal of this research is to develop new, cross-cutting materials synthesis and characterization techniques that, combined with existing BNL facilities for material testing and modeling, will impact the design cycle of a wide range of materials for advanced energy systems. A long-term goal is to develop techniques for studying energy related materials at the National Synchrotron Light Source (NSLS) that will be transitioned to a new beamline at the NSLS-II. Materials selected for this research have applications in advanced nuclear energy systems and enhanced geothermal systems (EGS).

Materials for Advanced Nuclear Energy Systems

APPROACH:

The goal for advanced nuclear energy systems is to develop materials that have a longer lifetime in high-temperature and high-radiation environments. Materials used for this research were obtained in collaboration with Dr. Stuart Maloy, Los Alamos National Laboratory (LANL) and are HT-9 (a ferritic/Martensitic stainless steel (13Cr-1Mo) for use in fast reactors) and PM-2000 and MA957 (oxide dispersion strengthened steels (ODS) that have 0.5% or less Y_2O_3 oxide nanoparticles homogeneously dispersed in a ferritic matrix). To better characterize radiation damage in structural materials, this research proposed using the Pair Distribution Function (PDF). The PDF is the probability of finding atom pairs separated by distance r and provides information about the atomic arrangement over short and intermediate distances. It is particularly useful for investigation of materials with only short-range structural repeatability, such as materials with a high degree of disorder. The resolution of PDF data is dependent on high-energy x-rays and having large detector coverage.

TECHNICAL PROGRESS AND RESULTS:

A diffraction pattern obtained at beamline X17B1 for alloy HT-9 is shown in Figure 1. While it is possible to obtain a PDF and conclude that the material has a body-centered cubic structure from the data (Figure 2), the resolution is not sufficient to allow the study of defects. Similar data for the ODS materials indicate that the concentration of the Y_2O_3 nanoparticles is too low to detect. Based on these results, four actions are planned:

1. Higher real space resolution data is needed to detect changes in structure due to radiation damage. A dedicated high energy beamline, X17A, with a large detector will become available in 2011. Data from this detector will be obtained. *Milestone Date: March 2011*

2. The HT-9 alloy system and ODS materials are complex. HT-9 has an engineered microstructure with precipitates and a controlled grain size that may change with irradiation. Copper, and perhaps tantalum and tungsten will also be used as samples to provide a

simplified model system. Irradiated samples may be provided from previous research or using ion irradiation. *Milestone Date: June 2011*

3. A new collaboration was formed with Dr. Amit Misra at LANL to look at defects in nanolayered composites. The ODS steels are believed to be radiation resistant because defects are annihilated at the oxide nanoparticle/matrix interface. However, the interfaces are difficult to characterize because they are small and located throughout the sample. The nanolayered composites provide large interfaces that can be characterized. Samples of Cu/Nb, Y_2O_3/Fe and TiO_2/Fe will be characterized using extended x-ray absorption fine structure (EXAFS) to determine the atomic structure at the interface and how it is altered by radiation. This also provides additional data for comparison to the PDF results. *Milestone Date: Beamtime Summer 2011*

4. Modeling has been initiated to calculate the PDF for defected structures. The PDF for a simple vacancy has been determined and indicates that defects must occur at more than approximately one percent of the atomic positions to have a detectable effect on the PDF. In addition, molecular dynamics calculations will be used to estimate more complex irradiated microstructures and the PDF of these atomic configurations will be calculated. This will facilitate the prediction of results from PDF, provide a closer connection with modeling radiation damage to better design experiments to validate the codes, and provide multiple atomic configurations to estimate different radiation doses. *Milestones Date: Fall 2011*

Materials for Enhanced Geothermal Systems

APPROACH AND TECHNICAL PROGRESS:

A new collaboration was formed with the Energy Resources Division to determine the feasibility of using supercritical carbon dioxide as the working fluid for Enhanced Geothermal Energy Systems (EGS). The structural integrity of the reservoir well is partially dependent on the susceptibility of minerals to reaction with sc-CO2 in an aqueous environment. Mineral powders and samples have been exposed to sc-CO2 in an autoclave. Results from scanning electron microscopy performed at the Center for Functional Nanomaterials include that the albite and biotite in granite rock are vulnerable to carbonation and that the rock surface develops a porous microstructure. X-ray photoelectron spectroscopy (XPS) will be performed at X24A to determine the amorphous reaction products and measure the depth of the reaction layer. This information will be used to estimate the reaction rate. A sample chamber (environmental cell) suitable for in situ investigations of CO2/water/rock at a beamline is being built. *Milestone Date: Summer 2011*

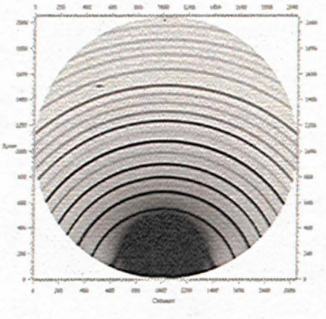


Fig. 1: Diffraction pattern for alloy HT-9 taken on beamline X17B1 (Beam energy of 75 keV).

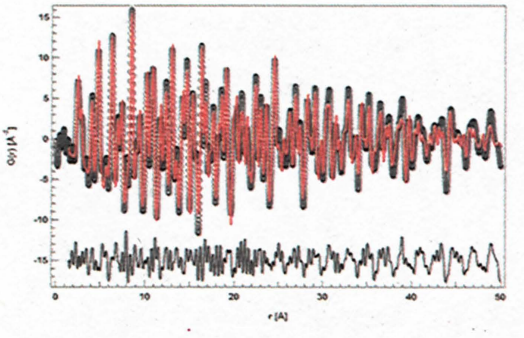


Fig. 2: PDF (lower curve) of alloy HT-9 calculated using a bcc model, lattice parameter a = 2.844 angstrom, Fe is 82.7 wt.%, Cr is 11.2 wt.% and C is 0.09 wt.%.

Development of an Ultrafast Electron Diffraction Facility for Condensed Matter Physics Challenges

LDRD Project 10-010

J.P. Hill, X. Wang, J. Murphy, C.-C. Kao, Y. Zhu and A. Cavalleri

PURPOSE:

The goal of this LDRD is to develop a unique Ultrafast Electron Diffraction (UED) instrument to study insulating ground states and fundamental photo-induced excitations in a class of materials called strongly correlated materials. The ground states in these materials are characterized by long range ordering of charges, orbitals, spins and lattice distortions. Using electron diffraction, we will probe several of these ordered degrees of freedom in a single diffraction pattern, allowing us to understand how optical radiation couples to these materials and how energy is subsequently distributed. Our instrument is based on a radio frequency (RF) photocathode, providing 100 femtosecond pulses of electrons at 2-5MeV, an order of magnitude higher in energy than all existing UED instruments. At high energies, space charge effects are reduced and shorter pulses can be achieved at large pulse charge. Once operational, this instrument will form the backbone of an ultrafast program within condensed matter physics and material sciences. Based on this work, it is anticipated that a proposal for a new FWP will be submitted to DOE BES to carry out a new program in ultrafast science at BNL.

APPROACH:

The primary objective is to study the novel orderings of charge, orbital, spin and lattice distortions in strongly correlated materials and understand how optical radiation perturbs these ground states and leads to non-equilibrium phenomena. There are no instruments that can accomplish all of these tasks in a simple, compact configuration. Table-top, optical, pump-probe experiments can infer dynamics but can't singly probe a discrete degree of freedom. X-ray methods can probe single degrees of freedom but can do so only one at a time and several ordered degrees of freedom are inaccessible (they lie outside the Ewald sphere). Ultrafast electron diffraction fills this instrumentation void. Using UED, we can probe several degrees of freedom independently in a single diffraction pattern, allowing us to understand how the excitation process affects different degrees of freedom on fundamental timescales.

There are several existing UED instruments capable of generating ultrafast pulses of electrons. However, in nearly every instance, these are pulsed sources based on DC acceleration of electrons with maximum achievable energies of 10s of keV to 100keV. While these instruments have contributed important science, there are several shortcomings associated with low kinetic energy electrons. Most importantly, at these energies, pulses of electrons suffer from Coulombic repulsion and hence, the pulse length is strongly dependent on the charge per pulse. Additionally, at low energies, the electrons have reduced penetration depth requiring experiments to be performed at grazing incidence in reflection geometry. In recent years, questions have been raised about results obtained from these low energy systems. Specifically, it was proposed that in the grazing incidence geometry, deflection of Bragg peaks (that might imply a deformation of the lattice) could also be caused by a low density plasma near the surface of the material. These unbound electrons near the surface (photo emitted electrons) are exactly what occur when the sample is photo excited.

In collaboration with scientists from the Source Development Lab of the National Synchrotron Light Source, we began construction of a high-energy, short-pulse, electron source that is based on an RF photocathode. There are several advantages to using a high energy (2-5MeV) electron source. For one, electron pulse length can be finely tuned by varying the phase of the RF driving field relative to the time the electrons are emitted from the photocathode giving us fine control over the pulse length. Additionally, at high energies the increased electron penetration depth allows us to perform these experiments at normal incidence and in transmission, reducing spurious effects caused the optical excitation process.

TECHNICAL PROGRESS AND RESULTS:

In this first year of funding we have hired a post-doc, Ron Tobey, and nearly completed construction of the instrument. The experimental hardware is all in place, with the exception of the high power RF system currently being installed. For reasons out of our control, we are behind where we would like to be - in particular there was a fire in the klystron requiring a long delay as a replacement was identified, modified and installed. At present we are planning on redirecting LDRD funding that was initially meant for a student to provide technical support with the goal of finishing the entire apparatus in April of 2011. Once the construction is completed we will be in a position to commission the instrument and measure existing samples in a very short period of time.

In the broader context of an ultrafast program within condensed matter physics, this year has seen excellent progress. Tobey has initiated several projects that are now coming to fruition, and we expect 2011 to continue this trend. In November we completed beamtime at the soft x-ray beamline of LCLS to study long range spin and orbital ordering in the Manganite $La_{1.5}Sr_{0.5}MnO_4$ using resonant diffraction. The beamtime was a resounding success and data are now being analyzed. Initial analysis suggests the surprising result that the orbital order melts faster and more completely than does the magnetic order, a result which if it stands, will raise direct questions about the conventional understanding of this ground state.

We have also applied for and been granted two additional blocks of beamtime at the soft x-ray hutch of LCLS for the upcoming allocation, amounting to 33% of the beamline's allotted time. Here at BNL, we are utilizing the CFN ultrafast optics to start an ultrafast Raman program to study the short range spin ordering in correlated oxides. Probing short range spin correlations through Raman scattering provides an excellent complement to the x-ray methods employed at e.g. LCLS, and the electron methods that are at the heart of this project. In combination, we map the effects of optical excitation on spin ordering at all length scales on sub-picosecond timescales.

Milestones for the remainder of this fiscal year are to:

1) Transport electrons down the beam path (April 2011)
2) Observe the first electron diffraction pattern (May2011)
3) Perform the first pump probe UED experiment at SDL (June 2011)
4) Perform soft x-ray pump probe experiments on cuprates (June 2011)
5) Perform soft x-ray pump probe experiments on Multiferroics (July 2011)
6) Submit paper on Raman pump probe experiments on nickelates (Sept 2011).

Design of Pt-free Electrocatalysts for Fuel Cell Oxygen Reduction Reactions

LDRD Project 10-012

Peter Khalifah

PURPOSE:

Although Pt-based hydrogen fuel cells have demonstrated impressive efficiencies (~50%), the current technology can never be implemented on a commercially relevant scale due to the extreme cost and the terrestrial scarcity of the platinum metal that is used to catalyze the recombination of protons with O_2 to form water in the oxygen reduction reaction (ORR). Furthermore, the ORR reaction is inefficient and requires a very large overpotential to proceed. A search for better catalysts will be initiated, integrating the materials synthesis and discovery experience of the Khalifah group with the fuel cell electrochemistry measurement expertise of the Adzic group. This search will focus on conductive transition metal oxide systems which offer the promise of activity, economy, and acid stability necessary to produce viable fuel cell systems. The objective of this work is the synthesis and characterization of a number of novel conductive and acid-stable transition metal oxide systems to explore their potential for electrocatalysis. The search for effective new catalysts is a high-risk exploratory project, but one which can potentially offer large rewards. Success in this endeavor will provide the preliminary results necessary to compete for programmatic funding in this area, and will establish a strong collaboration between synthesis (Khalifah) and characterization (Adzic) groups in the BNL Chemistry Department.

APPROACH:

While a good deal is known about the general features of oxygen reduction reactions mediated by Pt and other noble metals, exploratory work is necessary to identify transition metal oxides with ORR activity, and to understand the structural and electronic features that promote this activity. What is the recipe for a good ORR electrocatalyst? Our target systems will allow the incorporation of a variety of transition metals with variable oxidation states to participate in reactions, have good electrical conductivity to avoid potential losses at the electrode, and have the ability to accommodate defects which may serve as active sites for ORR reaction steps. Furthermore, we will focus on systems which are anticipated to have reasonable acid stability, whose lattice may accommodate hydrous species (H_2O, H_3O^+, OH^-), and whose structures are amenable to substitutional tuning, thereby allowing catalyst properties to be optimized.

We have chosen to focus on two main classes of compounds, pyrochlore and hollandite-type metal oxides. Ruthenate pyrochlores have been previously demonstrated to exhibit ORR activity; we will synthesize and test the activity of new and/or less well known conductive pyrochlores to see if similar activity can be achieved. Hollandite-type compounds (1D channel compounds with different sized channels) are close structural relatives of the rutile structural family, which includes two of the most active catalysts for water oxidation (RuO_2, IrO_2) – the inverse of the ORR reaction. Hollandites with metals which are both early (Ti, V, Mo) and late transition metals (Cr, Mn, Fe, Ru, Rh, Ir) will be synthesized and tested for ORR activity.

A complementary portion of this work will be the growth of large single crystals of materials with known or potential ORR activity, which will provide more complete information than typical powder preparations.

TECHNICAL PROGRESS AND RESULTS:

In the first year of this project, we have made progress in the following areas:

Aim 1: Explore conductive pyrochlores

Research in this area began with the investigation of pyrochlores compounds which are expected to have good acid stability – namely those with Ti, Nb, and/or Ta as the *B*-site cation. The first set of test samples combined these *B*-site cations with Bi and/or Ce on the *A*-site, as these two cations have been previously observed to improve the conductivity of other pyrochlore systems. Neither of these strategies was successful as all preparations resulted in samples with resistances exceeding MΩ values. Work then turned to mixing Ti, Nb, and Ta with stable divalent or trivalent cations such as Ca or Y. These compounds were then subjected to strongly reducing conditions to improve their conductivity. Judging by the observed color changes, these strategies are promising and more work is being done to fully structurally characterize reaction products.

Aim 2: Explore hollandite compounds

Synthetic efforts in this area have focused on the synthesis of Ti and Ru containing hollandites. A set of conductive compounds have been synthesized, and we have begun their structural characterization using powder x-ray diffraction tools. Electrochemical characterization tools have been purchased and installed; the initial characterization of these materials has recently begun.

Aim 3: Produce large single crystals

Our optical floating zone furnace has been recently installed. We have successfully carried out the growth of the reduced (+3.8) titanate ternary compound $La_5Ti_5O_{17}$ using fully oxidized (+4) titanium precursors, demonstrating that forming gas can be effectively used to access lower valence states of early *3d* transition metals. The first crystals were about 0.5 cm in diameter and 1.0 cm in length; scale-up to larger sample dimensions is planned. We will next be exploring some mixed Ti/Nb rutile compounds in this manner.

Additional crystals of some ternary niobate materials have been grown by what appears to be vapor transport or grain growth at very high temperatures (~1600 C) under reducing conditions. We have discovered two new reduced niobate compounds which are black in color and are anticipated to have good electronic conductivities. Single crystal diffraction data has permitted the full structural refinement of these two new phases.

In conclusion, we have identified routes for the production of acid stable transition metal oxides of both pyrochlore and hollandite type, and will test their ORR activity in the next phase of this project. It has been verified that our optical floating zone furnace will be an effective tool for the production of large single crystals of compounds central to this study.

Charge Generation and Transport in Films of Conjugated Polymers for Organic Photovoltaics BNL Part of a Collaborative NREL, BNL, ANL LDRD

LDRD Project 10-014

John Miller and Andrew Cook

PURPOSE:

This LDRD has three principal scientific goals that will be supported by two developments in instruments and technique. These and the APPROACH sections are similar to those described a year ago. In general, this project seeks to understand films of conjugated polymers in order to contribute to the development of high-efficiency organic photovoltaic (OPVs) devices. Specific scientific goals are:

1. Understand the nature of charge carriers (electrons and especially holes) in conjugated polymer films and determine their numbers (concentrations).

2. Measure and understand mobilities of charge carriers in polymers.

3. Measure and understand light-driven charge separation.

In addition to scientific and technical goals, one of the objectives is to build a connection between BNL and NREL in the area of organic photovoltaics, based on complementary knowledge and capabilities at the two institutions. A BES program manager has indicated interest in providing follow-on funding for a successful BNL/NREL collaboration.

