Laboratory Directed Research and Development Annual Report

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Pacific Northwest National Laboratory
Richland, Washington 99352
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Laboratory Director’s Message

The mission of Pacific Northwest National Laboratory is to transform the world through courageous discovery and innovation. Every day, scientists and engineers at PNNL set out to fulfill the promise of that mission by advancing scientific discovery and delivering critical solutions to the challenges that face our nation and the world. The science and technology that we work with, create, and improve upon inspires and enables the world to live prosperously, safely, and securely. Our investments in Laboratory Directed Research and Development are essential to our ability to advance our strategy and realize this mission. LDRD investments help us to nurture science and technology capabilities while capitalizing on the breadth and depth of talent that our staff members possess.

This LDRD annual report presents summaries of the results of our LDRD investments and describes how we conduct our LDRD program in compliance with DOE objectives and guidelines. These summaries highlight principal investigators and teams of scientists who are pursuing multidisciplinary approaches in their research and showcase how collective innovations are broadly applied across PNNL’s research portfolio.

With great pride in our researchers’ accomplishments, I present PNNL’s Fiscal Year 2014 Laboratory Directed Research and Development Annual Report.

Michael Kluse
Director, PNNL
Advanced Sensors and Instrumentation
Advanced Switching Concepts Applied to a Structure for Lossless Ion Manipulations (SLIM)

Richard D. Smith

This project sought to develop and initially demonstrate an advanced ion switching concept to a structure for a lossless ion manipulations (SLIM) device.

The role of mass spectrometry and other instrumental approaches based on ion measurements are continuously expanding in many fields of science. New opportunities to impact these fields significantly are becoming limited by conventional approaches currently used for ion manipulations, particularly the expensive fabrication and highly “lossy” nature. Possible applications include use in conjunction with massively parallel mass spectrometry analyzers, a development that would provide orders of magnitude gains in ‘omics applications. As ion manipulations become more sophisticated, conventional instrument designs and ionoptical approaches become increasingly impractical, expensive, and inefficient. The primary objective of this project was to simulate and test a switching concept in SLIM device. The switch is a cornerstone in the development of the SLIM device and would enable complex ion manipulation.

Specific Aim 1: Model ion motion inside the SLIM device and develop a realistic ion motion model to describe ions behavior. Simulations addressed ion motion in a circular path to determine optimum operating parameters. In addition, ion simulations modeled the advanced switching mechanism within the SLIM device and out-of-plane ejection of ions. Ion simulation aided in predicting the optimum resolution of separation while performing switching.

Ion simulation software SIMION 8.0 was used to calculate ion trajectories through the different switch configurations. A switch configured according to SLIM design concept was constructed in SIMION. Applying appropriate RF and DC potentials, field gradients can be applied that can switch ions into an orthogonal board from its initial location. The key challenges for optimum switch performance are the timing needed to switch the ions into the next section, which is dependent on the mobility of the ions and achieving the switching with as minimum (or no) loss of time resolution as possible. At the operating pressure of 4 torr, ions of standard mobility values (~1 cm²/V.s) need a voltage bias of 100V applied for at least >50 μs to the switching guard electrode. If the voltage is lower or switch time is shorter, the ions do not see the switching gradient, and switching efficiency is not 100%.

Once the ions switch into the orthogonal SLIM board, the critical question can be raised: what is the loss of resolution (potentially due to racetrack effect) while ions execute a turn? Ions at different positions in an ion packet executing a turn travel different path lengths (commonly known as the racetrack effect). This leads to loss of time resolving power; i.e., the ion packet becomes more diffuse in time after the turn. This loss must be minimized while ions execute turns if a complex device like ion cyclotron with multiple switches and turns has to be effective in high resolution separation or other complex ion manipulations. To achieve best switch design different configurations of the switch were evaluated for performance. The time resolution in a T-section while ions travel in the straight path was calculated at 13, which serves as a baseline. When ions execute the switch and turn, the resolution was calculated at 12. This slight loss of resolution is due to the ions executing a wide turn. By increasing field penetration into the straight section from the fields in the orthogonal T portion, there is potential for making ions execute sharper turns and avoid loss of resolution. A second design was evaluated on which the length of the switch trace was increased that allow ions to feel the switch gradient and thus make sharper turn. A third design with orthogonal electrode inserted inside the straight portion can also provide better field penetration. SIMION simulations help us see the relative benefits and caveats in each of these concepts.

The resolution with a long switching electrode was calculated as 13. The improvement in resolution is marked. However, there is increase in ion loss during switch. This was presumably due to the fact that there are several adjacent electrodes with same RF phase due to the orthogonal positioning of the switch electrode. This led to a drop in the pseudo potential well confining the ions. Increasing the length of the switch electrode was detrimental due to more poor pseudo-potential field through the relative field strength of DC focusing is higher resulting in better resolution. This loss in signal becomes more predominant when an insert electrode is added to further achieve field penetration as tested in the third design. This increased loss led to loss of resolution, even
though hypothetically an increase in resolution is anticipated.

**Specific Aim 2:** Fabricate and test a SLIM device with advanced switching. The SLIM device with advanced switching was fabricated and evaluated for performance. Schematic diagram of the experimental setup is shown. The switch performance was evaluated with a sample perfluoro compounds that produce singly-charged ions. Panel A in the accompanying image show the IMS-TOF 2D spectrum of all ions transmitted without any switching, while Panels B, C, and D show the SLIM switch successfully transmitting ions of specific mobilities. These results indicate that the SLIM switch is working as predicted by ion simulation.

The capabilities to perform these manipulations in a lossless fashion was not currently possible in any existing instrumental platforms that would allow exceedingly smaller mass spectrometry instruments and other devices to be built with the ability to perform multiple types of ion manipulations such as ion mobility, trapping, and transport. In addition to these abilities, this project developed new tools and techniques for advanced ion manipulations inside the SLIM device, creating the basis for constructing highly complex circuits of integrated ion manipulations. The results from this work were accepted for publication in the *Journal of Analytical Chemistry*.
The effectiveness of conventional measurement techniques for environmental monitoring is limited by background and other interferences. This project will develop and demonstrate a new concept in radiation detection that disentangles these interferences and reduces background to improve our ability to assay environmental samples dramatically.

Examples abound of how actinides have been used in environmentally related studies. By measuring the ratio of $^{240}\text{Pu}$ to $^{239}\text{Pu}$ for example, one can determine whether a source is consistent with local or global fallout. Transuranics are strongly associated with particulates in water so that they can be used to study scavenging, the removal from water by attaching to particulates. The activity of plutonium as a function of depth beneath the sea floor surface has been used to measure bioturbatory processes that mix the surface into the rest of the sea floor. Likewise, other elements have been used to date fossil corals or carbonate rocks and study seasonal variations in river and sediment flow. While the effort required to complete sample preparations is not particularly arduous, there are many studies in which thousands of samples are collected, as some environmental science questions require easily scalable measurement techniques. Thus, minimizing sample preparation is an important aspect of the overall environmental monitoring effort.

Any alpha-decaying radioisotopes have significant interferences when using current alpha-spectroscopy capabilities. By measuring other signatures that are generated in coincidence with the alpha particle, one can increase the probability of removing interferences between different radioisotopes. A good example of an isotope that may benefit from this approach is $^{238}\text{Pu}$, which is not typically measured with mass spectroscopy techniques because of interferences with much larger quantities of $^{238}\text{U}$. It also cannot be measured using alpha-spectroscopy without chemical separations because of interferences with alphas from $^{241}\text{Am}$. A system able to measure particles in coincidence with alphas from $^{238}\text{Pu}$ may eliminate the need for chemical separation and enable large-scale assaying of such samples.

Thus, the desired outcome is to develop a radiometric assay system for alpha-decaying radioisotopes that focuses on coincidence signatures to increase specificity of the system.

To assay actinides in environmental samples simultaneously and rapidly, we are developing a detector design that is capable of observing coincidences between conversion electrons and alpha particles to assay on complex samples. The first year of the project was an initial scoping study to evaluate the type of detection methods that could be utilized. In the second year, a more thorough examination of the impact of the sample, both in terms of preparation and background contributions, was completed. In addition, initial empirical measurements were conducted. For the third year, a demonstration of the detection concept on a prototype detector using an application-relevant sample will be completed. The overall objective of this project is to demonstrate a new detection modality that could significantly enhance radiometric assay capabilities for a variety of applications requiring assay of actinides in complex samples. This new approach has the potential to reduce assay time significantly, provide new sample diagnostic capability, and be a fieldable technology.

In FY 2013, we completed an initial scoping study to understand various aspects of designing the detector system. These aspects included an improved understanding of the signatures, an understanding of the substrate impact that holds the sample, and a comparison of two basic detector approaches: dual-gas proportional counters and double silicon-based detectors. The most important finding was that in the absence of background, the approach achieved reasonable measurement uncertainties in a few hours for relevant samples. In FY 2014, we evaluated the feasibility of the measurement approach for realistic samples while addressing issues such as intense backgrounds and absorptive materials. In addition, the project team gained significant experience with experimental techniques using different detectors. This experience enabled the development of a prototype measurement system.

During FY 2015, we will be conducting demonstration measurements relevant to the targeted post-detonation nuclear forensics and in-field environmental sample screening for safeguards applications.
We are developing a highly sensitive stable isotope measurement platform using capillary absorption spectroscopy. This technological development should enable advanced research in such diverse fields as microbial nutrient cycling, forensics investigations, and ecological studies.

Recent work with laser-based sampling methods demonstrated the effectiveness of laser ablation for spatially focused sampling over a solid surface without altering resultant isotope ratios. This work, however, used an isotope ratio mass spectrometer (IRMS) as a measurement platform. While it is the workhorse of stable isotope analysis, the technology has limited measurement sensitivity, translating to the need for larger sample sizes and therefore requiring harvesting at relatively large sample surfaces (~25 µm or above) for accurate measurement. This constraint limits both the spatial resolution of the method and ultimately the types of applications that can benefit from this approach (for instance, microbial interactions can occur on the sub-µm scale).

This project seeks to couple emerging laser-enabled surface sampling techniques with isotope analysis technologies to create a cutting-edge capability for making spatially resolved carbon (13C), oxygen (18O), and sulfur (34S) stable isotope measurements. Historically, analysis of these stable isotopes has been used for applications as varied as understanding nutrient cycling through microbial systems, forensic investigations, hydrologic investigations, a variety of ecological studies, and many others. Despite the clear utility of stable isotope measurements, there currently remains a capability gap in making rapid, spatially directed stable isotope measurements on solid samples. Combining laser ablation with a spectroscopy-based measurement, we seek to enable spatially specific isotope measurement (in both natural abundance and labeled studies) at scales not previously feasible, thereby enabling a suite of potential stable isotope applications.