APPROACH:

To pursue these goals the two Labs will develop new abilities based on the complementary capabilities and apply the instruments to the scientific goals. The instruments will include:

1. Two microwave conductivity instruments. One will be an upgrade of the laser excited instrument at NREL, where it will be sited. The second, at BNL, will measure charge carriers created by 9 MeV electron pulses at BNL's Laser Electron Accelerator Facility (LEAF). This electron pulse excitation is expected to produce electron-hole pairs that have escaped the Coulomb attraction that binds them.

2. NREL expertise will develop methodologies to create thick (1 mm or more) films of conjugated polymers to enable spectroscopic interrogation of charge carriers created by ionizing electron pulses at LEAF. BNL expertise will develop methods to investigate the nature of the charge carriers in these thick films using, principally optical spectroscopy and possibly also infrared spectroscopy.

TECHNICAL PROGRESS AND RESULTS:

Our start has been slower than hoped because two postdoc candidates at both BNL and NREL declined the Labs' offers. We located another candidate who accepted our offer and arrived recently (11/29/10). Meanwhile NREL now has its team on board and has started construction of a new microwave conductivity apparatus

A meeting with NREL colleagues Garry Rumbles and Nikos Kopidakos in late October generated a number of expanded ideas for the scope of this proposal. To understand the nature of charge carriers in polymer films containing aggregates of conjugated chains, Rumbles suggested that an intermediate step be investigation of aggregates in solution that mimic properties of the films. They have produced such aggregates in o-dichlorobenzene (ODCB), a popular solvent for preparation of films by spin-casting. The chemistry for production of holes in ODCB is not known, so experiments have begun at BNL's LEAF accelerator. The experiments seem to show efficient production of holes. One initial concern, fast geminate recombination due to the aromatic nature of ODCB, seems not to be a serious problem. During the next few months transient optical spectra will be obtained on aggregates in ODCB. A next step will be injection of charges into solid polymers samples at LEAF. For that purpose, our joint discussions produced two additional methods to produce sufficiently thick samples for transient absorption experiments at LEAF.

An additional component is experiments of conjugated diblock copolymers. These molecules have potential to carry out the basic requirements for successful organic photovoltaics (OPV): light absorption, exciton transport to a junction, exciton splitting, separation and electron and hole transport.

An important part of this LDRD will be linking of groups at BNL and NREL to perform joint experiments, but as importantly to engage, contrast, compare and merge our different visions of the best paths to efficient organic photovoltaics. To this end we plan frequent meetings. One occurred with the PIs. The next that will include the entire groups from both Labs is planned for early February.

Milestones 2011: Complete investigation of ion-production in ODCB; utilize results to obtain optical spectra of holes in aggregates of conjugated polymers. Submit papers on these subjects. Examine transient absorption of thick films and try pressed pellets. Complete microwave conductivity at NREL. Measure spectra and numbers of holes created in solid conjugated polymers by transient absorption at LEAF.

Milestones 2012: Install microwave conductivity at BNL. Compare microwave with information from optical spectra of holes to obtain hole mobilities. Perform microwave conductivity experiments, with electrons and holes injected into diblock copolymers at LEAF and on photoexcited polymers at NREL. Develop a grand vision for OPV based on expertise and views in the two Laboratories. Prepare a joint proposal to BES for ongoing funding.

Photoelectrochemical Fuel Generation from Water and Carbon Dioxide

LDRD Project 10-015

James T. Muckerman, Carol Creutz, Etsuko Fujita and Kotaro Sasaki

PURPOSE:

Our research focuses on efficient electrochemical water splitting and CO_2 reduction which are necessary to convert the electrical energy to hydrogen and reduced C1 compounds for fuels. Hydrogen and carbon paths can be separate (water splitting to form energy-carrying H_2; or CO_2 reduction to form energy-carrying CO or formate). Together such independent paths can produce syngas, H_2 + CO, for use in liquid fuel generation. The hydrogen and carbon paths can also be combined in CO_2 reduction directly to methanol. Current studies address fundamental questions regarding the coupling of multi-equivalent redox processes for H-H and C-H bond formation using transition-metal centers in complexes, in nanoparticles, and on catalytic surfaces. Experimental, *in situ* and theoretical studies of homogeneous catalysts and of electrode-attached catalysts and relevant intermediates are being carried out. Our studies strive to improve electrocatalysts for producing renewable fuels (H_2 and methanol) *via* low-energy pathways using earth-abundant materials.

APPROACH:

CO_2 reduction for syngas mixtures [Fujita, Muckerman, Ning (RA)]. Many 14-membered tetraazamacrocyclic complexes show promise as catalysts for water and carbon dioxide reduction. While electrode-adsorbed $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) and its derivatives produce only CO from CO_2 in saturated aqueous media, cobalt tetraazamacrocyclic complexes acting as homogeneous catalysts in both electrochemical and photochemical systems produce H_2 and CO. We and others have investigated the factors governing CO_2 binding and the reactivity of the CO_2 adducts for cobalt and nickel macrocyclic complexes using electrochemistry, flash photolysis and pulse radiolysis. Differences in the type and distribution of products formed by these macrocyclic complexes are mainly due to the differences in the equilibrium and rate constants for CO_2 and H^+ binding to the metal(I) macrocyclic complexes. Once the relevant thermodynamic and kinetic data are known, the optimum conditions for the formation of desired synthesis gas (CO/H_2) mixtures can be determined. Unfortunately, H_2 production has frequently been regarded as an undesirable side reaction in CO_2 reduction. The possible interaction of H^+ with reduced transition-metal complexes which may react with CO_2 has also been ignored in most cases. It is known that metal catalysts with conjugated π systems have a tendency to decompose *via* hydrogenation reactions by protons and electrons. Therefore a search for robust systems capable of prolonged electrolysis is also needed.

Homogeneous and heterogeneous electrocatalysis [Sasaki, Muckerman, Chen (RA)]. Homogeneous catalysts are suitable for elucidating mechanistic details of the reaction pathway because their structures and the reactivities of their functional groups are known and a variety of spectroscopic techniques can be used to identify reaction intermediates. However, most electrocatalysts are heterogeneous because of current-density considerations. In order to obtain high current density, the homogeneous catalysts developed in this project must be immobilized on conductive nanoparticle substrates such as metal oxides, metal carbides or conductive polymers. This approach bridges between homogeneous and heterogeneous electrocatalysis at the nanoscale interface. Our most promising molecular catalysts will be attached to appropriate

substrates through well-known routes for electrode modification. They will be placed on an ITO or glassy carbon electrode to test their ability to produce H_2 at various pH values. Mixed-metal heterogeneous catalysts such as NiMoN comprised of non-noble metals are also being explored for their activity and stability in acidic solution.

TECHNICAL PROGRESS AND RESULTS:

We have synthesized $Ni_xMo_yN_z$ nanoparticles (Ni:Mo = 4:1, 1:1, and 1:4) by annealing at 400C under H_2 and subsequent nitridation in a NH_3 atmosphere at 700C, in order to enhance the corrosion stability of Ni and Mo in acidic electrolytes. The polarization curves demonstrated that these $Ni_xMo_yN_z$ catalysts all showed improved activity for the hydrogen evolution reaction (HER) in comparison to pure Ni metal, Ni nitride and Mo nitride. The $NiMoN_z$ (Ni:Mo=1:1) showed the highest activity among the $Ni_xMo_yN_z$ catalysts. However, a notable loss in current density was observed during the cyclic potential sweeps, indicating that dissolution of Ni and Mo still has occurred in the acidic environment. Thus, further studies on improving their passivity to corrosion by incorporating other corrosion-resistant elements such as Cr are in progress.

We are exploring a new electro-deposition technique to produce highly active Pt clusters (smaller than 1 nm) on a carbon support for HER. With this new method, the loading of Pt can be reduced to an ultra-low level. Numerous supporting materials such as graphite powders, metal oxides, metal carbides, carbon nanotubes or graphenes can be utilized in this approach. The morphology of the carbon-supported Pt clusters was investigated by high resolution STEM at CFN. We observed small Pt clusters (< 1nm) formed on carbon; some clusters comprise just dozens of Pt atoms. Based on the Tafel slope analysis, the reaction rate of the Pt cluster electrocatalysts for HER is likely determined by a Volmer-Heyrovsky mechanism. As demonstrated by STEM images, the Pt atoms in a cluster were separated by a sufficient distance to impede the reaction between two nearby $M\text{-}H_{ads}$ at room temperature.

Molecular aggregates composed of a simple metal complex and a functional polymer can be easily prepared without employing complicated materials, such as supra-molecular and hybrid complexes. When using molecular aggregates as a catalyst, catalysis via a multi-electron transfer mechanism takes place with the intrinsic characteristics of the polymer employed. Such systems show unique and active catalysis that cannot be achieved by the neat complex in homogeneous solution. We synthesized polyaniline-wrapped carbon nanotubes by a simple free-radical polymerization method. We intend to encapsulate metal complexes, i.e., Co, Ni or Ru complexes between the polyaniline matrix and the walls of carbon nanotubes. Further studies in encapsulation of metal complexes on the sidewall are in progress.

Extensive electronic structure calculations have been carried out on the $Re(tBu_2\text{-}bpy)(CO)_3^+$ complex to explore its utility as both a H_2 production and CO_2 reduction electrocatalyst, and the factors that govern the distribution of products it produces. We will also examine the $Co(HMD)^{2+}$ macrocycle complex, which shows promise in our experimental screening studies.

2011 Milestones: Identify target catalyst systems (i.e., molecular complexes, mixed-metal compounds, etc.) that are the most promising for characterization and optimization.

2012 Milestones: Characterize and optimize the catalytic performance of the selected catalyst systems through extensive experimental and theoretical studies.

Structural Basis of Light Perception by Phytochrome

LDRD Project 10-016

Huilin Li

PURPOSE:

Plants and certain bacteria use light for photosynthesis and for sensing their environment as well. The protein phytochrome is a well-conserved photoreceptor responsible for sensing light in the red light range. The protein is unusually large, contains over 1000 amino acids and multiple functionally distinct domains. Despite its discovery almost half a century ago, and after numerous biochemical and biophysical studies, many fundamental questions regarding the structural and chemical basis of the process remain unclear. Cryo-electron microscopy (cryo-EM) is a powerful tool for elucidating the operational mechanism of large biological protein complexes via structural analyses. The Cryo-EM group at BNL Biology Department has been working on systems of biomedical importance. The group wishes to extend its research to bioenergy and plant biology, the areas of interest to the Energy Biosciences Program in the DOE Office of Basic Energy Sciences. The plant phytochrome project is of high scientific significance and is a research topic relevant to BNL and to the DOE Bioenergy Programs.

APPROACH:

The light sensing process relies critically on dimerization of the full-length phytochrome. Existing structural studies involve breaking the large protein into smaller pieces, and solving the structure of the fragments by X-ray crystallography. This approach is insufficient to understand how the multiple domains dimerize and cooperate to function as a whole. Our plan is to use cryo-EM and 3D image reconstruction approaches to reveal the structure of the biological functional phytochrome dimer.

Because phytochrome is well conserved from certain bacteria to plants, the structure of bacterial phytochrome will provide insight to the plant system. We plan to start our investigation with the bacterial phytochrome, which is much easier to produce in sufficient quantities (100 mg) and in a highly purified form. The next step is to study the structure of the purified plant phytochrome. In the longer term, we plan to reveal the conformational changes of the bacterial and plant phytochrome between red and far-red states. The latter is a highly challenging task.

We collaborate with plant biologist Dr. R. Vierstra in the University of Wisconsin.

TECHNICAL PROGRESS AND RESULTS:

During the first funding year (FY 2010), we worked on the bacterial system, specifically, the bacteriophytochrome from *Deinococcus radiodurans* (DrBphP). We received several batches of the highly purified DrBphP from Dr. Vierstra. We first examined and imaged the sample by negative staining electron microscopy. Through extensive search for EM grid preparation conditions, we established an optimum procedure for staining the DrBphP molecules that yielded good image contrast. We then collected a high quality data set and via computer-based image processing and 3D reconstruction, we produced a starting 3D model. We subsequently established proper conditions for freezing the purified DrBphP in vitreous ice and collected a dataset by cryo-EM. The new cryo-EM dataset was refined against the starting model. We eventually obtained a medium resolution cryo-EM structure to a resolution at which individual domains of the DrBphP dimer are resolved as different densities. This level of detail in the

structure enabled us to computationally "dock" into the 3D density map with several published crystal structures of the fragments of homologous bacteriophytochromes.

Our cryo-EM studies revealed that, contrary to the long-standing view that the two monomers are held together solely via their carboxyl terminal region, the amino terminal bilin-binding region of BphP also provides a dimerization interface with the C-terminal kinase domain appearing as a more flexible appendage. The BphP monomers were found to dimerize in parallel with the polypeptides intimately twisting around each other in a right-handed fashion.

The DrBphP work was recently published in the journal Proc. Natl. Acad. Sci. USA. The scientist who carried out the DrBphP research, Dr. Hua Li, left BNL recently to take up a position elsewhere as an independent scientist. A new postdoctoral research scientist with excellent training in protein biochemistry and structural biology has joined our group to work on this project. In this new funding year (FY 2011), we are focusing on the plant phytochrome system.

New Model Organisms for Analysis of Plant Metabolism

LDRD Project 10-017

Jorg Schwender

PURPOSE:

The objective of this LDRD proposal is to establish expertise at BNL in new model plants which have relevance as energy crops that can undergo metabolic engineering and flux analysis approaches. Transgenic lines which are affected in the synthesis of storage products will be produced and their central metabolism studied by flux analysis of developing seeds.

A target for future funding will be the establishment of a Bioenergy Institute linking genetics/genomics expertise at Cold Spring Harbor Laboratory (CSHL) (led by Dr. R. Martienssen) with expertise in metabolic engineering and flux analysis of Shanklin/Schwender at BNL. Therefore this project will foster improved integration of BNL's Basic Energy Sciences-supported groups (Schwender, Shanklin) as encouraged by our program officers.

APPROACH:

The criteria for selection of model plants are generation time, self pollination, suitability for genetic transformation, high sequence homology between genes of the new model plant and other well established model plants (*Arabidopsis*), and the complexity and size of the genome. For the purpose of studying seed metabolism by flux analysis, seeds must be of sufficient size. Developing embryos at an early stage of development will be dissected out of seeds under aseptic conditions and put into a synthetic liquid culture medium containing different organic substrates. The composition of storage compounds (oil, protein, starch) after culture should be similar between cultured embryos and seeds that matured in plants.

TECHNICAL PROGRESS AND RESULTS:

With the arrival of a new postdoctoral research associate, work on the project started in May 2010.

Identification of a model plant: As a good candidate for a new model plant we identified *Thlaspi arvense* (Field pennycress), a close relative to the widely used model plant *Arabidopsis thaliana*. *T. arvense* is a crucifer species that produces oil seeds. Its potential as a bio-energy crop has been reported in literature. While many crop plants are difficult to transform, different *Thlaspi* species have been reported to be easily genetically transformed by the flower dip method. Also the seed size appears to be adequate to allow for the intended cultures of developing embryos. The genomic organization of different *Thlaspi* species is reported to be diploid, which allows straightforward genetic manipulation.

We obtained a *T. arvense* strain from the Arabidopsis Biological Resource Center and determined the following growth characteristics: Growth from seedling to flowering 4.5 – 5.5 weeks and ca. 7.5 weeks until developing embryos can be dissected out of seeds for cultures. Weight per seed is ca. 1.0 – 1.3 mg. 3000 – 900 seeds are produced per plant.

Genetic transformation: We started genetic transformation of *T. arvense* with the vector DsRed, which includes a fluorescent protein as screening marker. Transformation of ovules by

floral dip and vacuum infiltration were used. To find optimal conditions, the composition of the infiltration solution was varied. So far the transformation experiments were successful but with only maximal 0.2% of seeds transformed.

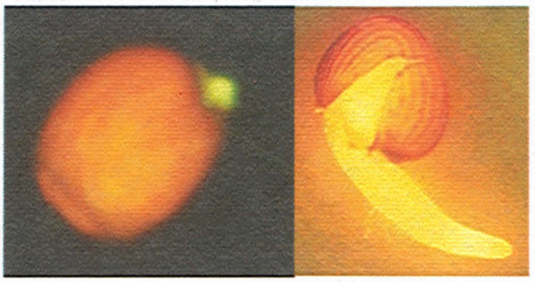


Fig. 1. Transformation of *T. arvense* with DsRed vector. Selection of transformed seeds is based on fluorescence of seeds under green light. Fluorescence of mature dry seed (left) and of the root growing out the seed coat during germination (right).

Genetic constructs: We designed two genetic constructs for overexpression in *T. arvense*, using the vector DsRed*:* The transcription factor WRINKLED will be cloned from *Arabidopsis thaliana*. Also a full length transcript of malic enzyme in *Ricinus communis* was identified in databases and will be cloned from *R. communis* plants.

Embryo cultures: To study metabolism in developing seeds, developing embryos were dissected and cultured in a synthetic medium. We started by dissecting developing embryos 12 days after flowering and culturing for 14 days in a medium formerly used for *Brassica napus* embryos. Experiments which varied the total osmotic pressure and different sugar carbon sources were performed. The effect on growth in the culture, embryo differentiation and storage compound synthesis was tested to identify growth conditions suitable for flux studies.

Future Goals (FY 2011):

- **Genetic transformation protocol**: Some of the experiments have to be repeated and varied to optimize the transformation efficiency. An already available vector construct for the manipulation of the fatty acid profile in seeds (Δ9 desaturase from *Doxantha unguis-cati*) will be used. The change in fatty acid profile in transgenic seeds can then be detected as proof of heterologous expression of a functional protein.

- **Genetic constructs**: The genetic constructs (WRINKLED, malic enzyme) will be transformed into *T. arvense*. Seeds of transgenic plants will be analyzed to assess changes in lipids, protein, and carbohydrate content. Flux analysis will be performed with developing embryos.

- **Embryo cultures**: Changes in seed composition due to overexpression of WRINKLED and malic enzyme should be reproducible in embryo cultures.

- **Genomic organization**: In collaboration with the group of Dr. R. Martienssen (CSHL), we will determine genome size and genome organization (ploidy, chromosome number) in *T. arvense*.

Future Goals (FY 2012):

- **Transcript profiling in developing seeds of *T. arvense*:** In collaboration with the group of Dr. R. Martienssen (CSHL), deep sequencing of gene transcripts in developing seeds will be performed. By homology to the *A. thaliana* genome, this sequence information will allow us to identify genes in central metabolism and the assessment of expression levels in developing seeds.

- **Flux analysis studies:** A biochemical reaction network will be established based on the transcript profiling. Flux analysis of the transgenics will be performed.

Development of Microprobe, Multichannel Optical Multimodality for Biological Tissue Imaging

LDRD Project 10-023

Congwu Du, Fritz Henn and Yingtain Pan

PURPOSE:

The objective of this project is to develop a multimodality image platform (MIP) that enables simultaneous imaging of microflow, tissue oxygenation and intracellular calcium from biological tissue such as rodent brain or plant leaves in vivo. The new optical image instrumentation will provide a new modality for future functional studies of biological tissue, which will complement other strategic 'Life and Physical Science Interface' initiatives. Our hypothesis is that an increased understanding of the physiology of biological tissue (e.g., plant) will facilitate the manipulation of plant physiology both for improved biomass and biofuel production. This instrumentation development directly supports BNL & DOE's missions while also providing technologies that are broadly transferable to other agencies.

APPROACH:

We have developed dual-wavelength laser speckle imaging (DW-LSI) and Rhod2 fluorescence techniques that enable qualitative flow and intracellular calcium imaging from rat cortical brain. In parallel, 3D Doppler optical coherence tomography (DOCT) was developed in Dr. Pan's lab that permits quantitative microflow and cellular morphology imaging. The central goal of this project was to integrate these three modalities into a multimodal image platform (MIP). Additionally, the capability of the MIP prototype to image the pathology and physiology with a high temporal and spatial resolution was tested in tobacco plants.

TECHNICAL PROGRESS AND RESULTS:

Development of MIP prototype: As being proposed in the Specific Aim 1, we have developed a multimodality image platform (MIP). Fig. 1. illustrates the MIP system that integrates DW-LSI and fluorescence imaging (upper dashed box) with 3D DOCT (lower dashed box). This MIP enables high-performance simultaneous detection of microflow, tissue oxygenation and $[Ca^{2+}]_i$

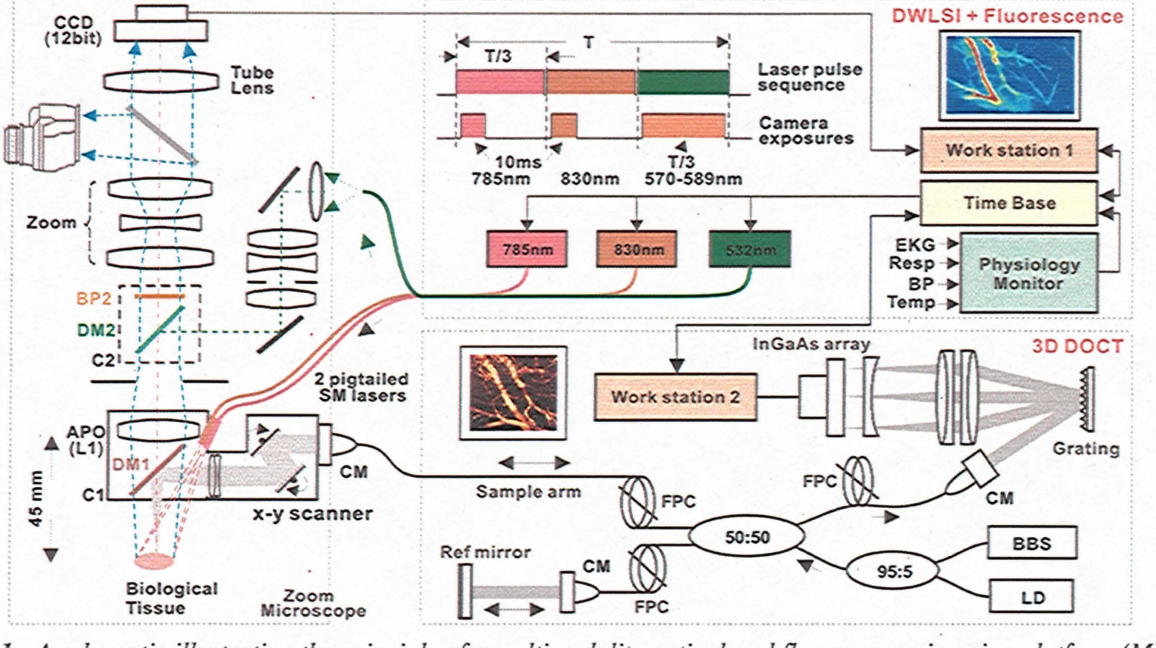


Fig. 1: A schematic illustrating the principle of a multimodality optical and fluorescence imaging platform (MIP) that combines DW-LSI and fluorescence imaging (Upper dashed box) and 3D DOCT (Lower dashed box).:

fluorescence from biologic tissue such as rodent cortical brain.

Validation of MIP technique: The MIP captures micrometer resolution, three-dimensional (3D) images from optical scattering media (e.g., biological tissue). The advantages of the technique include high spatial and temporal resolution over a wide field of view. Fig. 2A) illustrates the experimental setup of MIP to image tobacco leaves in vivo. Fig. 2B-C) show 3D OCT image of tobacco leaves, whereas Fig. 2D) shows the interior structure of the leaf, indicating the cellular resolution of the leaf structure in vivo. Fig. 2E)-F) show 2D sap flow of the leaf measured by using DOCT (2E) and DW-LSI (2F) of MIP system, which validate MIP's feasibility to image the pathology (2B-D) and physiology (2E & F) of leaves of the intact plant.

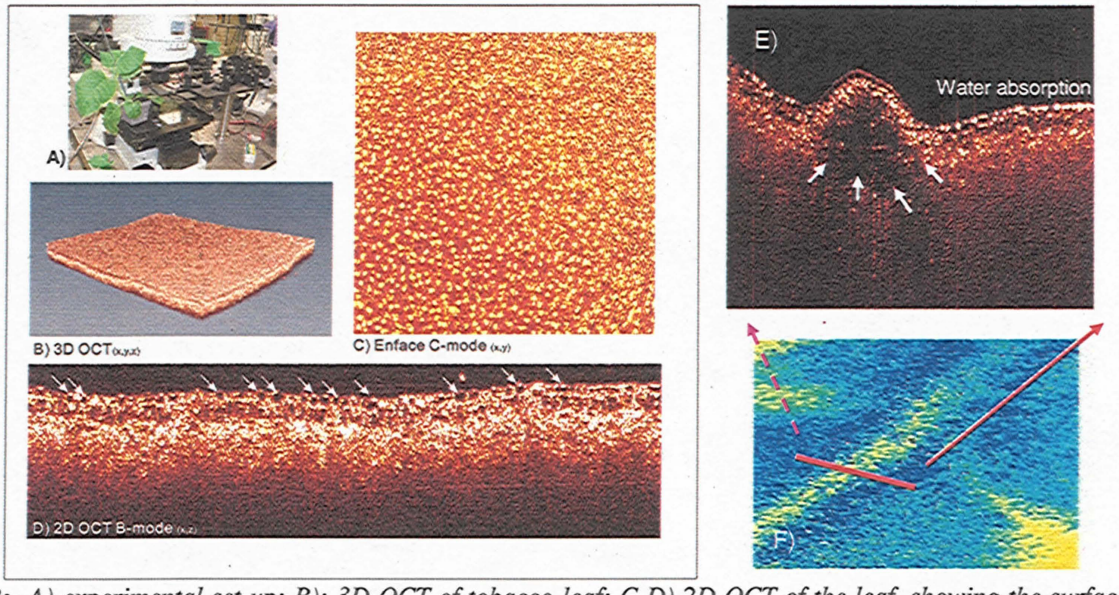


Fig.2: A) experimental set-up; B): 3D OCT of tobacco leaf; C-D) 2D OCT of the leaf, showing the surface and interior structure of the leaf, respectively; E-F) 2D sap flow of the leaf measured by DOCT and DW-LSI of MIP system, indicating the feasibility of MIP to measure the leaf physiology from intact plant.

Additional accomplishment: With the support of this project, we produced 1 peer-reviewed journal publication, that is in press in Neuroimaging. Also the work was included in several conference proceedings (3 in total) and we presented our data at both external and internal conferences and meetings (6 in total), including DOE's workshop of "Radiochemistry and radionuclide imaging instrumentation".

In summary, we have been developing multimodal optical techniques for in vivo imaging of biological tissues, including living plants. The merits of the techniques include high spatiotemporal resolution over a large field of view. Specifically, multi-wavelength laser speckle imaging permits direct assessment of flow changes in response to physiological or environmental changes. In addition, optical coherence tomography can provide 2D and 3D morphological imaging of living biological tissue at subcellular resolution.

FUTURE MILESTONES: 1). Further examine the utility and potential applications of MIP, and 2). Develop a high-resolution needle-based MIP (NB-MIP) to permit subcortical imaging.

Development of Large Liquid Argon Time Projection Chambers (LArTPC) for Future Neutrino Experiments

LDRD Project 10-025

Francesco Lanni

PURPOSE:

Liquid argon (LAr) has been successfully used in many high energy particle calorimeters since it was first proposed at BNL in 1974. More recently, there has been a growing effort to develop giant LAr Time Projection Chambers (TPCs) as an alternative to Water Cerenkov Detectors for neutrino physics measurements. TPCs, which are charged particle tracking 3D imaging detectors, provide detailed and precise information on all charged particles within the volume of the detector and therefore can provide much better background rejection and rare event discrimination. In order to develop and optimize LAr TPCs to exploit these unique capabilities, all of the physical processes that produce signals in LAr (principally charge and light) must be quantitatively understood. Much information is available (small LAr TPCs have been built) but scaling to future multi-kiloton detectors requires new information and higher precision data. This project will measure the fundamental properties of charge and light production and transport in LAr, investigate and optimize designs of devices and structures for charge and light collection, and develop the operation of electronics systems in LAr. The ultimate result of this project will be the knowledge to successfully construct a 100–kiloton scale LAr TPC for neutrino physics and proton decay experiments.

APPROACH:

This project emphasizes the fundamental physics and electronics that must be understood and applied in order to design the next generation of noble liquid TPCs. Basic properties of noble liquids are known only incompletely, and electronic systems optimized for operation in very large cryogenic detectors have not yet been developed. Aspects of the program include these:

Create the infrastructure for cryogenic measurements:

- Cryostats to contain the noble fluids, recirculating purification systems to achieve and maintain high fluid purity, and the required instrumentation will be constructed.

Measure basic noble liquid transport properties:

- Diffusion of electrons, electron attachment to impurities and electron-ion recombination will be measured to understand charge transport and production. Use of additives dissolved in the noble liquid to enhance charge or light production will be explored.
- Optical attenuation of the VUV scintillation light by impurities dissolved in the noble liquid and Rayleigh scattering limit the ability to collect light from the primary ionization. Quantitative measurements of the partition of impurities between the liquid and gas phase of noble liquids and of the kinetics of impurity generation and transport will be measured.

Readout electronics development:

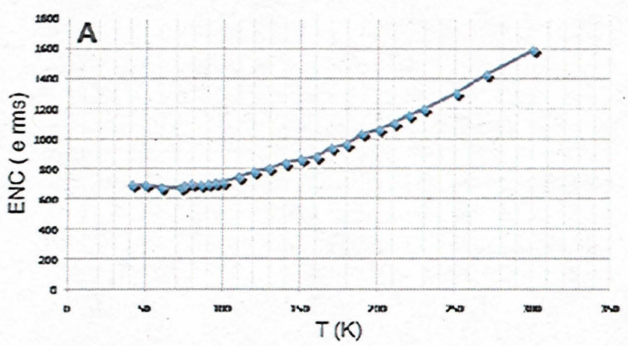
- For truly large detectors it will not be feasible to have one cable and cryogenic feed-through per readout channel. Electronic circuits must therefore operate in the noble liquid at cryogenic temperatures. This includes the full signal processing chain through digitization

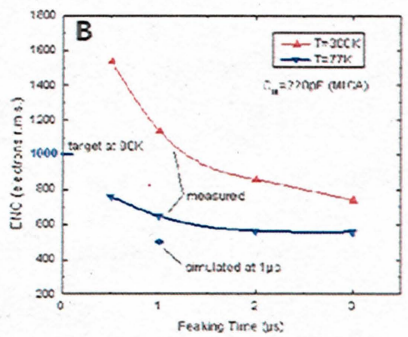
and multiplexing, so that only a minimum number of lines carry multiplexed signals through the large detector volume to cryogenic penetrations. The objective is to reduce the entire electronics system and the TPC structure to modules that are arrayed to scale to any detector volume or shape.

- Large detectors will be difficult to service, so cryogenic electronic systems must be designed for high reliability and long lifetime, and this performance must be verified.
- Modeling and measurement of the entire signal formation process, for both charge and light, using measurements of the basic transport properties described above.

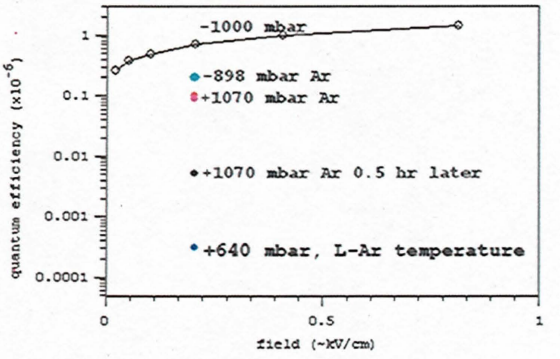
TECHNICAL PROGRESS AND RESULTS:

- Two large cryostats (0.3 and 0.8 m3) were acquired from within BNL; the smaller has been instrumented to evaluate electronics performance and reliability in LAr, and the larger has been reworked by the manufacturer and is being instrumented to contain and operate a small prototype LAr TPC (nanoBooNE) built in the Instrumentation Division. A small cryostat and purification system was designed and ordered.
- We characterized the noise at cryogenic temperatures of two CMOS ASICs: one is an existing device designed for room temperature (A) and the other is a new 0.18 um ASIC designed for cryogenic operation (B). The new ASIC works well at both room and cryogenic temperatures.





- A small variable-temperature helium cryostat was modified for work with LAr, and an apparatus is under construction, with the collaboration of the Instrumentation Division, to drift electrons up to 15 cm in LAr to measure transverse and longitudinal charge diffusion at low electric fields (below 1 kV/cm).
- Measurements (see below) were made of the quantum efficiency of Au photocathodes in LAr to be used as a source of high brightness electrons for transport experiments. The results indicated that the quantum efficiency was limited by the absorption of impurities on the photocathode surface.



Future Milestones (FY11):

- Electron diffusion measurements
- Effect of dopants on LAr transport properties

Future Milestones (FY12):

- Light collection in LAr through scintillating fibers, performance of PMTs, SiPMs, and APDs
- Time-stamp studies through cathode readout

Spin Waves in Artificial Magnonic Crystals: Fabrication, Imaging and Scattering

LDRD Project 10-034

Darío Arena, Aaron Stein, and Yimei Zhu

PURPOSE:

Spintronics, where the electron's spin in addition to its charge is central to the operation of the device, is one possible replacement for CMOS electronics based on silicon. A subset of spintronics, spin wave (SW) electronics, holds great promise in moving into the post-CMOS era. SWs are known to propagate over large distances (several mm) in materials with low damping. Logic gates based on the interference of SWs have been demonstrated. SW electronics may also form a part in reducing energy consumption as their function derives from the propagation of spin, not charge, and hence there is little energy loss from Ohmic heating. Advanced lithography techniques permit the introduction of periodic modulations in the magnetic permeability (μ) of ferromagnetic (FM) thin films in structures such as anti-dot arrays in FM films. The resulting structure is an artificial magnonic crystal (MC), where now, instead of electromagnetic waves, the relevant excitations are spin waves (quantized as *magnons*), that is, collective excitations of the spins of valence electrons in a FM. The purpose of this LDRD is to fabricate MCs with the advanced lithography tools available at the CFN (in collaboration with Dr. Aaron Stein) and then characterize the dynamic properties of the MCs with advanced TEM imaging (in collaboration with Dr. Yimei Zhu) and with x-ray techniques extant at NSLS and at other synchrotron facilities (primarily ALS and APS). The techniques at these non-BNL facilities (x-ray microscopy, ultrafast time-resolved x-ray scattering) may be developed at NSLS-II.