The finished capability that we are constructing will contain three main components: a UV laser ablation system for selective spatial harvesting of a solid surface, a thermal unit for converting ablated particulates to gas form for isotope analysis, and a capillary absorption spectroscopy (CAS) system for performing isotope measurement. In the first year of this project, we focused on development of the CAS system because this is the only component not commercially available. The second year will target combining the CAS with ablation and conversion systems to construct a complete system to be tested on suitable samples.

Thermal conversion of ablated particulates will provide CO2, CO, and SO2 gas used for carbon, oxygen, and sulfur isotope analysis, respectively. The CAS system uses a tunable IR light source to measure absorption bands correlating to different isotopes in each of these analyte gases. To date, our team has searched available HITRAN databases related to these analytes and identified key absorption regions that show high signal response, close energy proximity of absorption bands relating to each of the required isotopes, and exclude potential contaminant absorption (i.e., from water or air contaminants). Suitable previous data did not exist for measuring the 33S isotope, so we synthesized 33SO2 and analyzed the absorption spectra that we hope to incorporate into future revisions of the database.

We are testing different IR lasers for their ability to reach the selected absorption bands, and preliminary data for the CO2 and SO2 analytes indicate a suitable working range. We are currently evaluating the pressure ranges over which analytes can be accurately measured and, ultimately, the sensitivity of the approach. In parallel, we are developing software to accurately collect, process, and collate thousands of laser scans (generated on the order of seconds) over the absorption region and report a data summary. To date, this software is functioning and being optimized. Finally, we are exploring the optimal coupling to minimize sample loses when introducing a sample into the CAS system for isotope analysis. In total, we have performed the preliminary steps toward CAS development to enable our planned coupling to laser ablation sample selection.

The basic components of the LA-CAS system include a UV laser ablation system for sample harvesting, a thermal conversion unit to produce simple gases for analysis, and an IR spectroscopy system for isotope analysis.
Controlled Datasets to Inform the Study of Sensor Degradation for CBRNE Signature

Marvin G. Warner

We are examining sensor degradation and drift of signatures arising from physical sensor measurements under a specific set of operational conditions. This streamlined, formalized process may be broadly applicable across many application domains and will impact our ability to determine the operational reliability of a given platform and the signature it measures.

Measurements taken by a physical sensor are a composite of features derived from the target phenomenon, operating environment, and sensor itself. Signature detection entails interpretation of the measurement data and requires a fundamental understanding of how each of these impacts the observed measurements. This project is using a statistical design to avoid the explosion of experiments that arises from a full factorial exploration of a large number of variables. To that end, we are parameterizing possible environmental and sensor effects on measurements and plugging them in to a variety of design models prior to performing the laboratory experiments. The combination of subject matter expert-driven input, statistical design, and focused laboratory experimentation allows us to assess the relative impact each parameter has on observed measurement data and determine how an understanding of measurement effects can be used to improve signature detection and decision-making capabilities.

To accomplish this goal, a suite of different measurement systems representing fundamental classes of physical measurement (e.g., mass loading, electro-optical, electrochemical) are used to examine how the relative impact of different parameters remains the same (generalizable) or differs across sensor classes.

In the second year of this project, we focused the bulk of our efforts on investigating the use of statistically designed experiments to optimize the detection of RDX using atmospheric flow-tube mass spectrometry (AFT-MS), which was published in the journal Analyst. AFT-MS is an ambient mass spectrometry method that allows for the detection of explosives and other relatively low volatility chemicals with little or no sample preparation. AFT-MS has been demonstrated to detect low concentrations of explosive vapors at the parts-per-trillion level and below. We used statistical experimental design to probe the effects of various environmental and instrument parameters on the observable RDX detection limit.

For work done in FY 2014, an initial set of experiments was designed to study gas flow rate effects (1–4 L min⁻¹), desorption current (0.25–1 A), solvent evaporation time (2–16 min), and quantity of RDX (0.1–50 pg) on measured RDX peak height. Because little was known initially about how and how much experimental factors affected measured RDX peak height, a first block of 40 experiments was designed to help establish the effect on the response of all four main factors, determine which if any 2-factor interactions was statistically significant, and to test for possible curvature (higher-order polynomial effects) in any of the experimental factors. Results from the first block of experiments indicated that solvent evaporation time did not significantly affect measured peak height (at the 95% confidence level) and therefore this factor was maintained at 2 min. Once we determined the degree of curvature and 2-factor interactions, a second set of 26 experiments was constructed to allow us to fit a fairly complex predictive model. This model was then used to help interpret a real-world problem, the determination of the levels of RDX inside of a cargo-shipping container, by fitting data obtained from air sampling followed by AFT-MS analysis.

Models created using results from the experiments allowed us to identify the factors affecting measured RDX peak height and were used to predict conditions for optimal signal detection. Those conditions were employed to obtain data for a calibration model. Air samples collected within a shipping container that housed explosive magazines were analyzed and, using results from the calibration model, RDX concentrations within the container were determined to be in the range of 1 to 50 ppqv. This method not only establishes the ability to quantitate vapors within a container but also demonstrates the ability to detect these vapors with less than 5 min of sampling time.

A shipping container used to collect air samples containing RDX vapor.
Creating a Gas Phase Chemistry Workbench by Performing Manipulations in Efficient Ion Traps

Erin S. Baker

This project will demonstrate the feasibility of a gas phase chemistry workbench for performing lossless, highly efficient chemical reaction studies.

While sweeping advances in nucleic acid-based technologies continue to revolutionize biological research, the understanding of molecular-level processes is still limited. Proteomics, lipidomics, metabolomics, and other mass spectrometry (MS)-based ‘omic approaches can facilitate such understandings that are unobtainable from genomics. However, their collective impacts have remained relatively small despite recent advances in technical issues related to measurement reproducibility, sensitivity, throughput, and cost. Thus, additional technology developments are essential to understand these molecular-level processes. Because the genomics revolution was catalyzed by “next generation” nucleic acid-based technologies that drastically decreased cost and increased genome sequencing throughput, a new technology is necessary to catalyze ‘omic approaches.

The objective of this project is to develop new abilities for studying molecular-level interactions based on extremely high speed and lossless gas phase ion manipulations. These manipulations will be conducted in readily fabricated and modularized printed circuit board (PCB) devices, which will create a gas phase chemistry workbench.

Specific Aim 1: Develop a gas phase chemistry workbench utilizing readily fabricated devices for the characterization of ion/molecule reactions. During the first 6 months of this project, our goal was to evaluate ion/molecule reactions in the gas phase by creating a segmented quadrupole with PCBs. The novel PCB segmented quadrupole would transmit and fragment ions, allowing the efficiencies of both functions to be analyzed. Initially, the ion simulation software SIMION 8.0 was used to calculate ion trajectories and determine if any losses would occur when different configurations of the PCB quadrupole were utilized. Several voltage and frequency optimization steps were performed on each configuration, and eventually a design was found that had lossless ion transfer through the quadrupole. These simulation results were used to guide the electronic circuitry design for the PCB quadrupole in Eagle software and the plans for board fabrication and population of resistors and capacitors were sent for construction.

To perform the ion/molecule reactions, the fabricated PCB segmented quadrupole was mounted in the chamber of an existing ion mobility (IMS)-MS instrument, replacing the rod-based segmented quadrupole that coupled the IMS and MS regions. Using an existing instrument allowed for reduced machining costs, as only mounting brackets had to be constructed and also added more functionality to the instrument such as the ability to perform higher pressure collision induced dissociation (CID), which was not possible with the rod-based quadrupole. Once mounted in the chamber, the PCB segmented quadrupole showed good transmission for ions of a wide m/z range, similar to the transmission of the rod-based quadrupole. This indicated that no biases were occurring due to the PCBs and showed promising results for further implementations of PCBs for other instrumental components.

CID ion/molecule reactions were then studied with the PCB segmented quadrupole by increasing the voltage gradient at either the center of the PCB between two small lens elements or at the end of the PCB between a small lens and a larger lens. Both locations were able to fragment ions with efficiencies around 50%. However, it was found that higher fragmentation efficiency was possible between the small and larger elements at the end of the PCB, leading to knowledge about the optimum lens design for fragmentation.

The pressure around the PCB segmented quadrupole was also analyzed to understand if it had an effect on the optimum fragmentation efficiency. The quadrupole chamber
was separated from the other vacuum stages with conductance limiting orifices and pumped independently, allowing for systematic experiments as a function of pressure. The pressure was varied from 10 to 500 mTorr, and good fragmentation efficiency was observed for all pressures, which is not the case with the rod-based segmented quadrupole that operates better at lower pressures. Thus, the PCB segmented quadrupole allows new opportunities for fragmentation at higher pressures enabling new device configurations. Currently, further pressure and voltage optimizations are taking place to find the best operating conditions and lens arrangement for the PCB segmented quadrupole.

**Specific Aim 2**: Develop the ability to perform ion/ion reactions in the workbench. To address Aim 2, efforts are currently underway to conceptualize the initial ion/ion reaction chamber and components. Simulations of the proposed components will be performed early in FY 2015. Once good transmission is observed and optimized, we will use the simulations to guide our fabrication of the PCB components and machine the ion/ion reaction vacuum chamber. We estimate that we will be performing ion/ion reactions such as functional group-specific derivatization reactions by mid-year, and we anticipate completing Aim 2 during FY 2015.

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*a)* Parent and *b)* fragmentation spectra for leucine enkephalin, showing good fragmentation efficiency.
Development of an Ultra-Small Volume Detection and Sample Delivery System for Exploring Microscale Heterogeneity with NMR

Karl T. Mueller

We are developing methods and instrumentation that will ultimately integrate high-resolution NMR spectroscopy with lab-on-a-chip technology for studying samples with volumes in tens to hundreds of pL.

Microscale heterogeneity plays a key role in determining the outcome of attempts to decrease pollution, optimize industrial production, or understand cellular-level processes. Because of the unique capability of nuclear magnetic resonance (NMR) to characterize biological and chemical systems in detail without significantly perturbing them, we seek to extend the reach of NMR spectroscopy to routine analysis of microscopic samples. To this end, we are developing methods and instrumentation that enable high-resolution NMR spectroscopy as a tool for studying microscale heterogeneity. The current generation of commercial small-volume NMR detectors requires sample volumes of 5–10 μL, and we intend to show that high-resolution NMR can be used for practical studies of volumes that are several orders of magnitude smaller, allowing for novel studies that address individual microsystems such as cells and aerosol particles.

A key component of our experimental strategy is to improve sensitivity by decreasing the distance between the sample and the detector. In general, the sensitivity of inductive detection varies inversely with the distance to the detector. For the high-resolution probes described in the literature, the characteristic distance between the sample and the detection coil is ~0.25 mm or more. For our probe, samples can be placed within a few μm of the planar detector by preparing the sample in a thin-walled capillary or microfabricated chip.