APPROACH:

The program supported under this LDRD project consists of several tasks: (1) fabrication of MCs at the CFN; (2) characterization of the microwave excitation spectra of the MCs using ferromagnetic resonance utilizing a vector network analyzer (VNA); (3) examination of the SW standing wave patterns using Lorentz TEM microscopy; (4) measurement of x-ray scattering patterns of SWs in MCs; (5) imaging of SWs in MCs using x-ray microscopy. Task 1 will be conducted primarily at the CFN, although we may call upon the experience and capabilities of outside experts (Prof. Andy Kent of NYU and Assoc. Prof. Adekunle Adeyeye of the National University of Singapore) to assist with the fabrication issues that can not be resolved at the CFN. Task 2 will be performed at the NSLS using equipment purchased for this purpose under the LDRD program. Task 3 will be carried out at BNL in collaboration with Dr. Yimei Zhu. Task 4 will be executed at NSLS at beam line U4B, although access to more advanced facilities at 3rd generation storage rings may be required. Task 5 will be carried out at the XM-1 soft x-ray, full-field transmission microscope at the ALS at LBNL.

TECHNICAL PROGRESS AND RESULTS:

Year 1 efforts have been focussed on: (A) identifying a suitable Research Associate to carry out the research program; (B) acquisition of major capital equipment items and other electronics required for the project; (C) interfacing of the new equipment into a complete measurement system; (D) initial fabrication of MCs at the CFN. (A) has been completed with the hiring of Dr. Peter Warnicke as a Research Associate. The majority of activities under sub-task (B) have been completed. This has entailed identification and purchase of several electronic items including:

(a) Agilent HP 8720D Vector Network Analyzer, (b) 1.6 Tesla electromagnet, (c) 70 Amp power supply for electromagnet, (d) Agilent 6 GHz oscilloscope model #54855A, (e) data acquisition and experiment control computers, and (f) ancillary electronics and laboratory equipment. These items are now in-house and appropriate control software has been coded using open-source Python modules. Finally, Dr. Warnicke has been actively pursuing sub-task (D) at the CFN. This last task has entailed a fair amount of calibration work and dose tests on the e-beam lithography equipment at the CFN. The difficulty is producing a uniform pattern of ~500 nm anti-dot arrays over a large area (several square millimeters) onto FM thin films (in this case $Ni_{80}Fe_{20}$). Progress in this task has been steady (see Fig. 1), and we can now produce MC arrays over areas large enough to proceed onto the other tasks under the LDRD.

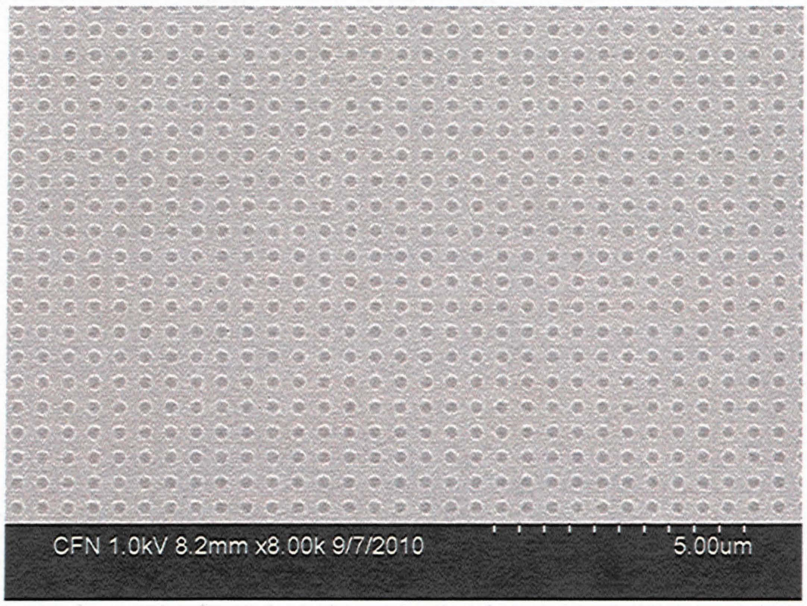


Fig. 1: *Anti-dot array etched into a ~25 nm thick film of $Ni_{80}Fe_{20}$. Sample fabrication at the CFN.*

We are now in a position to undertake the characterization of the MCs, and also to modify the lattice structure of the anti-dot array to explore the role of symmetry alterations on the excitation spectra of the MCs. Also, we will soon begin to undertake the tasks that will make use of the advanced characterization tools at the CFN, NSLS and elsewhere.

The milestones for the remainder of the LDRD are:
12 months: Produce CPWs and MCs optimized for Lorentz TEM. Commence TEM studies of MCs under rf excitation. Produce MCs on flat substrates for XRMS studies. Begin preliminary measurements on beam line U4B at NSLS. Initiate research trips to the APS or ALS.

18 months: Commence data analysis using open-source micromagnetic simulation software. Continue TEM and XRMS measurements. Begin research trips to ALS (microscopy) and / or APS (XRMS). Prepare manuscript on initial results (growth, FMR, TEM imaging, XRMS). Begin fabrication of MCs with different symmetries and investigate symmetry affects SW dispersion. Examine new MCs with tools available (FMR, TEM, XRMS, *etc.*).

24 months: Initiate time-resolved measurements to examine non-standing wave modes of the SWs. Continue research trips to ALS and APS. Continue Lorentz imaging. Begin investigations of magnetic multilayer samples and sample with non-cubic symmetry in collaboration with Prof. Andy Kent of NYU and Assoc. Prof. Adekunle Adeyeye of the National University of Singapore. Prepare manuscripts on results.

Atomic Structure and Bonding of Cellulose

LDRD Project 10-038

Michael McGuigan and Yan Li

PURPOSE:

This is a project to study theoretically the atomic structure and bonding in crystalline cellulose and its interaction with water. Such studies are important to aid in the discovery of methods to break down cellulose for biofuels. The project is a collaboration between the Biomolecular Sciences Division at the National Renewable Energy Laboratory (NREL) and members of the Biology Department and Computational Science Center at BNL.

APPROACH:

The project will utilize large scale quantum mechanical and molecular dynamics simulations on NewYorkBlue, the 128 Teraflops Blue Gene/L,P computer complex located at BNL. The goal is to provide a new understanding of the possible structural rearrangements in cellulose and to provide realistic parameters for large scale molecular dynamics studies of the interaction of cellulose with cellulose degrading enzymes.

TECHNICAL PROGRESS AND RESULTS:

We have studied the structural, energetic and electronic properties of crystalline cellulose I using first-principles density functional theory (DFT) with semi-empirical dispersion corrections. The predicted crystal structures of both Ia and Ib phases agree well with experiments, and are greatly improved over those predicted by DFT within the local and semilocal density approximations. The cohesive energy is analyzed in terms of interchain and intersheet interactions, which are calculated to be of similar magnitude. Both hydrogen bonding and van der Waals (vdW) dispersion forces are found to be responsible for binding cellulose chains together. In particular, dispersion corrections prove to be indispensable in reproducing the equilibrium inter-sheet distance and binding strength; however they do not improve the underestimated OH•••O distance in DFT. The computed energy gaps of crystalline cellulose are 5.7 eV (Ia) and 5.4 eV (Ib), while localized surface states appear within the gap for surfaces. The interaction of cellulose with water is studied by investigating the adsorption of a single water molecule on the "hydrophobic" Ib(100) surface. The formation of hydrogen bonds with the adsorbed water molecule is shown to depend sensitively on its adsorption site, e.g. above the equatorial hydroxyls or the CH moieties pointing out of the cellulose sheets. VdW dispersion interactions also contribute significantly to the adsorption energy.

EIC Polarized Electron Gun

LDRD Project 10-039

Ilan Ben-Zvi, Xiangyun Chang, Jörg Kewisch, Vladimir Litvinenko, Gary McIntyre, Alexander Pikin, Triveni Rao, Brian Sheehy, John Skaritka and Qiong Wu

PURPOSE:

The eRHIC project requires a highly polarized electron source with high average current which sounds ambitious based on state-of-art polarized electron source technology. Average current of about 2 mA of polarized electron beam has been obtained in Jefferson lab. But eRHIC requires 50 mA of average current. There are other requirements which make the source more challenging: the final transverse emittance, one of the most important parameters describing the beam's quality, needs be less than 20 mm.mrad; bunch charge should be about 3.5 nC; final bunch length should be less than 3 mm. A natural way of obtaining the 50 mA of average current is to employ multiple cathodes, for example 20 cathodes, and to combine the beam bunches from each cathode together to form one bunched beam. It works like a "Gatling gun". The goal of this project is to study the feasibility of the Gatling gun method of generating the eRHIC required electron source.

APPROACH:

Obviously, 20 cathodes will generate average current which is 20 times that of a single cathode. But it introduces many other problems if we want to combine the beams together like a Gatling gun (Fig.1).

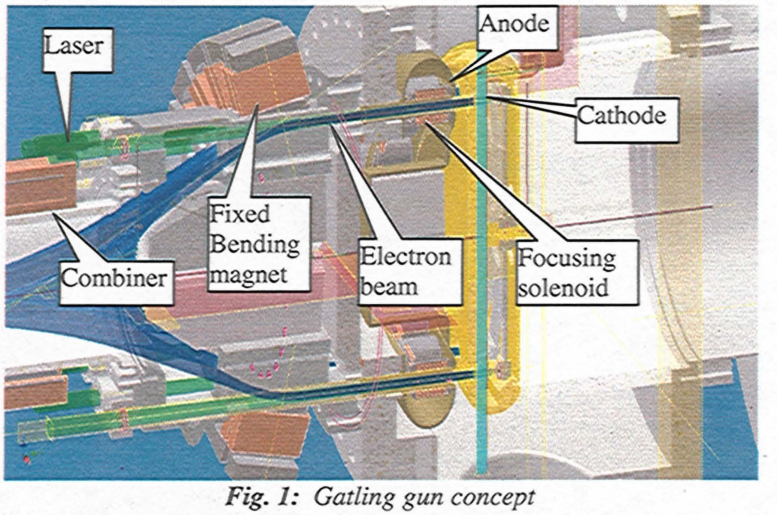


Fig. 1: *Gatling gun concept*

The cathode for generating polarized electrons must work at ultra-high-vacuum (better than 10^{-11} torr). But a cathode with emission will degrade the vacuum depending on its current and design, thereby compromising the performance of the cathode. So the first question is that do the cathodes in Gatling gun affect each other because they will all be operated in the same vacuum chamber? Also, as there are many pieces including some moving parts in the system, how can we achieve the ultra-high-vacuum under this circumstance? The solution is to use enough vacuum pumps (NEG pump).

The key issues to be addressed are the long term performance of the cathode in the presence of energetic high current electron beam, design of the Gatling gun/cathode preparation system that

is compatible with XHV vacuum while providing for the frequent replacement of the cathode and the design of the combiner that can merge individual beam-lets from 20 cathodes without degrading the quality of the electron beam.

TECHNICAL PROGRESS AND RESULTS:

In the past fiscal year we have completed the following:

- The electron beam transport in the Gatling gun was studied in detail using 2D simulations. The design for cathodes and anodes, design for the focusing of the beams after anodes, design of fixed bending magnets turning beams toward the common axis and the combiner combining the beams together were optimized. These parts are all shown in Fig.1.

- We completed most of the mechanical design of the system. It is mainly composed of 2 parts, the cathode preparation chamber and the gun chamber. All the necessary parts for this fiscal year have been designed and ordered. This is a milestone of the Gatling gun project in the past fiscal year.

- We made the decision to use magnetic bendings instead of electric bendings because the magnetic bending is much more efficient than that of electric bending at our designed 200 keV electron energy level. The combiner (Fig. 2) has been designed carefully. We also did some proof of principle tests based on our simple prototype. The prototype was designed carefully especially in its winding. The tests showed us clearly that we could achieve our desired high quality combined dipole and quadrupole field in the same ferrite tube and operate it at 700 kHz rotating frequency. The dipole and quadrupole field were independent of each other with our special winding technique. This is another milestone of the Gatling gun project.

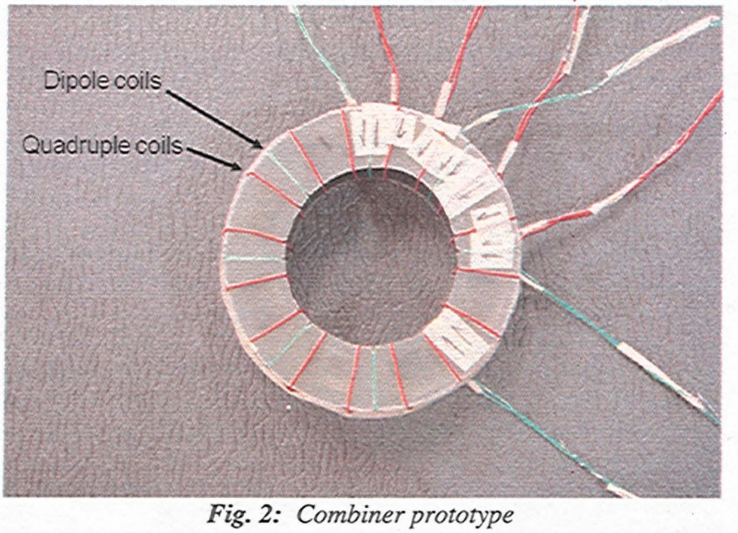


Fig. 2: Combiner prototype

- We have determined the requirements for the building and a site has been allocated for construction in Bldg 912, awaiting removal of existing equipment

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

APPROACH:

The BNL design for the EIC calls for a 200 mA polarized electron beam at the interaction region. Such high current is achieved by an ERL design where 50 mA current from the electron source is recirculated 4 times in an energy recovery mode. Even this reduced current puts a very high demand on both the laser and the cathode. The current state of the art in the polarized electron source is ~ 1 mA with significantly reduced cathode life time.

In this program, the scope is expanded to address both the development of the laser system and understanding the negative electron affinity of the cathode in order to increase the life time of the cathode.

The quantum efficiency of the polarized electron source is in the range of a fraction of a percent at 780 nm. The beam transport in the eRHIC project dictates the pulse duration of the electron beam at the source to be ~ 0.5 ns and the Gatling Gun design set the repetition rate at a single cathode to be ~ 10 MHz. The laser system for such a source, with ~100 W of power in ~0.5 ns at ~ 10 MHz does not exist. One approach is to irradiate each cathode with a separate laser beam of reduced repetition rate and hence reduced average power. In collaboration with Brian Sheehy of CAD, 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.

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. At BNL, the oxidizing agent used in the cathode preparation is oxygen whose purity is determined by its source and the scrubbing process used before letting it into the vacuum system. Two alternate sources are being investigated: a manganate compound in a silver capsule that releases pure oxygen upon heating and oxygen from a commercial high purity oxygen cylinder that is precooled to remove residual contaminants

such as water vapor. Future measurements include establishing the correlation between the QE and the surface properties of GaAs upon heating.

TECHNICAL PROGRESS AND RESULTS:

Three different laser systems: Ti:sapphire, directly modulated diode laser and fiber laser were compared in terms of their performance, upgradability and the cost. Although the Ti:sapphire laser has been the workhorse in many facilities for driving the polarized electron source, it can not deliver the 100 W required for eRHIC, not even the 4 W required for driving a single cathode. It was ruled out as a possible candidate because the performance requirement is too far beyond its current state of the art, the system would be too complex and cost prohibitive. Significant effort was expended in investigating direct modulation of a diode laser. However, this system also could not meet the specifications such as power level, repetition rate, and synchronization. After extensive discussions and preliminary research and development studies with industry experts, we decided that a fiber based system is more appropriate for driving the Gatling Gun. The system architecture is shown in Figure 1.

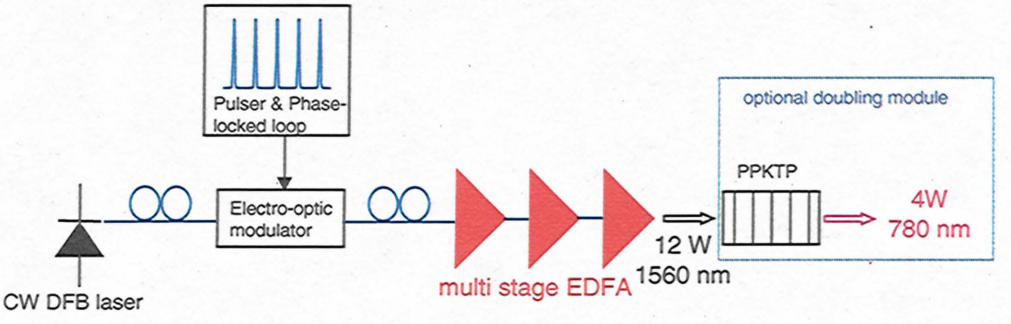


Fig. 1: Architecture of fiber based laser system to drive a single cathode of the Gatling Gun

It will be of master oscillator – power amplifier (MOPA) design, in which the oscillator is a low power, continuous wave (CW), distributed feedback (DFB) laser, the output of which is modulated electro-optically to produce the required pulse structure. The one- or two-stage electro-optic modulation stage will be driven by a pulser that can be locked in phase with an external RF reference. This is followed by a multi-stage erbium doped fiber amplifier (EDFA). There is sufficient interest in the laser industry to build such a laser. Currently, the procurement process is ongoing to purchase this custom made laser. The second year of the project will focus on evaluating the performance of the laser and establishing the path for the upgrade.

An existing cathode preparation chamber was modified to accept the two oxygen sources. This XUV vacuum chamber has been pumped to as low as 10^{-12} Torr vacuum. Bulk GaAs in this chamber has been heated to different temperatures ranging from 540° C to 600°C and QE of a sample with two oxygen sources was measured. Preliminary measurements indicate that the manganate source leads to a higher QE. These results will be followed up by more systematic measurements. A program to measure the QE after heating the bulk GaAs to various temperatures ranging from 540° C to 600°C and correlating it to the surface changes at these temperatures has already been launched. The surface changes will be measured using X-ray beams at the NSLS. These studies, not executed so far to our knowledge, will lead to a better understanding of the formation of NEA surface and hence better cathodes

2011 Milestone:

Install and characterize the laser system

Correlate QE of the cathode to its surface morphology

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

LDRD Project 10-041

Vladimir N Litvinenko

PURPOSE:

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 RHIC to the LHC. We are addressing issues, theoretical and numerical, that the FEL community have put aside for at least two decades. We are modifying the well-benchmarked 3D FEL codes specifically for the CeC cooler. It is very unlikely that we can readily employ existing wiggler designs with their very small gaps suited for light sources and short wavelength FELs. Accordingly, we are designing and fabricating a prototype of such a wiggler to address possible shortcomings and limitations. This LDRD is the front-runner project for testing the CeC mechanism in a proof-of-principle (PoP) experiment. With the success of the CeC PoP, the CeC cooler certainly will greatly benefit future medium- and full-energy eRHICs. Importantly, it will ensure that we maintain our competitive edge against EIC projects, such as the ELIC.

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 IP between two DX magnets. It should have an aperture adequate to avoid imposing any constraints on the 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:

Table 1. Main parameters for the CeC demonstration experiment

Parameter	**Units**	
Electron beam energy	MeV	**21.8**
Length of the CeC straight section	M	**14**
Length of the modulator straight section	m	**3**
Length of the kicker straight section	m	**3**
Length of FEL wiggler	m	**7**
Type of wiggler		**Helical**
Wiggler period	cm	**4**
Wiggler parameter, a_w		**0.437**

During this fiscal year we established the base-line requirements for the accelerator and FEL in the PoP CeC experiments, listed in the Table 1. We established that with these parameters, a 7-meter long FEL wiggler is sufficient to amplify density modulation (commonly called the

bunching factor by FEL researchers) by the designed number of one hundred. Fig. 1 shows results of Genesis-3, 3D FEL simulations for the beam's peak current of 100 A. As apparent in Fig. 1(a), the initial spike is amplified about 500-fold in a 7-m long FEL, which is five times higher than our design requirements for the CeC. This signifies that we have a significant margin for errors. It was also demonstrated (Fig. 1(b)) that with these parameters the group velocity of the FEL density wave-packet is equal to that of hadrons – the feature critical for CeC mechanism.

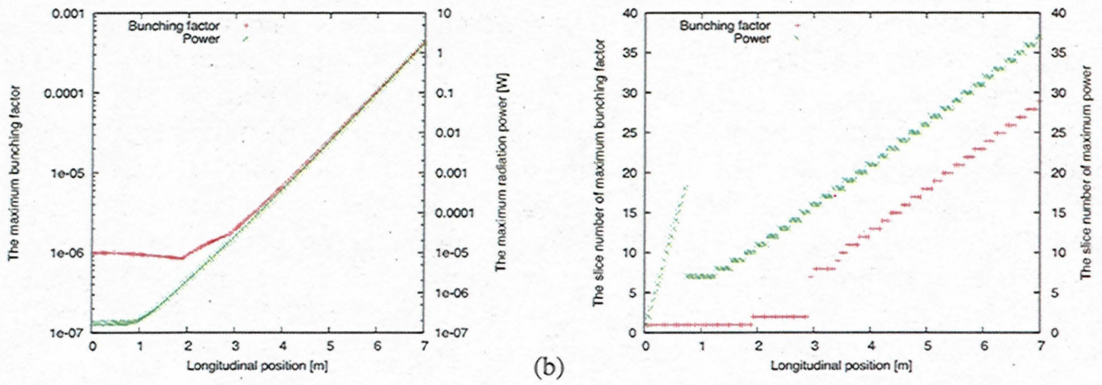


Fig. 1: *Left plot (a) shows the evolution of optical power (green +) and the bunching factor (red +). Right plot (b) depicts the position of the maxima of optical power (green +) and the bunching factor (red +) with respect to the initial spike, expressed in units of the FEL's wavelength (i.e. 10 μm).*

Based on these simulations we submitted a $5.8M 5-year proposal to the DOE NP office for the CeC PoP experiment at RHIC. The proposal was fully funded for its first year at $1.46M. In addition, we had published six papers containing results of our theoretical studies.

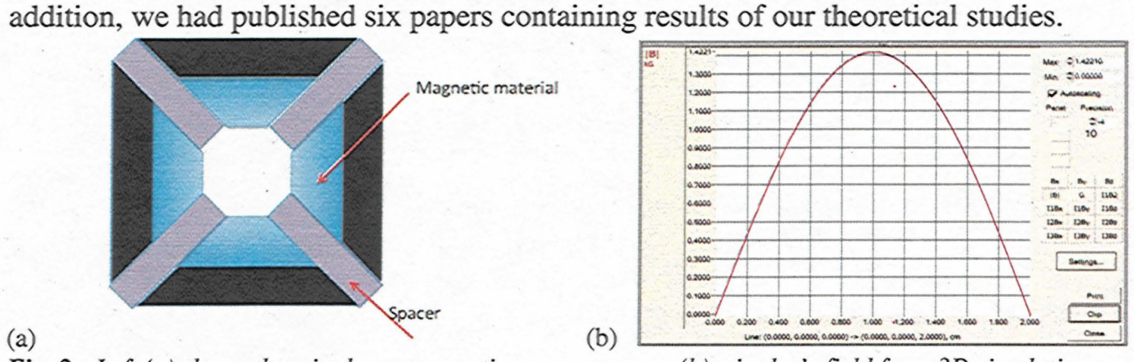


Fig. 2: *Left (a) shows the wiggler cross-section (b) wiggler's field from 3D simulations.*

We had also identified a company capable of building the prototype of the helical wiggler with required parameters and tolerances, as well as of making high precision magnetic measurements. We are in the process of placing the order.

Next year milestone - demonstrate that we can design and manufacture a helical wiggler with required parameters and accuracy.

[1] V.N Litvinenko, Y.S. Derbenev, PRL **102**, 114801 (2009)
[2] B.T. Schwartz et al., Journal of Physics: Conference Series (2010)
[3] Physics of FEL in an infinite electron beam, G. Wang, V. N. Litvinenko and S. D. Webb, Submitted to PR ST-AB, September 2010
[4] G.Wang et al., In Proc. of 32nd International FEL Conference, Malmo, Sweden, August 23-27, 2010
[5] S. Webb et al., In Proc. of 32nd International FEL Conference, Malmo, Sweden, August 23-27, 2010
[6] B.T. Schwartz et al., Proc. of SciDAC 2010 Workshop, July 11-15, 2010, Chattanooga, Tennessee
[7] G. Wang et al., Proc. IPAC'10, Kyoto, Japan, May 23-28, 2010, pp.873-875, http://accelconf.web.cern.ch/AccelConf/IPAC10/papers/mopd077.pdf

Realization of an *e*+A Physics Event Generator for the EIC

LDRD Project 10-042

Thomas Ullrich and Raju Venugopalan

PURPOSE:

A future Electron-Ion Collider (EIC) embodies the vision of the field of High Energy Nuclear Physics for reaching the next QCD frontier: the study of gluons that bind all atomic nuclei. An EIC, which provides high-luminosity collisions at centre-of-mass energies from 30-100 GeV with polarized electron and nuclear beams may be sited at either BNL (eRHIC) or JLAB (ELIC).

There is a plethora of compelling physics that can be conducted with a future Electron Ion Collider both in *e*+*p* and *e*+A collisions. Especially in the latter, many of the proposed measurements have substantial discovery potential. To observe the new phenomena expected in this regime, it is important to verify that the proposed measurements can be conducted with both sufficient statistics and kinematic reach. An essential element of this program is a Monte-Carlo event generator that covers the broad range of physics to be investigated and goes one step further to generate events in a nuclear environment including all known and conjectured nuclear effects. Such a generator does not exist and it is the aim of this LDRD project to provide such an *e*+A physics event generator, which will be able to simulate all interesting QCD physics in *e*+A collisions well into the saturation regime. This will then be a crucial tool for the design of detectors for an EIC. The generator will provide input for the 2012 NSAC Long Range Plan.

APPROACH:

To work on the realization of an *e*+A event generator a postdoctoral fellow (Tobias Toll) was hired in summer 2010 after an extensive search. He works 100% on the LDRD project.

We realized the complexity of *e*+A collisions cannot be encapsulated in a single generator but that a suite of generators in a common framework will be necessary, *i.e.*, the overall generator will consist of various packages that provide a common input and output format. As a first step we have focused on the key measurements at an EIC in *e*+A, the study of diffractive events. Diffractive events are expected to constitute up to 30-40% of all events in an EIC and allow the determination of the gluon momentum distribution and, as the only known probe, to measure the spatial distribution of glue in a nucleus. We first focus on exclusive vector meson production (J/ψ, φ, ρ) based on existing dipole models (b-Sat, b-CGC). We then will add DVCS (Deep Virtual Compton Scattering) and afterwards extend the generator to arbitrary final states. In parallel we have to simulate the breakup of the nucleus, since the fragments need to be detected to distinguish between coherent and incoherent diffraction. It is absolutely vital for an EIC detector to detect the nuclear breakup with essentially 100% efficiency. The design of the required detectors and the design of the interaction region (IR) depend heavily on the physics of the nuclear breakup. Once completed, we move to DIS (deep inelastic scattering) using the experience gained in the diffractive part. For DIS there is a rich set of *e*+*p* generators available and the main task will be to adapt existing Monte Carlo programs to *e*+A. A detailed strategy for this will evolve during FY11.

TECHNICAL PROGRESS AND RESULTS:

So far we almost completed a generator for diffractive exclusive vector meson production for *e*+A collisions. Here we pursued two approaches. In one the nuclei are only represented in the form of a simple overlap function that is limited to the simulation of coherent diffraction but

allows quick turn-around times (optical model). This work is completed. The other path is more elaborate since the nuclei are constructed in detail (MC Glauber model). This approach allows for the simulation of coherent **and** incoherent events and avoids approximations used in the optical model. It is, however, by far more complex and requires extensive studies. Since this is the superior approach, Tobias is working full time on it and great progress has been made. We expect this part to be finished within a few weeks.

The goal in coherent diffraction in e+A collisions is to get a handle on gluonic spatial structure. The key observable is the spectrum of *t*, the transverse momentum transferred from the initial nucleus to the final state in diffractive events with only a vector meson in the final state, *i.e.*, events of the type e+A→ e′+A′+V. Here *t* can be reconstructed from the kinematics of the final state particles. The observed dσ/dt represent a Fourier transform of the transversal spatial gluon distribution of the initial nucleus, which can be regarded as the gluonic form factor. This distribution is depicted in Fig. 1, which is generated by "*xdvmp*" the simulation package under construction. It shows the *t*-spectrum from coherent J/ψ production of vector mesons. To obtain this distribution, the amplitude of many nuclear configurations has to be averaged over to obtain a single event order to calculate the cross-section. To obtain a precise result at small *t* one has to average very few nuclei, while to get a precise answer at large t (small impact parameter b) several hundred nuclei need to converge to the final shape. The different curves represent the resulting cross-sections from averaging the amplitude over 40, 80, 160 and 320 configurations, respectively. A Fourier transformation of this diffractive pattern gives the desired source distribution F(b). The nuclei in this study were constructed by using a nominal Wood-Saxon configuration with parameters measured in low energy elastic electron scattering.

It is conjectured that at higher energies, the Wood-Saxon distribution is not applicable but that rather Color-Glass-Condensate inspired distributions will be observed. One of the key questions a generator needs to answer is if the EIC will be able to distinguish between these two scenarios. Figure 2 shows the comparison of such a distribution (KLN) with a standard Wood-Saxon distribution. For this study the optical version of the *xdvmp* generator was used. These results are encouraging since the two distributions show clear differences that can be easily distinguished in measurements at an EIC. In summary we have made good progress in the first few months. A first preliminary version of a generator for diffractive events is close to completion.

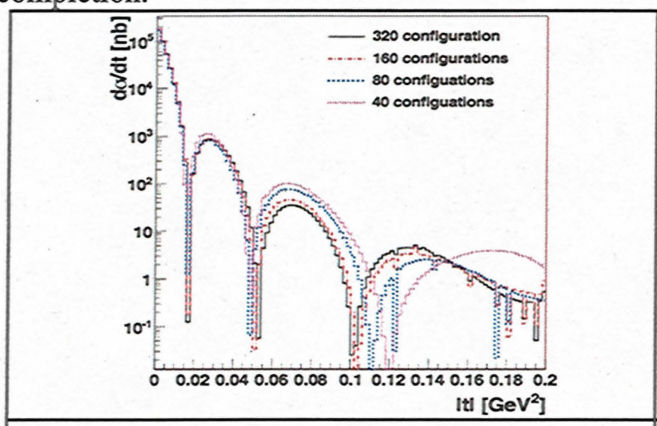


Fig. 1: dσ/dt after averaging over different number of nucleon configurations

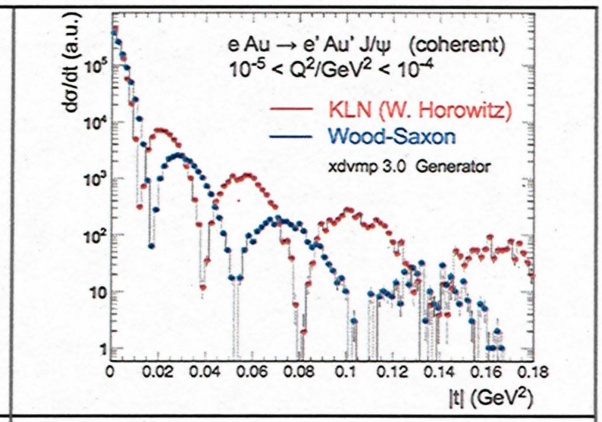


Fig. 2: dσ/dt from different initial spatial nuclear distributions

Exploring Signatures of Saturation and Universality in e+A Collisions at eRHIC

LDRD Project 10-043

Raju Venugopalan, A. Dumitru, J. Jalilian-Marian, A. Stasto, and T. Ullrich

PURPOSE:

A powerful motivation for an e+A collider is to study the properties of gluonic matter in nuclei at high parton density. A prediction in QCD is that the stability of matter requires that the occupation number of gluons in nuclear wave functions saturate at a value proportional to the inverse of the QCD coupling constant. A dimensionful scale $Q_{SA}(x)$ separates "soft" modes that are maximally occupied from "hard" modes that are not. This scale grows with energy and with nuclear size—so, for large nuclei, gluon momenta up to GeV scales are saturated. An important consequence of saturation is universality. Even though different nuclei can have different saturation scales at a given energy (Q_S^2 proportional to $A^{1/3}$), theoretical models predict that at very high energies, the saturation scales of all nuclei will approach a common value independent of the properties of the nuclei in which the gluons are confined. The properties of matter in this universal regime relate to the fundamental structure of the strong interactions itself—such as, for instance, a novel fixed point for the running of the QCD coupling constant or the Froissart bound for the total cross-section.

What are the signatures of saturation in deep inelastic scattering (DIS) off nuclei and can we extract the saturation scale uniquely from these final states? Which signatures are most sensitive to saturation? Can we anticipate precocious onset of saturation in these final states? Can they be clearly distinguished from alternative descriptions? Can one reliably extract the nuclear dependence, the impact parameter dependence, and the energy dependence of the saturation scale? By varying x and A, can we observe hints of the onset of a universal fixed point—what energy range is optimal? While qualitative answers to these questions exist, we do not at present have reliable quantitative answers to all these relevant questions.

In DIS at high energies, final states can be expressed in terms of multi-parton "Wilson line" correlation functions. The state-of-the-art description of the evolution of these correlation functions with energy is given by the JIMWLK renormalization group (RG) equations. Numerical solutions of these equations are feasible albeit challenging; one group of researchers has previously tackled the problem [4]. It is absolutely essential to have solutions to these equations to answer the fundamental issues raised above.

In addition to computing the properties of final states in e+A collisions, the solutions of the JIMWLK RG equations are also inputs in factorized expressions for multi-gluon production in A+A collisions. They are therefore important for a first principles understanding of thermalization in the Quark-Gluon Plasma, the development of elliptic and radial flow, and jet propagation (parton energy loss) in heavy ion collisions.