Specifically, our developed NMR probe integrates a sensitive planar detector with a versatile microfluidic platform for sample delivery, and we intend to demonstrate that this probe can be used for a wide range of applications. Together with a microfluidic platform for sample delivery, a prototype probe has been built and tested. The preliminary tests have demonstrated that customized pulse sequences can eliminate the line broadening that has for decades impeded attempts to miniaturize high-resolution NMR. These tests suggest that NMR spectroscopy could be used routinely in a size regime that has previously been inaccessible.

To realize the sensitivity gains associated with the close approach to the detector, optimization of the probe circuit and the detector was needed. In FY 2014, we performed the necessary optimizations. Characterization of the probe circuit showed that most extraneous noise has been eliminated: the noise has been reduced to a level near the intrinsic thermal noise of the detector. Simulations and circuit analysis led to design changes that insure the detector is grounded, as needed for optimal sensitivity. The signal-to-noise ratio also depends on the efficiency with which nuclear spins can be manipulated. For efficient manipulation of spins, the radio-frequency magnetic field generated by the detector must be as homogeneous as possible. The field homogeneity was optimized by polishing the planar detector to eliminate rounding and by matching the dimensions of the detector to the dimensions of the capillary that contains the sample.

For the initial tests of our probe, we prepared aqueous samples manually in a thin-walled capillary sealed at each end with wax. Replacing this wax with an elastomer chip at each end of the capillary yields a versatile microfluidic platform for sample preparation and delivery. A simplified prototype has been tested successfully for flow properties and sample immobilization.

For FY 2015, we will develop a detailed design for a two-channel transmission-line probe as well as fabricate and test both single-channel prototype and two-channel transmission-line probes. Alternative pulse sequences will be investigated for use with the transmission-line probe. Should our investigations yield constraints for small-volume NMR, we will explore alternative pulse sequences for this method and proceed with demonstrating the technology in key applications.
Enterprise Deployment of Hone at PNNL

Glenn A. Fink

**Hone is a host-based cyber security tool that correlates packets to processes accurately, a fundamental gap in Internet protocol design. It enables powerful insight for cyber defenders and makes both cyber security and operational analysis more accurate at a lower cost.**

When cyber analysts investigate a potentially compromised computer, they spend much time comparing their network sensor output to the actual effects on a target machine and deciding whether the system is actually infected. Hone makes it possible to determine the accurate process responsible for each communication, a key aspect of this investigation. Experts estimated that fielding Hone fully would garner a 20% cost savings in analysis costs (about $10,000/month in 2013 dollars), increase the accuracy of findings, and would locate 10% more of the infections (i.e., false negatives) that currently go undetected in the enterprise. Equally important, scarce security resources would be freed to examine more unusual events, and the exposure of the enterprise to compromise would be reduced. With Hone, analysts would do more intelligence work rather than constantly reacting to the latest threat.

Many other technologies, such as DARPA’s PAINT, NNSA’s WLS, Microsoft NetMon, and others attempted to perform functions similar to Hone. However, these technologies do not attribute traffic at a per-packet level, are not as accurate, and are easy to subvert. More poignantly, many work only for limited applications. This project’s aim was to prototype and demonstrate key commercial features of Hone for cyber security. Three major objectives were anticipated: demonstrate to potential commercialization partners that Hone enables a “killer app” that stops exfiltration of data via malware; minimally reduce to practice key features used to garner intellectual property and increase the commercial value of Hone; and publish an academic paper on Hone to document its critical features.

Our project produced a high quality Hone sensor for Windows and Linux, and we fielded it on over 200 operational systems. We navigated the difficult process of operational software deployment and experienced few problems in fielding. Data from Hone sensors were gathered and examined by operational security personnel at PNNL. Our work showed that Hone could be fielded successfully, but better logging systems were needed and more compact, flexible delivery of data to the central analysis effort was required.

Hone sensors produced the highest quality packet-process correlation data available in the government or industry, and its accuracy and speed of collection was unparalleled. The market shifted, however, and within a few months, there were many other tools available that could do limited forms of packet-process correlation. Unfortunately, cyber analysts and security folks determined that their existing tools were adequate for their needs, especially with being already integrated into existing frameworks. We decided that it was unwise to continue fielding Hone because new market pressures made differentiating Hone too difficult and weakened its value proposition.

To enhance the state-of-the-art and benefit researchers everywhere, we released Hone’s high-quality code in open source under a three-clause, BSD-style license (https://github.com/HoneProject). We hope that Hone’s code will help improve cyber security work that others do. We gained valuable experience in fielding PNNL cyber research tools to the operational side, which will help streamline future efforts to transition government cyber research to practice.
EUV Laser Ionization Mass Spectroscopy

Andrew M. Duffin

The objective of this project is to collaborate with the laser developers to research the application of state-of-the-art extreme ultraviolet (EUV) lasers for rapid actinide analysis.

The recent development of reliable, tabletop EUV lasers has enabled performing laser ablation mass spectroscopy at the nm spatial scale (two orders of magnitude improvement over current UV/Vis systems). EUV light also moves the ablation into a linear absorption regime that could solve many of the technical challenges presented by the necessity of multiphoton absorption required by traditional laser ablation sampling. In addition, traditional fs-laser ablation coupled to multi-collector inductively coupled mass spectroscopy (fs-LA-MC-ICPMS) has proven an effective analytical tool. We are able to develop fs-LA-MC-ICPMS into a robust method for rapid actinide analysis; unfortunately, however, traditional laser ablation can result in unruly transient signals that wreak havoc on analytical measurements. The cause of these unruly transients is thought to be related to the laser wavelength and laser spot size in relation to the size of the ablation target.

EUV laser light can be focused down to approximately 100 nm spots, a roughly two orders of magnitude improvement over the fs-laser ablation system at PNNL. In addition, each EUV photon is sufficiently energetic to ionize any material. These features give EUV light great potential to dramatically improve the state-of-the-art in laser ablation coupled to mass spectroscopy. Development of tabletop EUV lasers mainly comes from the National Science Foundation (NSF) Engineering Research Center for Extreme Ultraviolet Science and Technology in Fort Collins, CO, and this group has demonstrated the ability to couple EUV ablation to a mass spectrometer.

This project received funding at the very end of FY 2014. This initial funding was used to meet with our collaborators at the NSF Research Center. The goals of this meeting were to align the expectations of the two research groups, develop a research plan, coordinate schedules for future experiments, and familiarize ourselves with EUV laser operation. As a result of this meeting, we identified a few key samples and pieces of equipment for purchase. We also agreed to a schedule for conducting experiments. These accomplishments make us positioned well to start meaningful work during FY 2015.
Free Form Millimeter-Wave Imaging

David M. Sheen

This project develops novel millimeter (mm)-wave imaging techniques that couple optical camera-based motion capture with linear mm-wave arrays to enable flexible new three-dimensional (3D) imaging modalities that will provide enhanced performance.

Microwaves and mm-waves can pass through many optically opaque materials. This property is the fundamental basis for developing imaging systems for concealed weapon detection, in-wall imaging, ground penetrating radar, non-destructive evaluation of materials, and other security applications. A variety of novel imaging techniques have been developed at PNNL, all of which require precise scanning of a radar transceiver or array over uniformly sampled planar or cylindrical apertures. These techniques are seriously limited in their performance and range of applicability by the need for precise regular scanning over the aperture. Freeform imaging seeks to eliminate the requirement for standard aperture shapes and instead use the motion of freely moving targets (or a freely moving linear array) to effectively sweep out a two-dimensional (2D) irregular aperture. This new scanning freedom will allow for new applications such as scanning for weapons using a small mm-wave hand wand, scanning people as they walk freely past fixed linear arrays, and scanning walls using multiple overlapping manual scans. Realizing the vision of freeform mm-wave imaging requires low-cost optical camera-based techniques to capture precisely the complex motion of the target or moving transceiver array and computational techniques to form focused 3D mm-wave images from data collected during the scanning.

This year, a large number of 2D (range by cross-range) and fully 3D imaging experiments were conducted. These experiments were of two fundamental types, moving target and moving transceiver, both of which use a precise optical motion capture system to measure and track 3D positions and orientations of both the transceiver and target over time. Results from all of this work demonstrated conclusively that diffraction limited imaging is possible for these freeform scanning configurations if accurate motion capture of both the target and array is obtained.

Research conducted in FY 2014 focused on developing freeform image techniques using synthesized and experimental data; acquiring and implementing a camera-based motion capture system; and experimenting with freeform imaging using the motion capture system coupled to a single channel transceiver for 2D imaging and a linear array for full 3D imaging. Prior to experimentation, custom numerical modeling was performed to assist in developing image reconstruction algorithms and to guide our work. This numerical modeling performed end-to-end simulations of both the moving target and the moving radar transceiver freeform imaging configurations.

Our major focus in FY 2015 will shift to developing the optical motion capture technology. Experiments conducted in FY 2014 demonstrated that the mm-wave data were successfully focused into 2D or 3D images using freeform scanning.

Freeform 3D imaging result in which a flat metal F test target was manually rotated (photo inset) in front of a 2.4 m linear array to collect 3D mm-wave radar data. A single x-y slice of the focused image is shown in scaled 3D space in front of the effective aperture (blue). Note the non-uniform nature of the effective aperture.
We are developing a rapid, ultrasensitive, quantitative chemical analysis platform based on capillary electrophoresis (CE) coupled with electrospray ionization (ESI)-mass spectrometry (MS) using a novel microfluidic sample injector.

Rapid, quantitative and sensitive analyses are essential for advancing biological science and applications. We recently developed a novel injection mechanism for microchip CE, a powerful analytical separation technique widely used for proteomics, pharmaceutical, and biotechnology applications, that enables rapid, reproducible injections with no quantitative bias and allows variable sample volume compared with conventional electrokinetic injection. A pneumatic microvalve separates an analyte introduction channel from a separation channel at an intersection. The analyte introduction channel was pressurized such that when briefly opened, a small and volume-controllable sample plug is introduced to the separation channel. The high voltage was continuously applied across the separation channel, and analytes were rapidly separated. Polydimethylsiloxane (PDMS) was used as substrate material because its elastomeric properties were necessary for pneumatic valving. Unfortunately, PDMS has some undesirable surface properties (propensity to adsorb and absorb biomolecules and unstable surface charge) that limit separation efficiency. Also, difficulty in interfacing microchip electrophoresis with MS limited the proof-of-concept demonstration to fluorescence detection.