APPROACH:

The technical advance required for quantitative studies for eRHIC is to solve the JIMWLK RG equations for multi-gluon correlators using functional Langevin techniques [1]. This goal is challenging albeit feasible as suggested by the one extant numerical computation [2]. A further

challenge is to include running coupling effects properly in the JIMWLK computations. An outstanding post-doc candidate (Bjoern Schenke) was identified as one of the few people who could perform such computations and he was hired. He joined us only recently (December 2010) and has already begun working actively on developing the numerical algorithms with the PI and co-investigators.

PROGRESS AND RESULTS:

In the past year, the PI and co-investigators have identified key final states in both DIS and hadronic collisions where solutions of the JIMWLK equations will be essential. This was not widely appreciated before and provides further motivation for our research effort. For instance, the PI and collaborators have shown that the LHC data on p+p collisions are reasonably well described by models constrained by HERA DIS data on e+p collisions [3]. However, to obtain quantitative agreement, assumptions have to be made which need to be confirmed by the JIMWLK solutions to give credence to this agreement. Even more urgency is adduced by the observation of an interesting phenomenon called the "ridge" observed in very high multiplicity p+p collisions at the LHC. We showed that the ridge can be explained in an approximation scheme called "kt factorization" which includes QCD evolution in a mean field approximation by does not include multiple scattering effects [4]. (A student supported by the LDRD was involved in the latter work.) We also showed that the ridge is present in the opposite framework where one has multiple scattering effects but no QCD evolution [5]. The JIMWLK framework has both effects included properly; while we anticipate based on [4] and [5] that the ridge will be present in the full formalism, one can't be certain. Moreover, it has been argued that the quantitative correction from the full result as opposed to [4] and [5] would be very large, so it will be essential for quantitative phenomenology at the LHC [6]. Another example is di-jets in p+A and in e+A collisions. Again, here the JIMWLK contributions are essential and give contributions which are the same size as the "mean field" contributions that were previously assumed to dominate [7]. There are other examples of final states (heavy quarks) where these considerations are of relevance.

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Electroweak Physics with an Electron-Ion Collider

LDRD Project 10-044

W. Marciano and A. Deshpande

PURPOSE:

We are examining the potential electroweak physics capabilities of an Electron-Ion Collider (EIC). Topics of study include:

- Parity violating deep-inelastic structure functions measured using high statistics polarized electron scattering.
- Precision determination of the weak mixing angle over a broad Q^2 range and its implications for "New Physics."
- Searches for lepton flavor violation.

The statistical and systematic errors required are being used to define the EIC electroweak program.

APPROACH:

The principal investigators along with Krishna Kumar (University of Massachusetts) and Werner Vogelsang (BNL, Tubingen University) have considerable experience in deep-inelastic, polarized electron scattering both at the theoretical and experimental levels. Their efforts are assisted by a recently hired post doc, Yingchuan Li, who has worked both in nuclear and high energy theory. The study of parity violating structure functions is being carried out by K. Kumar and W. Vogelsang. A related topic, the Bjorken Sum Rule and QCD coupling at intermediate Q^2 is being examined by W. Marciano. The precision weak mixing angle work is being pursued by Y. Li and W. Marciano. Lepton Flavor Violation is being studied by A. Deshpande with emphasis on e+p→tau+x.

TECHNICAL PROGRESS AND RESULTS:

Work during FY2010 and the beginning of FY 2011 progressed on several fronts and results were reported at several workshops including the following:

- Electroweak workshop, William and Mary (May 2010).
- European Centre for Theoretical Studies (ECT), Trento, Italy - Presentation title, "Precision Tests of the Standard Model: from Atomic Parity Violation to Parity-Violating Lepton Scattering," (November 2010).
- Gluons and Quark Sea at High Energies Physics Workshop - To facilitate the organization of the program, Dr. Marciano was a convenor in regards to the subtopic: Beyond the Standard Model - Test of the Bjorken Sum Rule and Electroweak tests, held at INT (September - November 2010).

Y. Li was in residence at the INT for the entire ten week program and coordinated the electroweak studies. An important outcome was the weak mixing angle sensitivity studies for DIS ep and eD scattering. As illustrated in the preliminary Figure 1, the EIC can map out the running of $\sin^2\theta_w(Q)$ for large Q with a total statistical error rivaling the best measurements at Z pole colliders. Systematic errors are still being evaluated.

For the case of lepton flavor violation, it was found that EIC can probe an interesting region of "New Physics," but only if very high luminosity – $L \simeq 10^{35} cm^2/sec$ is available.

Results from those studies will be included in the white paper from the INT workshop, "Gluons and the quark sea at high energies: distributions, polarization, tomography."

During FY 2011, we expect to present our results at the DIS conference, which will be held in Newport News, VA, April 11-15, 2011. In addition, publication quality reports will be submitted to scientific journals.

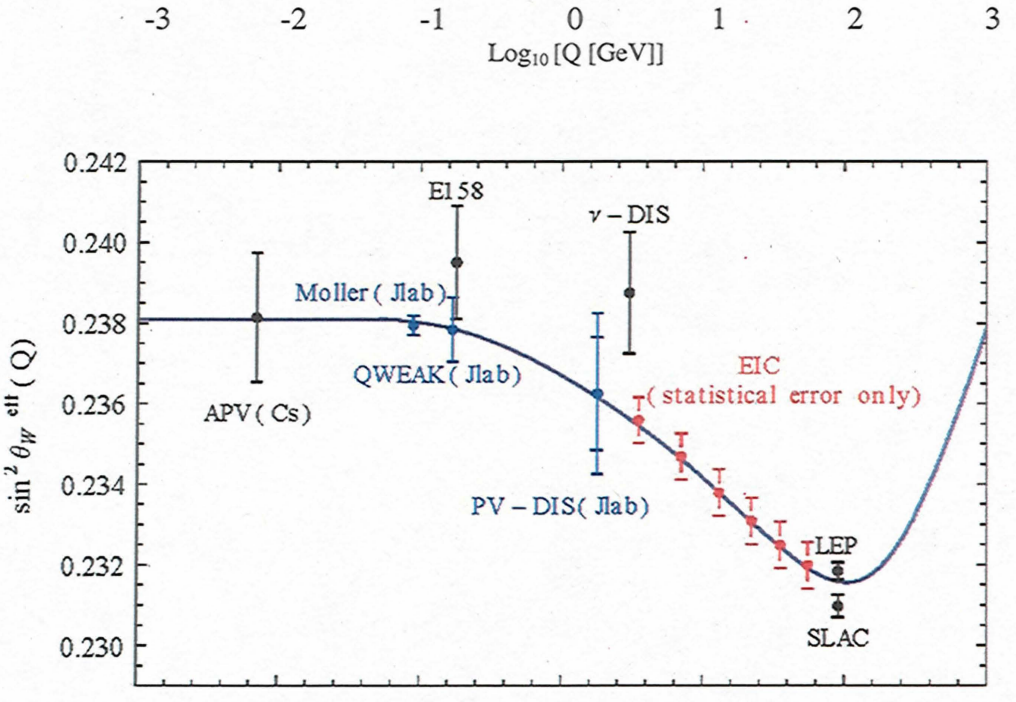

Fig. 1: *Existing Measurements (black) of $\sin^2\theta_w(Q)$ as a function of Q. Also shown are anticipated goals of JLAB experiments (blue). EIC capabilities (red) are shown for DIS polarized ep scattering assuming an integrated luminosity of $200fb^{-1}$.*

LSST – Astrophysics and Cosmology Initiative

LDRD Project 10-045

Erin Sheldon

PURPOSE:

The primary focus of this LDRD is on measuring gravitational lensing effects to probe the expansion history and growth rate of massive structures in our universe. Dark energy accelerates the expansion of the universe, dramatically increasing the volume in comparison to a matter-only universe. Dark energy also inhibits the growth of massive structures under gravitational collapse. Thus the number density of massive objects such as galaxy clusters as a function of cosmic time is directly related to the properties of dark energy, in particular the equation of state parameter w=pressure/density. Critical to using the number density to constrain cosmology are the masses of the clusters, which we will measure using gravitational lensing effects in DES (Dark Energy Survey). Data from BOSS (Baryon Oscillation Spectroscopic Survey) will also be used to constrain dark energy. The analysis and infrastructure development for DES will lead naturally to work on the Large Scale Synoptic Telescope (LSST) which was accorded top rank among large ground-based initiatives by the Astro2010 Decadal Survey. Brookhaven has a key role in the LSST project and science.

APPROACH:

Erin Sheldon is a member of DES, and is co-leading the lensing effort in DES. This work will be in collaboration with Mike Jarvis and Bhuvnesh Jain from the University of Pennsylvania. Erin Sheldon and post doc Zhaoming Ma are supported at 100% by this LDRD.

DES will see first light in late 2011. The intervening time is spent developing data reduction pipelines and realistic simulations to test these pipelines. After first light, DES will take data for five years, during which the data will be processed as it arrives and analyses performed to extract dark energy parameters.

Lensing measurements are critical to the goals of DES. The primary dark energy probes used by DES are the power spectrum of mass density fluctuations in our universe measured from gravitational lensing (cosmic shear) and the number density of galaxy clusters as a function of their mass and cosmic time. The masses of these clusters are also measured using gravitational lensing. DES will use the combined probes to constrain the equation of state parameter.

This cluster lensing work is a natural continuation of earlier work by Erin Sheldon in the Sloan Digital Sky Survey (SDSS), which remains the most sensitive measurement of this type to date. The processing pipelines for DES are an extension of those used in the SDSS, as are the analysis tools used to extract cosmological parameters. The volume and depth of DES is sufficiently large to allow these measurements to be made in many bins of cosmic time, with which the cosmological analysis will be extended to constrain the properties of dark energy.

Software pipelines were developed previously to measure gravitational shear effects in astronomical images. A framework was created to process the large amounts of DES data in parallel. The codes were tested on simulated DES data designed to accurately represent DES survey data.

TECHNICAL PROGRESS AND RESULTS:

The pipelines can now combine multi-epoch (multiple observations of the same object) data into a single best measurement for each detected astronomical object. The multi-epoch measurement code developed under this LDRD was a major milestone in DES lensing pipeline development. DES will visit each region of sky multiple times producing separate images at different epochs. This multi-epoch analysis is required to optimally process the data because each image is taken under different observing conditions, which results in a different point spread function (PSF). As this is the dominant source of systematic error in lensing measurements, it must be treated with care. The multi-epoch shear measurement code properly accounts for this effect when combining observations.

Using computers at BNL, all of the available simulated images were processed a large number of times during development; the quick turnaround of processing and code improvements has been important for efficient development. The processing includes the single-epoch exposures as well as the full multi-epoch simulated data.

Further DES simulations were created and tested which are a more realistic realization of DES observations and data, and have realistic gravitational lensing effects that can be used to extract the input cosmology. Significant progress was made in testing and stabilizing the code base. In 2010 Ma began developing an improved framework to determine and correct DES data for the PSF. Stellar images (point sources) are used to determine the PSF which is then interpolated from the positions of the stars to that of the galaxies. This project is in the early stages, but progress has been rapid and a useable code should be available soon.

DES will see first light in fall 2011 and begin science operations in 2012. To prepare for the survey data, processing pipelines and analysis codes to measure gravitational lensing are being written and tested at BNL.

The primary challenge for 2011-2012 is the processing of real DES data as it arrives and much of the group activities in the ramp-up to operations will be preparing for the data flow. We must adapt the workflow of getting images, processing, and feedback into a streamlined operation.

Because DES data management will only process the data a few times, development and testing of the lensing pipeline must occur externally. This testing must use all available data in order to probe low-level systematics, and is thus computationally intensive. BNL has taken on this responsibility, led by Sheldon. This careful attention to systematic effects will lead to accurate measurements of dark energy properties.

Epigenetics From Plants to Man

LDRD Project 10-046

Fritz Henn, Qiong "Alison" Liu, Jacob Hooker, Martine Mirrione and Daniela Schulz

PURPOSE:

The goal was to assess epigenetic changes using both in vitro molecular approaches and in vivo imaging approaches. Epigenetic changes are the mechanisms used to alter gene expression due to environmental factors. The in vivo approach for man involved developing an imaging ligand that will measure specific histone deacytalase (HDAC) activity in vivo which will provide a mirror of epigenetic change. The in vitro question involved: 1) determining the role of CO_2 and temperature changes in altering plant gene expression. 2) looking at the role of stress in altering gene expression and inducing depression in humans.

APPROACH:

The role of environment in altering gene expression has come to be a major area of biological research. In studies ranging from plant adaptation to environmental change to the role of early environmental stress as a causative factor in psychiatric disease, epigenetic changes appear to play a major role. This project was aimed at three targets. The first one was to determine if it is possible to develop an imaging method that would capture epigenetic change and allow an assessment of how important it might be in an organism's reaction to environmental change. The approach here is to create a labeled PET tracer that will assess specific HDAC activity. The HDAC family of enzymes are central controls in altering gene expression by changing the binding of histones to DNA. This was work of Jacob Hooker and Sung Won Kim.

The second area of research was to use molecular techniques, to identify controls that alter plant development in response to environmental changes. Here we found that changes in either temperature or atmospheric CO_2 alter a set of miRNAs which regulate plant growth. Several of these miRNAs act in an opposite fashion to elevated CO_2 and T increases, namely leading to enhanced growth with high CO_2 and decreased growth with high T.

In the final area we used a stress model to induce helplessness in animals and have defined the circuit that mediates the helplessness. Using this as a model for human depression, we confirmed the circuit alteration in man using human imaging. We then attempted to define how the circuit was altered and implicated the reward system and DA in this process. We are now attempting to define the pathological driver which appears to be overactive glutaminergic transmission in the medial prefrontal cortex.

TECHNICAL PROGRESS AND RESULTS:

The labeling of a histone deacytalase requires finding a compound which binds tightly and will cross the blood brain barrier. The first compound tried was entinostat (MS-275) which is a HDAC inhibitor .currently being considered as a possible drug to fight cancer. This required the development of new chemistry to get a fast one step reaction to incorporate CO_2 into carbamates. This led to the development of some novel and important chemistry that will have a positive effect on the synthesis of a variety of PET ligands using C^{11}. New HDAC inhibitors are being developed which will cross the blood brain barrier and this work will continue with follow on funding from NIH.

The analysis of the effect of increasing temperature on plant growth showed dramatic detrimental effects in yield and seed development. This appeared to be mediated by miRNAs. Those miRNAs which changed have been identified and involved 62 known plant miRNAs and 35 predicted miRNAs, which were unknown. In the case of CO_2, 17 known and 9 predicted miRNAs were found. CO_2 was found to increase yield and seed formation and interestingly 16 known miRNAs were found to change with both conditions, but most in opposite directions. This will provide a basis for understanding the effects of climate change on agricultural yield.

Looking at the effect of stress in inducing helplessness, a brain circuit was identified which was altered due to the stressor. This circuit was analyzed and found to be overactive and inhibit the reward circuitry of the brain. That is, no experience of reward or pleasure was noted after a positive experience. This clearly could lead to a depressed mood and the overactivity in this circuit was determined to be present in depressed patients using imaging studies in conjunction with researchers at the National Institute for Mental Health. We are now looking at the molecular controls leading to this circuit abnormality in an effort to identify new drug targets for more effective antidepressants.

New Methods for Analyzing Brain Function using MR

LDRD Project 10-047

David Schlyer and Elisabeth Caparelli

PURPOSE:

This goal of this project is to use multiple approaches to attempt to improve the type of information that can be obtained via magnetic resonance-positron emission tomography (MR-PET) studies. We have developed radioactive nanoparticles with an exterior shell of reactive carbon groups in order to create ligand specific markers for in vivo use in both PET and MR. These particles may be targeted through the use of external magnetic fields which would be a major therapeutic advance. We are also developing metabolomics and central nervous system neurogenesis measurements using magnetic resonance spectroscopy (MRS) and combining PET and MR measurements in one instrument.

APPROACH:

Nanoparticles can provide not only sensitive and specific imaging information in cancer patients, but also selectively deliver anticancer drugs to tumor sites (Gupta 2007, Hanessian 2008). Although recent advances have demonstrated the feasibility of using targeted magnetic iron oxide nanoparticles for tumor imaging and therapy, methods and strategies to produce tumor-targeted imaging probes with a high specificity and sensitivity are still greatly needed (Xie 2009). There are many examples of using nanoparticles as drug delivery agents and more recently magnetically guided nanoparticles have been used to deliver therapeutic drugs to the specific areas. The added benefit of using nanoparticles for therapy requires that the therapeutic drug stays attached to the nanoparticle until it reaches the desired site. After two decades of effort, iron oxide nanoparticles have become a powerful platform, but they are not in widespread use clinically (Xie 2009). There are still questions about how to optimize the nanoparticle-therapeutic drug constructs for delivery of the drug to the tumor site and how magnetic direction might be optimized for delivery using magnetically directed drug constructs. There are also questions about how these nanoparticle constructs may affect the physiology and what toxicological effects these constructs may have. As a result of great benefits which may be derived from these constructs and the potential undesired side effects, we have undertaken a study of the biodistribution using radiolabeled nanoparticles while at the same time observing the effects on normal metabolism using MRS at the local site of accumulation and also at areas which are connected through physiology, but not in direct proximity to the site of accumulation.

TECHNICAL PROGRESS AND RESULTS:

We have developed the synthesis of iron-52 labeled iron oxide nanoparticles as a basis for imaging them simultaneously with PET and MRI. The probe is a superparamagnetic MRI contrast agent in the form of a single iron oxide nanoparticle with a core containing a positron emitting radionuclide. This dual probe concept combines the strengths of both PET and MRI into a powerful new tool for quantitative molecular imaging. With the dual probe approach, the strengths of one modality compensate for the weaknesses of the other. With appropriate functional groups attached, this type of dual modality probe is the basis for the therapeutic construct we are studying.

Since Fe-52 is not always available to us, we have also developed methods to incorporate carbon-11 and fluorine-18 into several different types of nanoparticles with several different functional groups on the periphery of the particles. The results of these experiments are shown in Figure 1.

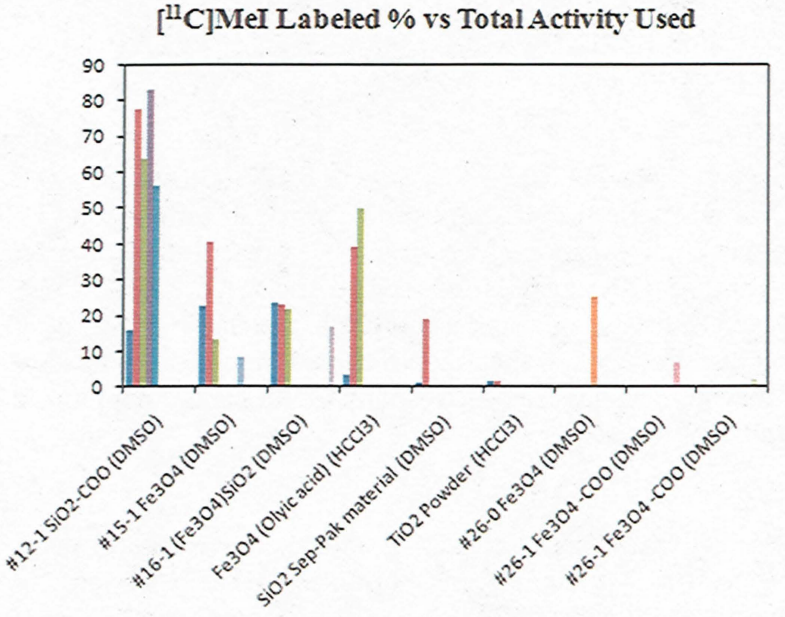

Fig. 1: Yields of [^{11}C]CH_3I labeling of different nanoparticles in several solvents

We have also carried out studies of simultaneous PET and MRI showing the uptake of the radiotracer at a specific site while simultaneously monitoring the metabolic profile in a remote region of the body. In the following example, we administered [^{11}C]raclopride and monitored the uptake in the striatum while at the same time monitoring the metabolic profile in the frontal cortex of the rat brain (Figure 2). We will expand these studies to the effects of nanoparticles.

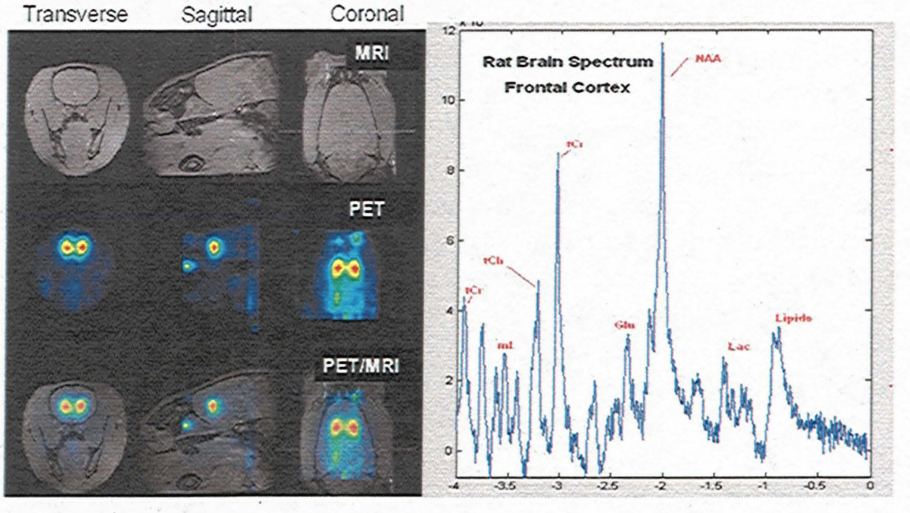

Fig. 2: Simultaneous PET and MRS quantifying the concentration of radiotracer in one region and monitoring the metabolism in a separate region of the rat brain.

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Radiotracer Development and PET Imaging for Obesity Studies

LDRD Project 10-048

Gene-Jack Wang, Anat Biegon, Jean Logan, and Colleen Shea

PURPOSE:

This project is aimed at developing new approaches to the study of common obesity in humans using new radiotracer technology applied to health problems. We have studied the nature of the reward system in drug addiction and have developed a fairly complete set of experimental approaches to defining alterations in this system in addiction. We have begun to apply these approaches to other human diseases such as adult hyperactivity disorder and obesity, conditions in which control and appropriate reward structures appear to be distorted. Obesity is perhaps the major underlying factor in the increasing cost of health care due to its increase in prevalence and apparent association with a variety of serious health conditions from increasing levels of diabetes to cardiovascular disease. For obesity, we found a distorted reward response, which was different between genders. This program will allow us to continue to explore this result using a variety of PET approaches including a new gender specific ligand, which may shed light on the differences between men and women in reward response.

APPROACH:

Brain dopamine function and insulin resistance: Laboratory animals with disruption of brain insulin receptors show enhanced feeding behaviors. A recent study using PET-FDG shows brain insulin resistance exits in subjects with peripheral insulin resistance, especially in striatum and insula, regions that relate to appetite and rewards. Dysregulation of insulin resistance responses in these regions may be very important in the etiology of insulin resistance in obesity. Subjects with insulin resistance may need to generate higher circulating insulin to experience the reward sensation of eating. Our imaging studies implicate the involvement of brain dopamine (DA) in normal and pathological food intake in humans. Increase in striatal extracellular DA is associated with food cue presentation in normal weight subjects, which provides evidence of an involvement of dopamine in non-hedonic motivational properties of food intake. Overeating in morbidly obese individuals reduced striatal DA D2 receptors (D2R) availability. Simple carbohydrate, such as sugar intake, is a major nutritional source, which contributes about one fourth of total energy intake. This leads us to hypothesize that subjects with insulin resistance will have higher circulating insulin and overeating behavior to experience the reward sensation of eating, which will enhance brain DA release and down regulate striatal D2R. We use PET with [C-11]raclopride to measure D2R and DA release with FDG to assess brain metabolic function.

Brain aromatase availability in overweight humans: Aromatase, the Cyp19A gene product, is the last enzyme in estrogen biosynthesis from androgenic precursors. The aromatase gene is locally expressed and differentially regulated in many organs and tissues, including fat cells and brain. Aromatase expression is reportedly increased in fat tissue of subjects with a high body mass index (BMI), but the relationship between BMI and brain aromatase availability has not been investigated to date. Vorozole is a potent and selective aromatase inhibitor, and [C-11]vorozole was found to be a useful PET tracer for brain aromatase in rodents and non-human primates. Our recent PET studies have revealed that the regional distribution pattern of aromatase in the human brain is unique, with the highest levels found in the thalamus. In

contrast, primate and rodent brain studies show low levels in thalamus and high levels in amygdala. We use [C-11]vorozole, an aromatase inhibitor tracer to assess aromatase availability in brain of overweight humans with PET.

TECHNICAL PROGRESS AND RESULTS:

Insulin resistance project: Four women and 4 men (51.5±4.2 years old, BMI = 24.1±6.2, range: 20.8 – 33.5) were scanned with [C-11]raclopride, after oral glucose (75 gram) and oral sucralose ingestion. Blood glucose and insulin levels were obtained prior to and at 10, 30, 60, 90 and 120 min after glucose ingestion. Self-report measures (i.e. three factors eating questionnaire-TFEQ, Dutch Eating Behavior Questionnaire-DEBQ) were obtained at baseline condition. Correlations analyses were used to assess the relationship between changes in brain dopamine D2 receptor availability and blood insulin, glucose levels and self-report measures. **Results:** Subjects with greater blood insulin levels at 120 min after glucose ingestion showed higher hunger scores in TFEQ ($p < 0.03$) and total TFEQ scores ($p < 0.02$). Greater blood insulin levels at 90 min are associated with higher total DEBQ scores ($p < 0.008$). Blood insulin and glucose levels are not associated with striatal D2R availability with sucralose and changes in oral glucose ingestion. Preliminary statistical parameter mapping analyses (SPM, $p < 0.05$) of distribution ratio images revealed 5 subjects with less blood insulin levels and decreased D2R availability in ventral striatum, hypothalamus, frontal cortex and parahippocampus after glucose ingestion (Figure 1); 3 subjects with greater blood insulin levels did not show changes. The preliminary finding suggested glucose ingestion induced DA release in brain reward regions and insulin inhibited these responses. Subjects with insulin resistance might decrease reward responses to glucose.

Aromatase project: Five healthy overweight subjects (3 women and 2 men, 39.3±14.8 years old, BMI = 29±2.8) and 13 age matched normal weight subjects (5 women and 8 men, 35.1±15.5 years old, BMI = 22.8±1.7) were scanned with [C-11]vorozole. PET data were acquired over a 90 min session and regions of interest placed bilaterally over selected brain regions (hypothalamus, amygdala, thalamus and cortical white matter). Brain and plasma time activity data were used to calculate the total distribution volume (V_T) from a two-compartment model. The results were analyzed by 2-way ANOVA with repeated measures (group x region) and Pearson's regression analysis. **Results:** High BMI was associated with a significant ($p < 0.01$), 25%, 27% and 30% decrease in V_T in the hypothalamus, thalamus and amygdala respectively with a smaller decrease (< 20%) in cortical white matter. There was a significant, inverse correlation ($n = 18$, $r = 0.59$, $p < 0.015$), between BMI and V_T in amygdala with trends in the same direction in the other regions of interest.

SPECIFIC ACCOMPLISHMENTS:

Reduced availability of aromatase in the brain of overweight subjects implies reduced conversion of androgens to estrogens in the brain. This finding is in line with animal data showing decreased food intake in animals administered with estradiol in the hypothalamus and other nuclei and supports the notion that human aromatase expression is regulated in a tissue-specific manner. The result of this study is submitted to the Society of Nuclear Medicine meeting in 2011. In the future, we will submit a NIH R21 grant application based on the findings of this project.

Imaging Plants

LDRD Project 10-049

Richard A. Ferrieri and Paul Vaska

PURPOSE:

Positron Emission Tomography (PET) imaging in plants is receiving increased attention as a new strategy to measure plant responses to environmental stimuli and as a tool for phenotyping genetically engineered plants. Both applications are relevant to DOE missions in the environment, addressing carbon sequestration below ground, and in bioenergy, imaging sugar transport to screen lines of potential energy crops. PET imaging in plants, however, poses new challenges to researchers. In particular, the leaves of most higher plants are so thin that a large fraction of positrons emitted from PET isotopes (including ^{18}F, ^{11}C and ^{13}N) escape. Even state-of-the PET cameras have significant partial-volume errors for such thin tissues. Although these limitations are acknowledged by researchers in the field, little effort has been given to bring this technology into a realm of yielding quantitative data.

APPROACH:

Here we measured the magnitude and distribution of escaping positrons from tobacco leaves, *Nicotiana tobacum* (cv. Samsun), for the radionuclides ^{18}F, ^{11}C and ^{13}N using the small-animal microPET scanner. Characteristics of these radionuclides are listed in Table 1. Leaves were encased in a Plexiglass housing that sat within the camera's gantry and field-of-view (Figure 1). Images were reconstructed by filtered backprojection after Fourier rebinning using commercial software (Micropet Manager 2.3.3.0) and displayed for visual comparison using microPET software (ASIPro VM 6.2.5.0) enabling construction of regions of interest (ROI's) on the leaf surface (Figure 2). Image results were compared to radionuclide concentrations measured from tissue dissection and counting, and to a Monte Carlo simulation using GATE (Geant4 Application for Tomographic Emission).

Table 1.

Isotope	Half-life (min)	β+Endpoint Energy (MeV)	Mean Range in water (mm)	β+ Range distribution [18] – FWHM (mm)	β+ Range distribution [18] – FWTM (mm)
F-18	110	0.6	0.59	0.102	1.03
C-11	20.4	0.96	1.13	0.188	1.86
N-13	9.96	1.2	1.60	0.282	2.53

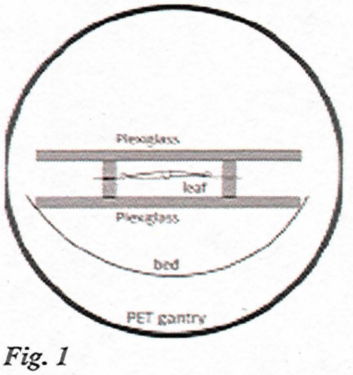


Fig. 1

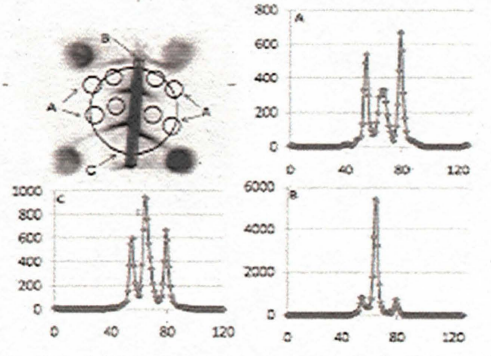


Fig. 2: ROI's for tissue (A), midrib (B), and whole leaf (C). The four circular foci of activity in the corners coincide with the location of the plastic spacers between the Plexiglass covers. Plots show ROI mean (nCi/cc) as a function of radial distance in the PET field of view. Distance units are plane number (each plane is 0.78mm think). Center peaks represent tissue activity while outer peaks represent escaping positrons.

TECHNICAL PROGRESS AND RESULTS:

Simulated and experimentally determined escape fractions were consistent. The fraction of positrons (mean ± standard deviation) escaping from midrib, leaf parenchyma and whole leaf was substantial for ^{18}F, ^{11}C and ^{13}N (Figure 3). Escape fractions were lower in thicker tissues line the midrib. We ascertained that partial-volume averaging underestimates the radioactivity concentration in the leaf blade by at least an order of magnitude. The foregoing effects combine to yield PET images whose contrast does not reflect the actual activity concentrations. These errors can be largely corrected by integrating activity along the PET axis perpendicular to the leaf surface, including detection of escaped positrons, and calculating concentration using a measured leaf thickness (Table 2).

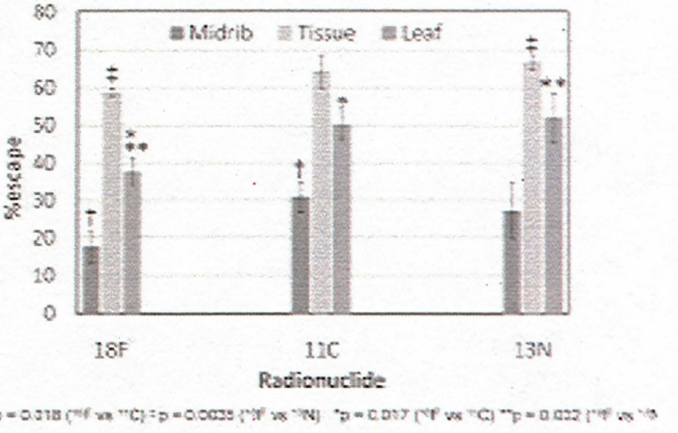


Fig. 3: Percent of radioactivity detected outside the designated leaf sections (escaping positrons) using ROI integration method depicted in Figure 2.

	Escape fraction (percent)		
Leaf thickness (um)	F-18	C-11	N-13
50	76.83	79.20	78.90
100	73.35	78.40	78.20
150	69.18	76.72	77.00
200	65.03	74.57	75.49
250	61.14	72.31	73.96
300	57.27	70.22	72.16
500	44.85	60.96	65.06
1000	26.65	43.30	49.88
2000	13.52	24.69	30.84

Table 2. Results of Monte Carlo simulations. The percent of positrons escaping the leaf and annihilating in the Plexiglass detection plates above and below the leaf tissue are tabulated for varying leaf thicknesses. Radioactivity is a line source of radioactivity placed at the center of the leaf with activity distributed evenly throughout the thickness of the leaf.

Proton EDM Research and Development

LDRD Project 10-050

Yannis Semertzidis

PURPOSE:

This LDRD supported the study of the statistical power and systematic errors associated with the elastic nuclear scattering of a polarized deuteron beam on a solid carbon polarimeter using the COSY (Juelich/Germany) storage ring. It also supported the development of a software program that can accurately track the particle momentum and spin vectors in a storage ring and the development of the electric field testing needed for the proton and deuteron electric dipole moment (EDM) experiments. One of the main issues in the experiment is to develop a very high resolution beam position monitor (BPM) at the pico-meter level. Some of the findings of this BPM development are being applied to R&D work for a BPM for RHIC.