In the present work, we are leveraging the numerous advantages of the microfluidic injector but performing the electrophoretic separations within fused silica capillaries to achieve high resolution separations. The platform will have significant advantages over either fully capillary or fully microfluidic systems. Also, the platform creates new analytical possibilities, including the facile coupling of liquid chromatography with CE-MS for ultrahigh peak capacity multidimensional analyses; as such, our work is expected to spur significant additional opportunities for development and application.

During FY 2014, we achieved our aim of developing a robust platform having microvalve-based microfluidic sample injection for CE separation within fused silica capillaries. We also succeeded in implementing MS detection. A zero-dead volume interface was developed between the microchip and the capillary by patterning a capillary insertion channel into the microchip. The geometry of the insertion channel was such that the capillary lumen aligned accurately to the microchannel terminus. To avoid leaks at the microchip-capillary interface, PDMS could be cured around the inserted capillary. Alternatively, the capillary insertion channel on the microchip could be undersized, requiring the PDMS to be stretched around the capillary, which also effectively eliminated leaking and dead volume at the interface.

For detection, a sheathless CE-MS electrospray interface was adapted from previous work. The interface was chemically etched to impart some porosity to the electrospray source, providing electrical conductivity through the capillary wall while preventing bulk flow. Combined with the absence of electroosmotic flow in the coated fused silica capillaries, the sheathless interface necessitated a pressure driven flow through the separation capillary to provide flow for ESI-MS. This worked well, but the process degraded separation efficiency somewhat. To overcome this limitation, we subsequently implemented an electrokinetically driven sheath flow interface that provided both high sensitivity as well as improved separation efficiency. We now routinely achieve >50,000 theoretical plates for our <10 min analyses.

Using the assembled platform, we were able to demonstrate on-demand, high throughput, tunable and quantitative injection for CE-MS. We also identified the conditions and performed separations to demonstrate Hadamard transform CE-MS for improved sensitivity and expect to publish on this soon. Additionally, we discovered that analytes can be preconcentrated under certain conditions at the closed microfluidic microvalves on the devices by applying an electrical potential across them. For FY 2015, we aim to complete the characterization of the devices for Hadamard transform CE as well as for membrane-based preconcentration-CE. We will then pursue a platform for multidimensional separations.
Laser Ablation Capillary Absorption Spectrometer for Trace Isotopic Sampling and Imaging

M. Lizabeth Alexander

The goal of this project is to advance laser ablation-capillary absorption spectrometer (LA-CAS) system development to perform stable isotope measurements at a level of precision and accuracy required for detection and imaging in key DOE research areas such as biogeochemistry, atmospheric sciences, and genomic sciences.

Precise measurements of stable isotope ratios are well established as a valuable tool for basic areas of chemistry, biology and geology as well as forensics and medicine applications. The current workhorse for stable isotope measurements of lighter elements (hydrogen, carbon, nitrogen, and sulfur) is the isotope ratio mass spectrometer (IRMS) coupled with traditional analytical techniques for sample preparation and introduction such as a gas chromatograph, elemental analyzer (EA), or offline methods. In recent work, we reported the use of LA-IRMS as a method for spatially resolved isotope analysis of samples. These measurements showed precision and accuracy consistent with IRMS measurement but required a much smaller (~1000-fold) sample size than traditional EA-IRMS. Most recently, we used a prototype LA-CAS that combines previous LA-IRMS work and carbon isotope measurements by IR spectroscopy into a single instrument.

The development of the LA-CAS was motivated by the need to track nutrients in microbial communities at the scale of one to tens of organisms or near 1 µ in size. Carbon isotope measurements provide one method of tracking nutrients from sources with differing \(^{13}\)C/\(^{12}\)C ratios such as C3 vs. C4 plants. The amount of carbon in this small area is under a picomole (pmol), far below the detection limits of IRMS (5–10 nanomoles [nmol]) or current IRIS systems (100–200 nmol). Our results further demonstrate that there is no loss in sensitivity when coupling LA to the CAS in a flow-through system ideal for the imaging application intended for LA-CAS. Previous results of CAS with the gaseous CO\(_2\) standards system demonstrated molar detection of 100 pmol at levels of precision sufficient to distinguish isotope ratios from different nutrient sources without the need for expensive, time-consuming isotopic labeling. Further improvements lowered detection to 2 pmol, and improvements are underway that are expected to measure carbon isotopes at the 100–200 femtomolar level. Spatially resolved isotopic measurements on this scale can find a wide range of applications. For instance, this approach could be utilized for performing detailed tracking of labeled substrates through a stratified microbial mat, probing the stable isotopes of microfossils embedded in a rock matrix, assist in performing individual analysis of prokaryote and eukaryote communities such as in the rhizosphere or microbiome. A key advantage of this system over previous spatially resolved work is the improved sensitivity over an IRMS-based method. The enhanced sensitivity of the LA-CAS system over LA-IRMS will permit coupling to smaller sample spot sizes, thus enhancing the spatial clarity of such measurements and permitting probing of smaller systems.

Work in FY 2013 addressed thermal drift in real-time. Software development for rapid summing and peak integration were successfully completed with the exception of automating the cursor control for peak selection and the data storage process. The identification and purchase of an appropriate QC laser became necessary when the existing Alpes Lasair laser for CO\(_2\) was unstable. The frequency slew rate was nonlinear and not constant, resulting in large apparent shifts in frequency. This additionally resulted in a dependence of output power vs. frequency, which translated into a large slope in the baseline that dictated the use of 2f detection resulting in bipolar peak shapes.

In FY 2014, the original code was reengineered and repurposed to increase data collection efficiency and provide more flexibility and accuracy in peak integration methods. All signal allocation is on the data acquisition board and directed to fill on board buffer. The result is an improvement in data acquisition rate from 100 scans in 30 sec to 1250 scans in 7 sec at 24-bit data acquisition. This is significant progress in moving toward the goal of real-time isotopic imaging. The use of real-time Python software for peak integration not only allows for faster data acquisition but also allows for more sophisticated signal processing, potentially including the use of Fourier Transform methods previously patented by PNNL for baseline suppression and noise reduction. This leads to a system that has higher sensitivity and is more robust.

Additionally, we are pursuing the use of a tapered fiber hollow waveguide to maximize the following properties:

- allows more light to be introduced into the optical waveguide while reducing volume and sample size 0.1 cc vs. 0.5 cc
- higher laser power yielding above shot noise limit and higher sensitivity
- more robust for routine use
• improvement using FT filtering (though noise was not eliminated as well by thermal roiling)
• improvement in a sensitivity factor of 10, allowing sub-picomolar detection.

The one disadvantage was the increase of noise at higher laser frequencies, but this can be suppressed by using FT filtering in the rapid post processing software and demonstrates the increase in noise at higher frequencies. Though not yet implemented, FT filtering would reduce this noise significantly, resulting in sub-pmol detection limits.

Another unforeseen issue was that with the previous design for a cryotrap and the introduction of CO₂ into the tapered fiber. There was too much dead volume to allow the rapid cycling needed for isotopic imaging with high sample throughput. The figure shows a solution that has been proven feasible but still needs work for implementation. The laser ablation instrument is used to drill a number of small holes in the side of the tapered fiber waveguide. It was found that this did not adversely affect the optical properties. The larger sample introduction capillary can then be butted up against the area with holes drilled. An existing problem is how to shape and seal this junction. Upstream of the junction, a rapid-cycling cryotrap shown schematically will alternately trap and then desorb CO₂, resulting from the ablation of specific sample locations and allowing the precise determination of the isotopic ratio to be mapped over the sample.
The objective of the proposed work is to design, construct, and demonstrate a segmented active photo-diode array (SAPDA) integrated circuit that targets high energy resolution.

A broad gap in capability exists in light imagers. Available commercial pixelated imagers are inadequate to the task of measuring the temporal structure of individual nanoscale scintillation, fluorescence, and luminescence light pulses. Measuring the temporal structure of these light pulses in real time allows for the identification of the nuclear and chemical conditions present in a sample and may enable a quantum leap in computer data storage that cross-cuts electronics from smart phones to exascale supercomputers, an extremely impactful area of human technical endeavor. Continued advancement in these technical subjects is critical to maintaining state-of-the-art capabilities and driving successful commercialization.

The result of this project will address numerous limitations of photo multiplier tube (PMT)/scintillator based radiation spectrometers. SAPDA would enable the creation of new radiation detection systems designed to be low power, smaller form factor and ultra-low background. Additionally, the SAPDA is magnetic field insensitive, tolerant of operating temperatures higher than traditional PMTs and can economically tile a large area of scintillating material. This breakthrough in photon measurement eliminates the usual trade-offs between photon detection efficiency, dark false hit rate, and eliminates backgrounds created by PMT primordial materials. The SAPDA technology will dramatically enhance the measurement reach of scintillating detectors. Data gathered during experimental measurements will demonstrate the utility of the SAPDA and provide defensible results critical to securing external funding necessary to develop complete solutions.

The wave function of scintillation light from recently developed scintillators such as Cs₂LiYCl₆:Ce (CLYC) allows for the determination of detected sub-atomic particle type via small differences in the dynamic light energy decay vs. time. This behavior drives our attempts to establish new methods to measure these effects. We are demonstrating new methods of recording these very fast nanosecond time-scale temporal fluctuations in light intensity, which will require imager architectures beyond the conventional. Additionally, the wave function of laser-induced fluorescence decay is a sensitive function of physical conditions in a sample to be measured. Measurements such as temperature, activity and concentration of the hydronium ion (pH), and the quantity of fluorescent inorganic or organic molecules in a sample have been demonstrated. Imagers optimized for these measurements have recently been reported.

Thus far, we have invested our efforts in establishing a new computer-aided integrated circuit (IC) design flow, a new imager architecture, and a number of new circuit inventions. Each pixel in this imager array functions as a miniscule sampling oscilloscope, shrinking the volume of a lab bench measurement instrument to the micron scale. A number of commercial complementary-metal-oxide-semiconductor (CMOS) semiconductor wafer foundries and IC prototyping services were competitively reviewed. This project has enabled the first ever collaboration between PNNL and commercial wafer foundries for the manufacture of our full-custom application-specific ICs.

Upcoming work for FY 2015 includes the tape-out of the design to a selected foundry, the manufacture and packaging of the new imager IC, establishing a full custom test platform and test plans with the goal of demonstrating proper operation of the new imager in the laboratory. A scholarly article will be authored and submitted to peer-reviewed scientific journals for publication.
This project is developing a low background liquid scintillation counter (LBLSC) to maximize cosmic ray shielding. The system will be sensitive to $\beta$ and $\alpha$ emitting nuclides at concentration levels 10–100 times lower than available from commercially available instruments.

PNNL’s shallow underground laboratory is intended for measurement of low-concentration levels of radioactive isotopes in samples collected from the environment. The development of a low-background liquid scintillation counter is underway to augment further the measurement capabilities of this laboratory. As part of lab activities, liquid scintillation counting is especially useful for measuring charged particle (e.g., $\beta$, $\alpha$) emitting isotopes with no or weak $\gamma$-ray yields. The combination of high efficiency detection of charged particle emission in a liquid scintillation cocktail coupled with the low-background environment of an appropriately designed shield in a clean underground laboratory provides the opportunity for increased-sensitivity measurements of a range of isotopes, including tritium ($^3$H), strontium ($^{89,90}$Sr), or $\alpha$-emitters in naturally occurring uranium/thorium (U/Th) decay chains.

The objective of this project is to design, construct, and demonstrate a world-class LBLSC to be installed in the shallow underground laboratory at PNNL. Our results will add an important capability to fill an existing gap for the quantification of low-activity beta-emitting radionuclides. To benefit fully from the low background environment of the laboratory, custom high-radiopurity components and low-background shielding design are essential. Success in these areas likely leaves the scintillation photon detector as the single largest contributing source of primordial radioactive isotopes within the shield.

A breakthrough in photon detection related to the usual trade-off between photon detection efficiency and impact of primordial background sources would dramatically enhance the measurement impact of the system. As a result, two high-risk, high-reward research paths are being pursued. Demonstration measurements of two beta-emitting fission products will be completed, whose data will show the utility of the LBLSC and provide experimental results useful to the eventual development of an automated system, integrating it into existing radiochemical analysis programs and providing a capability for measurements that were previously infeasible. The LBLSC system developed will be directly applicable to the measurement of tritium and 14C.

Our FY 2014 work covered three areas: low background shield design, novel light collection methods, and simulations for background estimates. The low background design follows a standard principle of nested active and passive shielding. From outer to innermost, the shield is composed of a radon exclusion box, plastic scintillator panels for cosmic ray rejection, neutron absorbing 30% borated polyethylene, 8 in of progressively lower $^{210}$Pb concentration lead bricks to shield against external $\gamma$-rays, and a 2-in thick copper liner that serves as the scintillation light collection guide designed as a hollow, highly reflective channel milled within the liner. The reflective channels guide scintillation light from decays measured in the scintillation cocktail vial to photomultiplier tubes (PMTs) “around a corner” within shielding to guard against trace radioactivity in PMTs from contributing to the instrument background.

The nested shield was modeling in the GEANT radiation transport simulation software to evaluate the background contributions from various potential sources, including external $\gamma$-rays, $^{210}$Pb in the lead shield, U/Th in the copper liner and light reflective coating, and radioactive $\gamma$-ray emitters in the PMTs. These simulations show that the instrument may obtain a background rate of ~0.01 counts/min, in contrast to commercial systems that typically have ~1 count/min. The second year of the project will fabricate the instrument.
Miniaturization of Multi-Modal Regenerative Feedback Sensor

Mark Jones

This project developed and miniaturized a class of multi-modal sensing platforms based on regenerative feedback resonator circuits. The resulting technology could be deployed as unattended wireless sensors for national security.

Recently, material-loaded regenerative feedback resonator circuits under evaluation as radiation detectors were discovered to exhibit unique responses to other phenomena during characterization. The circuits were originally intended to sense transient changes in detector material electromagnetic properties induced by ionizing radiation. However, prototype configurations demonstrated surprising sensitivity to a variety of other stimuli, including acoustic pressure, human proximity and motion, visible light, electromagnetic fields, and temperature. Recognizing the potential for multi-signal detection, we began to explore the use of these circuits in the broader context of national security missions.

The simplest implementation of a circuit being investigated consists of a microwave amplifier with a material-loaded cavity resonator in the feedback path and a directional coupler to measure the resonant behavior of the loop system. Other components may include a phase shifter for precise frequency control and a band-pass filter to reject undesired resonant modes. The sensing mechanism is produced by interaction of the resonator with the external environment. The circuit is compatible for use with any two-port resonator element, and we utilized 3D and planar split-ring resonators as well as resonant patch antennas.

Regenerative feedback technique has been widely used to increase the sensitivity and frequency selectivity of radio receivers. These circuits are attractive because of their simple, low-cost topology and the ability to generate dynamic quality factors many orders of magnitude higher than those quality factors available from resonators used in a passive configuration. For example, we measured dynamic quality factors as large as 60 million for circuit prototypes.

The sensing circuit can be compact and designed to transmit wirelessly real-time frequency response to a receiver located a safe distance away from the deployed sensor.

Our first step was to perform a baseline evaluation to assess the response of early prototype sensors to acoustic, electromagnetic, and proximal inputs. For each modality, we identified relevant sensor characterization methods to collect the appropriate standardized data. After reviewing the results, we selected human proximity and electromagnetic emissions as the modalities for detailed research and design efforts. It is expected that investments in these sensing configurations can be readily leveraged for other modalities.

Using a combination of 3D finite element electromagnetic simulations and experimental investigations, we examined sensor phenomenology, including resonator modal behavior, dielectric material loading effects, and transduction mechanisms. Excellent agreement was obtained between simulated and measured characteristics of the various resonator configurations. Additionally, research revealed that the proximal sensor modality operates as a short-range radar review of active integrated antennas and self-mixing transceiver, where the resonator functions as a reciprocal antenna that transmits and receives propagating waves. Phase shifts corresponding to reflected signals from nearby objects are converted into excursions from the nominal carrier frequency. In addition to proximity sensing, direct detection of incident electromagnetic signals is enabled by the self-mixing operation of the amplifier as it is driven into its nonlinear regime. The received signals appear as frequency-modulated sidebands on the carrier frequency.

Miniaturized multi-signal sensor developed for use at 5.8 GHz. The integrated design includes a resonant patch antenna and feedback circuit on opposite sides of a multi-layer circuit board with overall dimensions of 50 mm × 50 mm × 2 mm.
The sensor form factor was reduced from bulky initial prototypes consisting of coaxial components to a small printed circuit board and resonant patch antenna operating near 2 GHz. This more compact design exhibited significantly improved performance for both proximity and electromagnetic inputs when tested using the characterization methods from the baseline evaluation. In addition, we confirmed that the sensor can detect human presence and movement through internal walls of typical office buildings. We performed a preliminary demonstration of the use of multiple identical sensors operating in wireless exfiltration mode with external directional antennas to detect and track movement through an area. This simultaneous operation was possible because the sensor was designed to enable precise tuning of the frequency response of the regenerative feedback circuit.

After confirming the successful operation of the 2 GHz printed circuit sensor, we designed the next iteration of the multi-modal sensor. To miniaturize the form factor and maintain performance, the operating frequency was increased to 5.8 GHz, and the resonant patch antenna and feedback circuit were placed on opposite sides of a multi-layer circuit board. The overall dimensions of the 5.8 GHz sensor are 50 mm × 50 mm × 2 mm. The resonator element was designed using electromagnetic simulation. We fabricated and tested the miniaturized sensor, which exhibited significant improved performance compared with previous prototypes.

We also developed an enhanced 2 GHz sensor that incorporated a microwave circulator to separate the transmit from the receive paths. This design increased radiated power, reduced noise power, improved frequency stability, and allowed for a greater flexibility in the antenna selection. This configuration was also used to demonstrate the monitoring of human activity through an exterior cinderblock wall of a facility. In addition to motion tracking, the sensor detected simultaneous transmissions from a hand-held FRS radio.

For FY 2014, we published a peer-reviewed journal article in *Applied Physics Letters* that described considerations to optimize the resonant response and demonstrated sensitivity to low-frequency electromagnetic emissions. Additionally, the technology from this project relates to a U.S. patent awarded during this fiscal year.
Mössbauer Spectral Imaging

Lucas E. Sweet

Actinide Mössbauer spectral imaging is a novel concept targeted at improving the limit of detection and chemical characterization of actinide-containing solids. This development is potentially a new tool in the field of radioactive material detection.

Mössbauer spectroscopy has been an underutilized chemical characterization technique for a couple of reasons. First, the radiation sources required to probe actinide nuclear resonances have been difficult to prepare and required significant radiological material handling infrastructure. Second, this has been a bulk solid analysis technique that required up to several days for a single spectrum to be collected on a sample. At these sample quantities and data collection times, other analytical techniques are more effective for chemical characterization.

Recent advances in iron (57Fe) Mössbauer spectroscopy have drastically improved detection limits and data collection efficiency, including use of gamma detectors with high spatial resolution, gamma-ray focusing optics, and technologies for Mössbauer measurements using high flux synchrotron light sources. Our focus is to apply these advances in iron to actinide Mössbauer spectroscopy. These developments are intended to produce a novel ultra-sensitive characterization technique for actinide-containing solids that can have applications in nuclear safeguards and non-proliferation.

In FY 2013, we evaluated options and chose our detector, which was integrated into the spectrometer. We confirmed that the new configuration would allow for the high efficiency detection of the correct gamma-ray lines for performing our targeted actinide isotope Mössbauer measurements. In addition, we explored alternative measurement geometries, tested several different measurement geometries, and compared real data collection efficiencies of some of these geometries using our spectrometer.

The majority of our FY 2014 efforts focused on instrument design and the acquisition and fabrication of parts to make the design a reality. Several more custom parts were fabricated than originally anticipated because vendors were unable to produce parts that met our required specifications. We determined what kinds of gamma detectors were optimal for actinide Mössbauer measurements and the type of instrument geometries we wanted to use for optimal speed and sensitivity. With the identification of a new cryostat at the end last year, our instrument design was rethought, which resulted in an instrument that will be more versatile and safer to operate.

Among the most helpful activities last year was a visit to the Institute of Transuranium Elements in Karlsruhe, Germany to consult with the scientists who built and operate one of the few (if not only) currently operating neptunium Mössbauer spectrometers. This was extremely informative and helped guide our instrument design, particularly for the vertical velocity transducer and safer source containment. In parallel, we have been working on a real-time noise reduction filter for Mössbauer data collection, as the Kalman type filter we developed improved signal-to-noise ratio by 51% over unfiltered data. This development will decrease data collection times for Mössbauer measurements. We received acceptance of a journal article describing our work to Nuclear Instruments and Methods in Physics Research.

Finally, we have been working on electronic structure modeling to understand and interpret actinide Mössbauer spectra. Our calculated Mössbauer spectra generated by modeling matched well with spectra previously reported in the literature. This type of application of electronic structure calculations for interpretation and prediction of Mössbauer has been applied to iron Mössbauer spectroscopy but is much less understood for actinides.