APPROACH:

The polarimeter is the main detector used to probe the spin vector of the stored protons in the proton EDM experiment. Since the signal is small, the requirements on the systematic errors are very strict and we set out to test them at COSY by exaggerating certain beam parameters and conditions. Extrapolating to the expected beam parameters and stability conditions during the experimental run, we could estimate the expected polarimeter systematic errors.

The polarimeter collaborators supported by this LDRD were Dr. Astrid Imig (BNL-post doc), some travel support for Dr. Ed Stephenson of the Indiana University Cyclotron Facility and travel support for William Morse and me. The travel support was for visits to COSY where we have used stored polarized deuteron beams to scatter off solid carbon targets and detect the scattered particles with scintillation detectors arranged in a toroidal geometry. The needed statistics required extensive running times, i.e., a period of two to three weeks of dedicated time twice a year.

The EDM requirements for the storage ring are very strict. In addition, the commonly available programs don't regularly include electric fields since they add a substantial complication. This complication arises from the fact that while magnetic fields conserve the particle kinetic energy, the electric fields conserve only the total mechanical energy (kinetic plus potential energy) and not just the kinetic energy. During the last year we have developed a thorough understanding of the issues involved and for the most part we have solved them. Selcuk Haciomeroglu, a Ph.D. student from Istanbul Technical University is doing this work with me.

Regarding the electric field development, we have borrowed a high voltage testing system from Cornell University and have installed it at the AGS experimental floor. We also borrowed specially made plates, one made out of stainless steel (SS) and the other titanium (Ti). After meeting the safety requirements, we were able to turn it on and take data.

On the BPM development, we have run several simulations, made measurements and made numerous systematic error studies. We have eliminated several options as potentially vulnerable to systematic errors. The good news is that we have developed three alternative options that look promising, since we couldn't find serious systematic errors.

The state of the art for BPM resolution is of the order of 10 nano-meters for a single measurement. We want to use this accomplishment and build upon it. We want to average the

BPM measurements effectively by several orders of magnitude and achieve a *resolution* level of 0.1pm between two counter-rotating beams.

Previously, we developed the modifications needed to a detector in the COSY ring so that it could work as a polarimeter for our tests. Those modifications included a major data acquisition development as well as electronics evaluation and testing. Other modifications included the development of a suitable beam extraction system onto the carbon target and timing of the RF-solenoid system to perform the needed spin flips.

TECHNICAL PROGRESS AND RESULTS:

During the last year, we developed a Monte Carlo (MC) program and confirmed the statistical power we obtained at the runs for various geometries. This helped benchmark the MC program and enables us to predict the statistical power at the proton EDM experiment and furthermore optimize it. We took data under various conditions for extensive periods of time, analyzed them, and presented them at collaboration meetings and conferences. We have also shown that the systematic errors are well below the statistical reach of the experiment. We have prepared a major paper and it will be sent for publication soon.

The issue of changing of the particle momentum during horizontal oscillations complicates the equations of motion and the integration method. We decided to use a small step for particle and spin tracking giving adequate accuracy for the needs of our experiment. This development is still going on until the end of March 2011, when we expect to finalize it and write the papers for publication.

The electric field testing helped us understand the issues with very high electric fields on metallic surfaces. Usually, the E-field that can be safely applied on metallic surfaces is of the order 5-10 MV/m, but it can go up to 30 MV/m when the surface is treated with high pressure water rinsing (HPR). We have tested the plates without HPR to set the baseline. We have caused several sparks to find out the recovery time and have also applied high pressure glow discharge, which helps clean up the plates after a severe spark. We have now asked Cornell University to provide us with new plates after HPR treatment to compare their E-field performance.

The most promising system we have developed conceptually is to look at the DC component of the magnetic field generated by a stored beam outside the beam pipe. The magnetic field from the beam is expected to be of order of 0.2mG, which is mostly cancelled by the counter-rotating beam. However, this cancellation will not hold when the two beams separate in space due to the presence of magnetic fields. The amplitude of the separation also depends on the vertical tune of the ring lattice. We decided it would be beneficial to modulate this tune so that the induced magnetic field would show up at a specific frequency. That magnetic field is below a pG, which low temperature SQUIDS would be sensitive enough to probe.

We are preparing a proposal for the DOE Office of Nuclear Physics that will be submitted by the end of spring 2011. We have proposed the BPM idea for an R&D project at RHIC and separately for the US-Japan program.

In-situ Reaction Cell Development for Studying CO2 Sequestrations with the X-ray Microprobe at the NSLS

LDRD Project 10-051

Jeffrey Fitts

PURPOSE:

This project will extend current synchrotron-based X-ray microprobe capabilities to enable imaging of geochemical reactants and formation products under in situ temperature and pressure conditions in the caprocks and well cements that are expected to entrap CO2. The major technical milestone of this project is to develop an in-situ reaction cell capable of operating at geologic storage reservoir temperature and pressure conditions and with the freedom of movement and angular acceptance necessary to perform 3-dimensional diffraction tomography.

APPROACH:

Capture and geologic sequestration of carbon dioxide has emerged as a promising option for mitigating the increasing carbon dioxide concentrations in the atmosphere (IPCC, 2005). The DOE predicts that widespread adoption of carbon capture and geologic sequestration (CCS) will occur only if CCS technologies achieve 99% CO2 storage permanence and only add a 10% electricity cost premium. Among the most significant technical challenges and cost uncertainties is ensuring long-term entrapment of the injected CO2 with minimal leakage (Bachu 2008). This project set out to develop an in-situ reaction cell for microprobe beamlines at the NSLS (X27A & X26A beamlines) and NSLS II (SRX and HXN beamlines) to enable studies of CO2 geochemistry under geologic storage conditions

The heterogeneous reactions controlling carbonate precipitation and mineral dissolution will only be revealed empirically by an experimental probe that combines micron-scale spatial resolution to focus on individual mineral surfaces within pore spaces and sensitivity to detect the very onset of mineralization/dissolution with the ability to make measurements under in situ temperature and pressure conditions of geologic CO2 storage reservoirs. Support for this LDRD was used to purchase the components needed to develop an in-situ cell and motorized stage capable of operating at geologic storage reservoir temperature and pressure conditions and with the freedom of movement and angular acceptance necessary to perform 3-dimensional diffraction tomography.

The new stage motors will significantly improve all modes of operation of the microprobe. The x-ray beam focal length and working distances of the fluorescence and CCD detectors, however, impose a tight operating volume on the in-situ cell and tomographic stage, and therefore, would require significant modifications to the endstation configuration to collect images under active flow conditions. Therefore, the experimental plan was modified to enable an 'online/offline' mode of operation, where the high pressure pumps, heat baths and flow equipment are operated in the 'online' mode in an auxiliary lab away from the beamline. At periodic intervals that accommodate beamtime scheduling, the flow experiment is temporarily stopped by stop-cocking the section of PEEK tubing containing the sandstone sample and transferred to the NSLS while maintaining pressure and temperature, and thereby the tomographic imaging is conducted in the 'offline' mode. The online/offline mode is also beneficial for conducting long-term (weeks to

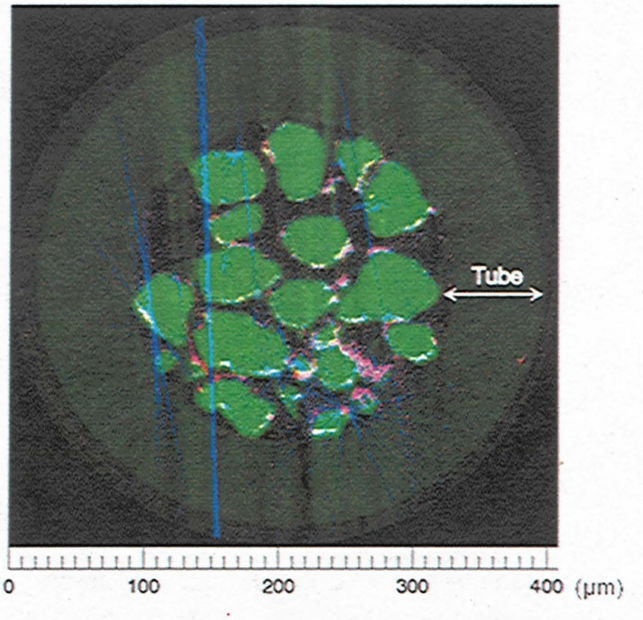
months) flow experiments while preserving the ability to collect multiple time points over the course of the experiment.

The plan is to develop the microprobe imaging capabilities provided by the newly developed in situ reaction cell to establish a resource at the NSLS that is unique among DOE operated synchrotron facilities. This unique capability will is now being used to pursue follow-on funding for the following technical and scientific activities required to 1) establish micro-diffraction tomography at the NSLS, 2) build collaborative ties with researchers within the region (especially Stony Brook University and Princeton University) to pursue a research center scale program for CCS, and 3) produce the data necessary to attract follow-on funding from DOE Fossil Energy and Basic Energy Sciences

TECHNICAL PROGRESS AND RESULTS:

The first aspect of the technical progress entailed identifying and purchasing the components for the pressure and temperature flow apparatus needed to develop the online mode of the experiment. This process was aided significantly by modifying a flow through system being used in Professor Martin Schoonen's lab at Stony Brook University. A high precision ISCO pump that can operate at the necessary pressures and temperatures was purchased and tested. The necessary fittings, tubing and gauges were also purchased. The components are currently in building 815 lab C-5 awaiting follow on resources for labor support to conduct flow-through experiments.

The second aspect of technical progress centers on the 'offline' mode of operation at the NSLS x-ray microprobe beamlines. Significant effort was put into identifying and testing the cell material that would contain the sample at pressure and temperature while allowing sufficient transmitted and fluoresced x-rays for the 3-D imaging. Diamond or sapphire window designs were abandoned because of cost and geometry constraints, and finally, the high density polymer tubing, PEEK accommodated the largest sample diameter (1.4 mm). The tubing and connectors are also low cost and relatively easy to integrate into the beamline stages. A new goniometer was also purchased for NSLS operated beamline X27A.



The Figure shows a single x-ray fluorescence tomographic slice through PEEK tubing packed with size selected sand grains from the Mount Simon formation, which is targeted for geologic CO2 storage in western New York. The image combines Sr, Rb and Fe fluorescence with absorption image which shows density contrast. This image shows that adequate x-ray penetration and fluorescence emission makes it out of the cell to the detector and that in situ imaging at this scale and in a PEEK tubing size, which is rated for the pressures and temperatures needed to simulate geologic CO2 storage formation conditions, is feasible.

Enzymatic Control of Plant Cell Wall Properties that Impact Conversion to Biofuels

LDRD Project 10-052

Paul Freimuth

PURPOSE:

The biofuels research sponsored by the DOE Office of Biological and Environmental Sciences is focused on production of ethanol from cellulose, the major carbohydrate polymer in plant cell walls. Separation of cellulose from other cell wall polymers, including hemicellulose and lignin, has emerged as a major obstacle. Efforts to address this problem have underscored the lack of knowledge of how cellulose is assembled with other polymers into a recalcitrant network during plant cell growth. Broadly, the goal of this LDRD project is to investigate the mechanisms of polymer network assembly in plant cell walls, and, in particular, to study the role of carbohydrate-active enzymes and binding proteins in this process. Our technical objectives are to produce a representative set of these plant cell wall proteins using recombinant expression technology, and then characterize their biochemistry. Successful achievement of these objectives will lay the foundation for structural characterization of the plant cell wall proteome by X-ray crystallography using the BNL light sources and for determining how plants use these enzymes to regulate the molecular architecture of their cell walls. Increased basic understanding of the physical-chemical nature of plant cell wall polymer networks will provide insights for development of more effective methods to deconstruct this material for biofuel production and for discovery of novel uses for this highly abundant, renewable natural resource.

APPROACH:

Background, scope and methods: Plant cell walls consist of roughly equal amounts of cellulose, hemicellulose and lignin. Cellulose is a homogeneous linear polymer of glucose subunits. Hemicellulose is a branched, heterogeneous carbohydrate polymer that cross-links cellulose fibers, thereby increasing their tensile strength. The mechanisms of establishing these cross-links and of regulating their number and distribution along cellulose microfibrils are not known. Lignin is a complex phenolic polymer that is synthesized at late stages of cell wall biogenesis and serves to further increase cell wall tensile strength and overall hydrophobicity.

In addition to these 3 major polymers, the cell wall contains numerous proteins that are secreted from plant cells and function in cell wall biogenesis, although the precise roles of most of these proteins have yet to be determined. Whole genome sequencing of several plant species has revealed a large number of genes for cell wall-localized glycoside hydrolases, which are enzymes that hydrolyze the chemical linkages between subunits of carbohydrate polymers. The genomes of Arabidopsis and rice, for example, each contain about 45 genes specifying different cellulases, which hydrolyze the linkages between glucose subunits of cellulose polymers. It is widely held that many of these cellulases introduce chain breaks along newly-synthesized cellulose polymers that then serve as points for introduction of hemicellulose cross-links or for expansion of the cell wall during cell growth. These hypotheses remain largely untested, due in large part to technical difficulties in producing plant cellulases (and eukaryotic secretory proteins in general) using recombinant expression technology. Recently our collaborators at Cornell University reported that the catalytic domain of a tomato cellulase and the carbohydrate-binding module from the same enzyme could be independently produced by recombinant expression in yeast and bacteria, respectively (Urbanowicz et al., 2007, J. Biol. Chem. 282:12066).

TECHNICAL PROGRESS AND RESULTS:

In FY 2010 we evaluated recombinant expression of 6 glycoside hydrolases from the model plant *Arabidopsis thaliana*. These particular proteins were chosen based on results of an initial homology modeling survey, performed in collaboration with Dr. S. Swaminathan (BNL), to identify proteins that will likely differ substantially in structure from prototypic microbial enzymes of known structure. Analysis of the amino acid sequences of these proteins indicated that they (*i*) have N-terminal signal peptides and thus are secreted from plant cells; (*ii*) have sites for post-translational glycosylation; and (*iii*) have separate structural domains for catalytic and carbohydrate-binding functions. None of these 6 proteins could be produced with both domains intact in either the *Escherichia coli* cytoplasm or in the secretory pathway of the yeast *Pichia pastoris*. We therefore tested the "divide-and-conquer" strategy as described by the Cornell group for independent expression of the catalytic and carbohydrate-binding domains of the tomato cellulase. Preliminary results suggest this approach will be at least partially successful. One of 2 cellulase catalytic domains tested was successfully produced in *P. pastoris* (Fig. 1A), although the catalytic function of this expressed domain has not yet been determined. In addition, the carbohydrate-binding module (CBM) of a hemicellulose hydrolase was successfully produced in *E. coli* (Fig. 1B), and crystals of this protein, grown in collaboration with Dr. Swaminathan's group, diffracted to about 4 Å resolution. The study is ongoing and production of several proteins is still being evaluated.

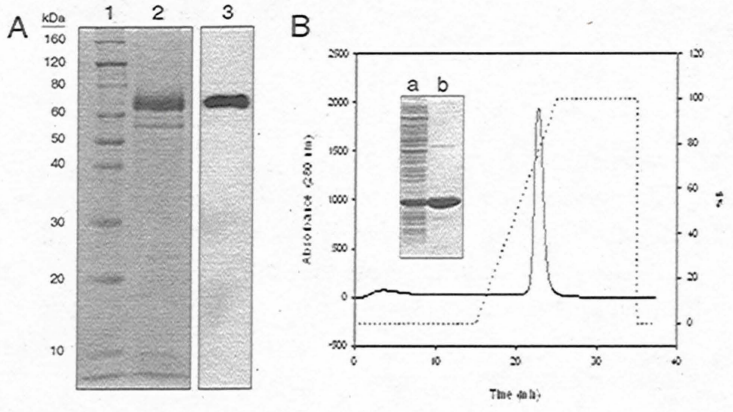


Fig. 1: Recombinant expression and purification of glycoside hydrolase domains. A, SDS-PAGE analysis of cellulase catalytic domain (Strep-tagged) after purification (left panel, lane 2, coomassie blue-stained gel) or in raw culture supernatant (right panel, lane 3, western blot). B, elution profile of CBM from ion exchange column. Inset, SDS-PAGE analysis of CBM protein before and after purification (lanes a and b, respectively).

Milestones for FY 2011 and FY 2012: (a) complete evaluation of recombinant expression of the initial test set of 6 proteins; (b) scale-up production of successfully-expressed proteins for biochemical characterization and where possible, for structural characterization; (c) perform biochemical and structural characterizations; (d) conduct protein engineering experiments (construct chimeric proteins) to study the basis for differential success in the production of closely related proteins (e.g. the 2 cellulase catalytic domains described above), with the long-term goal of developing an approach for uniformly-successful recombinant protein expression; (e) investigate lab-scale (table-top) fermentative growth as an approach to increase yields of proteins made in yeast, where it is often not feasible to produce amounts of proteins needed for structural characterization using standard shake-flask culturing methods. For example, the cellulase catalytic domain described above accumulates to about 0.2 mg / L in shake-flask cultures. Fermentative growth typically increases production yields by a factor of 10 or more relative to shake-flask cultures. The cell wall proteome contains many proteins similar to this one whose structural characterization will depend on advanced technologies such as recombinant protein expression in eukaryotic host cells and fermentative growth.