For FY 2015, we will complete construction of the Mössbauer spectrometer and begin 237Np measurements. We will demonstrate that the instrument can also do 238U Mössbauer measurements by procuring a 242Pu source. By year’s end, we should be able to demonstrate Mössbauer imaging of a mixed uranium and neptunium sample with a pixelated gamma-ray imaging detector and pinhole configuration.
Platform for High-Throughput Determination of Enzyme Kinetic Parameters for Hemicellulose Saccharification

Ryan T. Kelly

We developed an analytical platform based on droplet microfluidics to monitor reactions involved in the enzymatic breakdown of biofuel precursors. This process will enable the rapid screening of new reactants and automated optimization of reaction conditions.

With increasing efforts to develop viable biofuel alternatives to fossil fuel energy sources has come the need to understand the fundamental enzymatic reactions involved in natural lignocellulose degrading systems and to screen recombinant libraries of engineered glycoside hydrolases for feedstock degradation efficiency. Existing methods to monitor enzymatic saccharification are low in throughput, often involving liquid chromatography separations or fluorescent labeling, and require large amounts of material. We are developing a platform to monitor degradation efficiency with higher throughput and minute amounts of reagents.

Our platform is based on droplet microfluidics coupled with ion mobility spectrometry/mass spectrometry (IMS/MS). Picoliter to nanoliter sized volumes comprising enzyme, substrate, and dilution buffer are controllably dispensed into an immiscible oil stream. Rapid mixing of enzyme and substrate droplets upon contact initiates the degradation process, and the reaction occurs as droplets travel through the microchannels towards the detector. We aim to demonstrate the ability to monitor reaction of multiple (hemi)cellulases with a panel of cellodextrins with high throughput and to detect the products in a label-free fashion using IMS/MS. This will be the first time that droplet-based microfluidics have been combined with IMS/MS, which should prove powerful for high throughput screening and online reaction monitoring.

The nature of the project required that a number of iterations in microfluidic device design be performed to develop a working prototype. These iterations were required to produce properly sized droplets, achieve rapid mixing, ensure adequate incubation time, and optimize the extraction of droplets from the oil stream for downstream analysis. Each successive generation required multiple photomasks to accommodate different microchannel heights and cross-sectional shapes. The production of 3–4 photomasks, which takes about a day each to produce, for every design change became an impediment to optimizing the microfluidic platform. We solved this issue by devising a strategy to enable designs using a single photomask while maintaining the same alignment tolerances between layers achieved using separate photomasks. The results of this innovation were published in the international journal RSC Advances.

We found that conventional analog regulators to control the pressure with which droplets are introduced into the oil stream tended to drift over time and with changing input pressures. We purchased a digital pressure controller that quickly responds to such changes and allows for consistent droplet generation performance over extended periods of time (hours). We also explored different channel geometries to enhance mixing and found that increasing the tortuosity of the flow path while varying the cross-sectional area indeed increases mixing efficiency.

The final component of the microfluidic platform was the ability to generate a series of droplets with a range of substrate concentration spanning several orders of magnitude to obtain accurate kinetic parameters. We accomplished this by developing a microfluidic serial dilutor, which generates quantized droplets and subsequent serial dilution by using a mechanical valve-based injection method. This is highly flexible and independently controls the timing of droplet formation, size, merging, and mixing. Our diluter consists of a chamber, an oil channel where droplets are generated, and two ports for reagent and buffer, respectively. To characterize our dilution method, we established the relationship between droplet number and corresponding concentration droplets and plotted a dilution profile. To plot dilution profile, we generated a series of 35 droplet microreactors containing different concentrations of the fluorescein, where its concentration varied from 1–160nM. The fluorescein concentration inside each droplet was determined from the intensity of the initial fluorescein droplet observed in the captured video. This approach to serial dilution combined with the previously developed functionality enabled the online reaction monitoring of the conversion of xylobiose into xylose.
Platform for Large-Scale Determination of Protein-Ligand Binding

Ryan T. Kelly

We are developing a new platform based on microfluidics coupled with ion mobility spectrometry-mass spectrometry (IMS-MS) for solution-based, label-free determination of protein-ligand binding that will broadly advance fundamental and applied biological research.

Noncovalent protein-ligand interactions play a major role in many biological processes, including signal transduction, enzymatic catalysis, and immune response. Determining the binding affinities and kinetics of these interactions is of great importance for applications ranging from biofuel development to drug screening. Existing methods for measuring protein/ligand interactions include both label-based and label-free technologies. Labeling assays can be robust and highly sensitive, but require modification of reaction components, which can interfere with the interactions under study. Label-free technologies avoid such artifacts and require minimal manipulation of reaction components. The most widely used label-free techniques are microcalorimetry and surface plasmon resonance, which both require highly purified samples and can only measure one interaction per detection volume.

Our microfluidic/IMS-MS platform will overcome many limitations of existing approaches. By targeting protein-ligand interactions, we will provide a completely solution-based, label-free, multiplexed method for obtaining binding and kinetic parameters unlike any commercially available method. It will also be high throughput, enabling a combination of multiple proteins and ligands to be evaluated in an automated fashion with extremely low sample consumption. The platform will use microfluidics combined with IMS-MS: microfluidics will enable rapid mixing and extended incubations of very small (nanoliter [nl]) volumes without dilution, thus making them ideal for high throughput screening and reaction monitoring. Similarly, IMS-MS will enable sensitive gentle measurement of noncovalent complexes in the gas phase, making nanoESI-IMS-MS an ideal method for studying noncovalent protein/ligand interactions and determining binding locations. Interfacing IMS with time-of-flight (ToF) MS also permits the simultaneous acquisition of ion mobility and high accuracy MS information that covers a broader m/z range than most trapping instruments (~10,000 vs. ~3,000) for detecting large protein complexes. We aim to optimize the IMS-MS platform for the characterization of noncovalent interactions and develop a microfluidic chip combined with the optimized IMS-MS system to perform multiplexed binding and kinetic assays.

During FY 2014, we laid the groundwork for the data collection and analysis that will be performed next year. The nature of the project requires that a number of iterations in microfluidic device design be carried out that are necessary to achieve rapid, complete mixing of protein and ligand; ensure measured and controlled incubation time; and optimize delivery of protein/ligand complex from the oil stream for IMS-MS analysis. In addition to developing the planned droplet-based incubation chamber, we developed a droplet-free method, which substantially simplifies device operation while providing the same functionality. The droplet-free platform comprises valve-controlled protein and ligand inputs, a reservoir for holding the mixed reagents, and a means of dispensing the reagents to the mass spectrometer. The design needed to balance requirements for rapid reservoir filling and maximizing volume. A larger volume can require more time to fill and naturally uses more reagents, but it enables more time points to be collected by IMS-MS or for consumption of larger amounts of reagents at each sampling point. The latter point is advantageous for difficult-to-detect complexes that require additional signal averaging in the IMS-MS platform to provide adequate signal. The disadvantage is that it takes longer to fill, which puts a lower limit on the first time point that can be measured; hence, the tradeoff between the ability to track rapid binding events accurately and having sufficient sample to measure weak signals. We alleviated this tradeoff to some extent by filling the reservoir at high pressure and then reducing the pressure substantially for lower flow rate MS analyses. Our current design has a 300 nL reservoir, enabling 10 time points to be collected that consume ~30 nL each. At a typical nanoESI flow rate of 100 nL/min, this will enable IMS averaging of 20 s per data point. Reservoir filling can be achieved in <10 s, sufficient speed to track a binding event that takes just a few minutes to reach equilibrium.
We also made substantial progress in optimizing the nanoESI-IMS-MS platform for measuring noncovalently bound complexes. The conditions for ionization, ion transmission, IMS separation, and mass analysis all must be sufficiently gentle to avoid breaking apart the weakly bound complexes, as any difference in binding between binding pairs in solution and in the gas phase will lead to errors in the calculation of binding rates and dissociation constants. Instrument parameters were carefully tuned to ensure minimal disruption of the weakly bound complexes. We verified that equilibrium binding constants measured by IMS-MS were similar to literature-reported values.

While the microfluidic platform was under development, it was necessary to electro spray large numbers of samples for IMS-MS measurement and platform optimization. Throughput was extremely limited using conventional sample delivery procedures that involved loading sample into a glass syringe and using a syringe pump to drive the sample through tubing to the ESI emitter. This process involves consumption of a minimum 15 µL of sample prior to the actual sample used for measurement. It was labor intensive, as the syringe and tubing required thorough washing between samples, but we developed an automated process to alleviate this shortcoming. The sample was electro sprayed by first injecting the sample into a sample loop on a valve using a robotic auto-sampler. The valve was then actuated, and the sample was moved from the loop to the electro spray tip using a nanoLC pump. Narrow diameter lines limited the diffusion of the sample as it traversed the lines. Because the pump delivers solvent continuously, the electro spray tip never dries out, which significantly reduces emitter clogging and increases platform robustness. The pump was also capable of delivering much higher pressures than the manual syringe pump. Only 7µL of samples is required at a time to ensure that the 5µL sample loop is filled. All of the sample gets electro sprayed, eliminating sample wasted to clear lines and establish stable electro spray. Also eliminated is the risk of complete sample loss due to unexpected disconnects. Automation using in-house developed software has addressed the issues of robustness, sample size, and time stamping and will allow more complete exploration into protein ligand binding. While this automated direct infusion platform will lack the temporal resolution provided by the microfluidics for high rate kinetic measurements, it provides an elegant and practical solution for equilibrium binding measurements and other studies involving direct infusion measurement of large numbers of samples.

For FY 2015, we will combine the developments described above in IMS-MS platform development and microfluidic design to achieve a high rate kinetic rate constant measurements in a label-free, solution-based and automated platform. We will first evaluate the platform using lower cost model systems before testing with kinases and kinase inhibitors. We expect that the results will enable scientific discovery in otherwise intractable systems given the broad relevance of the platform to biological interaction analysis.

Charles H. Henager Jr.

This project explores the development of physical models of materials deformation as determined by non-linear ultrasonic methods.

The development of advancements such as small modular reactors (SMRs) is projected to be a significant contributor to future global energy resources. Safe efficient operation of nuclear reactors is contingent on a more complete characterization of materials, particularly at the elevated temperature anticipated for several new designs. The ability to monitor and predict component life augments the safety features of the new reactor concepts. Characterization of materials is key to the life assessment from the perspective of material degradation. One particular mode of deformation, creep deformation, can cause distortion of structural materials that can be life limiting, especially in close tolerance areas where radiation creep and thermal gradients exist. Plastic deformation and creep deformation, in particular, can be correlated to density changes and elastic moduli changes in materials that are observable using ultrasonic measurement technologies. Radiation-induced hardening from radiation damage and defect accumulation is observable using non-linear ultrasound (NLUS) methods and second harmonic peak detection. The theory of defect scattering needs to be improved to help understand how NLUS methods can be used to detect certain microstructural defects.

This research uses high-resolution in situ nonlinear ultrasonic measurements of deformed and deforming samples characterized for density, microstructure, and strain. NLUS measurements will be used on deforming and thermally aging samples to determine second harmonic signal generation compared to undeformed, unaged samples. A new test system was constructed to allow in situ pitch-and-catch NLUS measurements with cold grip end sensors and heated gage length regions undergoing creep deformation and precipitation. 316SS and Fe-1%Cu alloys will be used for this work to validate the experimental data.

The new test frame is complete and is ready for initial testing. The system allows loads up to 10k lbs and temperatures from RT to 900°C with positional accuracy of 0.0055 in. Tension-tension fatigue at elevated temperatures is also possible with this new computer-controlled system. Ultrasonic sensors are mounted in water-cooled grips to maintain them at 50°C or less during testing. The 22-in long sample has a 2-in long 0.25-in diameter gage designed at PNNL to minimize wave distortion.

A specimen of 316SS was tested successfully at a 125 lb load and 50°C temperature to show that the system was operational. A clear second harmonic peak was observed. Further testing is underway, and rods of Fe-1%Cu are being prepared for thermal aging studies of Cu-precipitates in Fe as a simulation for radiation-induced embrittlement of reactor pressure vessel steels. Initial results are included in a new DOE proposal concept for FY 2015.

State-of-the-art mesoscopic phase field models of deformation and materials ultrasonic response are being developed and validated using experimental data. The use of these models to predict deformation and ultrasonic response simultaneously has not been accomplished previously and represents a genuine multi-physics approach. The information will be integrated in finite element codes as a microscopic damage model to achieve a multi-scale methodology by predicting material response at the macroscopic scale. The mesoscale phase field modeling will provide effective material properties in defected materials such as effective elastic modulus tensor $C_{ijkl}$, kinetic properties of material response to applied fields such as ultrasonic wave propagation, and interaction mechanisms between defects and ultrasonic waves.
Secondary Signatures for Provenance Attribution

Jon H. Wahl

This project investigates “natural” tagging and tracking signatures present in the atmosphere for correlating nuclear process signature detections. Our research will improve the U.S. government’s ability to associate the nuclear signature materials in a given sample with the environs of or the effluents from a region.

Many nuclear measurements are often highly dependent on meteorological data and modeling input, which may be limited, unavailable, or in many cases unreliable. Consequently, additional provenance information would be valuable to improve and bolster confidence. The overall objective of this project is to develop a robust methodology to determine signatures or features that inherently exist in the environmental background (i.e., features of opportunity), which can be volatile organic compounds (VOCs), particles (in the form of soot, dust, or pollen), and microbial cells (earth microbiome). Importantly, a certain fraction of all these types of backgrounds will be due to transport/dispersion to a region. Identifying and utilizing this fraction, which will likely be a feature set of the background, can offer an indication of the directional region or origin of an air sample.

One of the most readily available chemical background features are VOCs, the collection and analysis of which are at the heart of our chemical approach. Our technical approach is based on proven technologies and analytical methods, including large volume air sampling and concentration utilizing sorbents, sample extraction, and analysis by gas chromatography/mass spectrometry (GC/MS), which is the modern day “gold standard” for VOC analysis. In general, a robust volatile compound map needs to be screened because neither the type, number, or amounts of components are known a priori, although certain chemical classes (e.g., hydrocarbons) may be anticipated. As such, GC/MS is used to examine specific chemical characteristics within a variety of environmentally collected samples to determine the statistically significant signature components. This chemical and environmental data, as well as any other additional material such as regional information of known industrial activity or endogenous backgrounds, will be mined for “features of opportunity.”

In this project, the chemical organic methods for provenance signatures have been developed, and the signature statistical framework has been established. Specifically, a robust air collection and chemical analysis approach has been examined utilizing a thermal desorption unit GC/MS system.

A statistically derived method for denoising complex GC/MS data files was developed to analyze a collection study that contained numerous GC/MS generated chromatograms. In general, this approach is based on the assumption that well-separated, higher intensity compounds are the most significant and reproducible. Additionally, this method evaluates each chromatographic peak in terms of its combined retention time, m/z value, and intensity. A probability or significance level for the peak’s location and intensity is calculated. If the combined significance level is greater than a pre-determined threshold, then both the location and intensity are typical of background peaks, and the peak is eliminated from consideration. If it falls below the significance threshold, then either the location or intensity or both are unique, and it is retained as a signature peak for the compound.

For FY 2014, we further developed and assessed those signatures measurable by the GC/MS approach based on sampling scenarios. Additionally, we assessed the statistical likelihood of those signatures being present in the concentrations needed for detection.

Schematic representation of two extracted chemical fingerprints from two regions.
Single-Step 2-D Ion Mobility Separations Technology

Keqi Tang

This project is developing a single-step concurrent ion mobility spectrometry (IMS) and field asymmetric waveform IMS (FAIMS) technology for two-dimensional (2D) rapid gas phase ion separation with high resolution and sensitivity.

Historically, breakthroughs in chemistry and biology are enabled by new methods for molecular structure characterization. Over the last decade, IMS coupled to mass spectrometry (MS) has emerged as the next powerful analytical and structural tool of broad utility. This situation has included the rise of FAIMS based on the dependence of ion mobility on electric field intensity. Strong orthogonality between FAIMS and linear IMS has prompted their coupling for 2D gas phase ion separations of impressive combined resolving power (>1000). However, large ion losses at FAIMS/IMS and IMS/MS interfaces made the sequential addition of these separation stages a major challenge, preventing the practical utility of this extremely complex hybrid instrument.

The primary goal of this project is to develop a new instrumentation that allows single-step concurrent FAIMS and IMS separations by using a novel concept of field-driven FAIMS with electrodynamic ion funnel interfaces to achieve exceptional overall instrument sensitivity. Specifically, the project aims to achieve three major goals: to build a novel segmented FAIMS device and integrate it with an MS platform; to convert the field drive FAIMS into a hybrid one step 2D FAIMS/IMS separation device; and to demonstrate the performance of the new hybrid IMS/FAIMS/MS instrument for high throughput, high resolution, and high sensitivity chemical and biological sample analysis.

In FY 2014, our primary effort was focused on designing and building the first 2D FAIMS/IMS device based on a well-known segmented FAIMS concept. The device mainly consists of two parallel segmented electrode assemblies that are capable of simultaneous FAIMS and IMS separation.

To determine optimum geometric dimensions of the device and its operating parameters, a detailed theoretical analysis was performed in FY 2014. An optimum operating pressure was selected to allow high resolution ion separation and the effective ion focusing and transmission by ion funnels at both the entrance and exit of the FAIMS/IMS device. A gap width between the two parallel segmented electrode assemblies was selected to achieve optimum FAIMS separation at the selected operating pressure. With the selection of the overall assembly, optimum ion residence time (~100 ms) and field uniformity were expected for the new device. A FAIMS resolving power of 200 and an IMS resolving power of 30 were expected, with an estimated combined FAIMS/IMS resolving power of $10^4$ to $10^8$, more than an order of magnitude higher than the resolving power achievable by any currently available IMS-based gas phase ion separation technologies. Guided by the comprehensive theoretical analysis, a prototype 2D FAIMS/IMS was successfully built in FY 2014.

We successfully powered up the new 2D FAIMS/IMS device with a commercial asymmetry waveform power supply. This situation will significantly simplify follow-up integration of the 2D FAIMS/IMS device with a high performance MS platform and shorten overall technology development time for the complete 2D FAIMS/IMS MS instrument, which is planned for FY 2015.
Super Resolution Fluorescence Barcoding and High Throughput Microfluidics for Quantifying the Expression of Multiple Genes in Individual Intact Cells

Galya Orr

With this research, the ability to interrogate individual cells in complex communities accelerates the discovery and design of new molecular functions for sustainable biofuels and carbon cycling.

Fundamental limitations in averaged cell population measurements often dominated by the most abundant processes have led to new developments in single-cell analysis. These techniques can identify variability between cells rapidly and accurately unmask molecular details buried otherwise in population measurements. However, these methods are available at few expert laboratories and mostly in low throughput.

This project provides an automated high throughput platform for large-scale applications in microbial community research, biodefense, or medical care. Fluorescence in situ hybridization (FISH) will be used, where fluorescent probes are designed to recognize and bind mRNA molecules for specific genes. While the number of fluorescent colors that can be differentiated within a single cell is limited to about seven, the combinatorial use of these colors to create fluorescent barcodes can significantly increase the number of probes that can be differentiated in a single cell to more than 60. Our newly developed technology will provide a tool for rapid, accurate interrogation of single pathogens or diseased cells for immediate diagnosis and treatment and support research in environmental microbial communities, where complex relationships between species make it impossible to regrow isolated cells in culture.

We established combinatorial barcoding of FISH probes and their detection and quantification within intact individual cells using super resolution fluorescence microscopy. Building on our expertise in molecular biology, we established protocols and optimal probe configurations for generating barcode FISH probes and inserted them into the cells. We have been using eukaryotic cells that are larger and easier to work with, later focusing on bacterial cells. Building on our expertise in single-molecule fluorescence imaging techniques in living cells, we assembled a multicolor stochastic optical reconstruction microscopy (STORM) system, which currently includes four lasers. By adding a fifth laser, we can detect nearly 30 different barcoded FISH probes in a single intact cell. By systematically increasing the number of barcoded FISH probes imaged in a single cell, we can work our way through the technical and computational challenges to achieve unambiguous quantitative evaluation of the expression of multiple genes in individual intact cells.

In addition to our above progress, we established the trapping of single cells in a microfluidic array for subsequent high-throughput tagging and imaging. The array is fabricated using multilayer soft lithography and consists of multiple inlets, each has a corresponding microvalve to control fluid delivery. The cells flow into the array and are confined in geometrical traps designed to accommodate just one cell each. Once the traps are filled, microvalves close around each trapped cell to hold the cells in place for imaging. Further refinement of this process will increase the fraction of traps containing a single cell to approach full capacity.

In FY 2014, we refined the trapping of single cells in the microfluidic array and the delivery of multiple reagents needed for preparation and fluorescence labeling. We also implemented additional lasers on the STORM system to a total of 6, allowing us to scale up the number of detectable barcoded mRNA probes to more than 20. Finally, we established the computational approach for automated image analysis to distinguish between barcodes and quantify the expression of multiple mRNA species in single cells.

A) A differential interference contrast (DIC) image; B) a wide field fluorescence image; and C) a super resolution STORM image of cells tagged with FISH probes specific for GAPDH, a key enzyme in the conversion of glucose to energy.
Vapor Detection of Illicit Substances in an Atmospheric Flow Tube Mass Spectrometer

Robert G. Ewing

Detection and interdiction of chemical weapon compounds and illicit drugs are important national security issues. This project is enabling real-time detection that is below the occupational safety exposure levels and significantly lower than previous detection technologies.

The recent development of an atmospheric flow tube-mass spectrometer (AFT-MS) enabled the real-time vapor detection of some explosives at unprecedented levels, approaching a single part-per-quadrillion (ppq). These remarkable detection limits enable standoff or non-contact detection for a variety of scenarios, including cargo screening. In turn, this discovery led to wanting to determine what other substances might be detectable at these levels, such as narcotics or chemical weapons. The challenge is that many of these compounds form positive ions, unlike explosives that form negative ions. Preliminary studies using AFT-MS have demonstrated complex positive ion spectra for background laboratory air. The primary scientific challenge associated with using the AFT-MS to detect positive ions of illicit substances is ionizing the target substances selectively in the presence of a variety of compounds in room air. The goal of this investigation is to identify and select appropriate ionization chemistries to reduce the interference of background chemicals while enabling the detection of illicit substances.

In FY 2014, two narcotics and two chemical weapon surrogates were evaluated with an AFT-MS to determine the substances’ ability for ultra-trace vapor detection. It was determined that with the proper selective ionization chemistry, all four substances were detectable. For the narcotics, vapors from micro-gram quantities were detectable; for the chemical agent surrogates, vapor was detected from material permeating through the septa of a sealed 2 mL glass ampule. Preliminary data based on calculations of signal intensities suggest detection limits approaching single digit ppq. Further, vapor concentrations coming from the sealed vial with a dilution flow of ~7 L/min were estimated to be ~5 parts-per-trillion.

To varying degrees, all four substances responded differently to changes in the selective ion chemistry. In one instance, the selective ion chemistry produced a response 1600 times greater than that measured in room air. The selective ion chemistry in conjunction with the AFT-MS provided unprecedented detection limits for the compounds investigated. The system also provided unparalleled selectivity with the combination of selective ionization and mass spectrometry for positive identification with MS/MS for additional compound confirmation. With ppq detection levels in real-time without solute pre-concentration, this technology not only enables a revolutionary detection capabilities but it also provides a means to monitor analyte breakthrough at ultra-trace levels that will be useful in material development for personnel protection equipment such as gloves or protective suits.

The initial success of detecting ppq levels in both illicit drugs and organophosphorous compounds merits additional research and development that are necessary to optimize the whole detection process. Efforts planned for FY 2015 include the following: 1) further expansion and refinement of ionization chemistries; 2) investigations into the effects of several common background interferences on the detection capabilities; 3) quantitation of the detection limits for selected analytes with optimal experimental design; and 4) evaluation of additional analytes to determine the ability to expand the detection library. Perhaps the greatest challenge for FY 2015 is in confirming the detection limits. Preliminary data suggest detection limits in the low ppq range; however, these values result from calculations based on ratios of signal responses and an estimate reaction rate constant. A second method will be required to confirm these concentration levels.
Biological Sciences
**Agrobacterium tumefaciens-Mediated Transformation of Oleaginous Yeast**

Ziyu Dai

Oleaginous yeast strains are one of best known biological systems for effective conversion of lignocelluloses to bio-hydrocarbons. Development of effective genetic tools is pre-required for productivity improvement.

Concerns about the fossil fuel supply and the environmental impacts of their use have stimulated a sustained interest in the development of sustainable renewable transportation fuels. Drop-in fuels can be obtained from the catalytic conversion of lipids or fatty acids from oilseed crops, oleaginous (oil-producing) algae, or yeasts. The oleaginous yeast is appealing for this process, with its use of lignocellulose-derived sugars for conversion to lipids. In particular, *Lipomyces starkeyi* can accumulate lipid at up to 70% of its dry weight. In addition, it can use a variety of monosaccharides and disaccharides that are found in lignocellulosic biomass. Because a transformation method for integration of homologous or heterologous genetic material into the chromosomes of *L. starkeyi* does not yet exist, it cannot be manipulated for improved productivity or customized product profiles.

Ultimately, the purpose of this study was to establish an effective transformation system for oleaginous yeast such as *L. starkeyi*. Although its genome has been sequenced recently, there are no genetic tools for engineering the organism; therefore, it was therefore crucial to establish effective transformation methods, determine suitable selectable markers (antibiotic resistance genes), and define the necessary genetic elements (promoters and terminators) for the expression of genes. We developed the first successful transformation method for *L. starkeyi* using *Agrobacterium tumefaciens*-mediated transformation (ATMT). Additionally, further research and development is needed to capture the methods proposed for sustainable fuel via a robust patent application that is well supported by quantitative data and examples of use.

The technical progress for this project in FY 2014 is outlined below:

1. We first established effective selection doses of antibiotics, such as, barstar, G418, hygromycin B, pyrothiamine and Zeocin, which would be potentially used for genetic transformation on proper culture media. A couple of antibiotics exhibit their potency for selection of *Lipomyces* species.

2. Two transgene expression cassettes were constructed accordingly, where one was for marker selection and the other served as reporter gene to determine the effectiveness of genetic elements in the transgene expression system. Five strains of *L. starkeyi* and six other *Lipomyces* species were then selected for examination of the genetic transformation.

3. The antibiotic selection, polymerase chain reaction (PCR), and southern blotting analysis all confirmed that the transgene expression cassette was integrated into the chromosomes of those specifically transformed *Lipomyces* strains.

4. The transgene expression cassette carrying the reporter gene under the control of genetic elements, along with the antibiotic selection marker gene, was transferred into the *L. starkeyi* strains. From there, it demonstrated the strong expression of the reporter gene in 90% of transformed strains.

With the successful demonstration of DNA integrated into the *L. starkeyi* chromosomes by ATMT, we needed to maximize the transformation efficiency, uncover the method for homologous gene replacement, increase the feasibility of the transformation in other related species (e.g., *L. knockii* and *L. lipofer*), and study the effectiveness of gene regulatory elements (various promoters and terminators) for gene expression. In addition, these tools are needed to alter targeted genes and realize improvements in lipid and other chemical productivity in oleaginous yeast. Through establishing an effective genetic transformation system and evaluating those genetic elements identified from *L. starkeyi* for genetic improvement, an effective genetic transformation system can be established for select *Lipomyces* species.
Biogeochemical processes regulate soil carbon dynamics and CO$_2$ flux to and from atmosphere, influencing global climate changes. Integration of biogeochemical processes into earth system models (e.g., community land models [CLMs]) currently faces three major challenges: 1) extensive effort required to modify modeling structures and rewrite computer programs to incorporate the latest biogeochemical processes with increasing complexity; 2) computational cost to spin-up CLM to steady state of coupled carbon–nitrogen processes is prohibitively expensive due to the long residence time of soil carbon; and 3) various mathematical representations of biogeochemical processes exist, with some too simplified to reflect fundamental mechanisms and others are too complex for pragmatic application. The objective of this research is to develop a generic biogeochemistry module to address the challenges mentioned above that will enable significant future research with reduced cost and minimize coding error. The model can also facilitate the whole community to test different mechanistic process representations and data to gain new insight on what is most important in the system in response to climate change.

In the first year of the project, we developed a new biogeochemical module with a computational framework that incorporated mechanistic biogeochemical reactions into earth system models for simulating carbon-climate feedbacks. The module uses a generic algorithm and a reaction database to collect and compile biogeochemical reactions. The advantage of our module is that new, updated processes can be incorporated into earth system models without the need to set up mathematical equations manually for describing biogeochemical reactions. The compiled reaction database consists of processes of nutrient flow through the terrestrial ecosystems in plants, litter, and soil. The database has a structure to incorporate new and updated reactions readily. The module was first integrated in CLM, the land component of the Community Earth System Model (CESM), and benchmarked against simulations from the original CLM-CN code. We also incorporated a phosphorus cycle in CLM using the new module.

In the last year, we developed an algorithm based on the new framework to estimate global soil organic carbon (SOC) using satellite-derived canopy leaf area index (LAI) and CLM, as soil carbon plays a key role in the carbon cycle that is important in global climate models. Traditional estimation of soil carbon stock using modeling-based methods involves spin-up of carbon-nitrogen (CN) models, which is to perform hundred to thousand years’ long simulations until the carbon-nitrogen pools reach pseudo steady-state. This has become the bottleneck issue for global modeling and analysis, especially when new physical and/or chemical mechanisms are proposed.

In our novel approach, SOC is estimated by solving steady-state equations using the Newton-Raphson iteration and annual averaged parameters. Potential annual average carbon input is figured given LAI derived from the multi-year Moderate Resolution Imaging Spectroradiometer (MODIS). This is the first time that SOC was calculated using MODIS-derived LAI, and the results are comparable to those using the spin-up approach. The work is a promising to estimate global SOC distribution, evaluate efficiently, and compare aspects simulated by different CN mechanisms in the model. We also developed an algorithm to speed up the traditional spin-up approach, and improvement was made compared to the best available approach in the literature. Our work is especially suitable for simulations at high latitudes where spin-up time is the longest. The previous soil hydrology model in CLM caused instabilities in SOC simulation, making steady-state SOC solution impossible.

This research has generated three manuscripts to date: a published work in *Geoscientific Model Development* and two other submittals. For the next step, our approach in this research will be used to incorporate new mechanism-based models and apply the model to the Disney Wilderness Preserve site.
Development of Bromotyrosine Antibody Assay for Blood and Sputum Samples

Richard C. Zangar

This project seeks a quantitative empirical test for assessing inflammation in asthmatics.

Asthma is a common disease that currently affects about 9% of the United States (approximately 23 million Americans) and world populations with a lifetime risk of around 15% and substantially decreases worker productivity and quality of life. Asthma is particularly problematic in children ages 1 to 4, such that 0.24% of these are hospitalized as a result of this disease, a rate that is higher than any other cause except respiratory infections. Along with no medical cure, asthma symptoms may disappear on their own for unknown reasons. The immediate medical goal is to control symptoms through the use of anti-inflammatory drugs or by reducing exposure to environmental factors such as allergens or cigarette smoke. The inability to cure this condition means that treatment of this disease is designed to control symptoms. Currently, there is no practical test for assessing inflammation in asthma patients, which means that this information is inferred from patient questionnaires regarding asthma symptoms. However, patients often have differing perceptions of similar symptoms, so questionnaires are not truly reliable.

We have been working with asthmatic patients by indirectly assessing the eosinophil peroxidase (EPO) activity. Eosinophils appear to be the sole source of EPO, and this activity seems the sole physiological source of bromine bleach (hypobromous acid [HOBr]), which reacts with proteins to produce bromotyrosine residues and appears to be specific markers for inflammation in asthma patients. Notably, a variety of studies have demonstrated that total levels of protein bromotyrosine are altered in asthma and are promising biomarkers for inflammation in asthmatics. Even so, these studies did not evaluate bromination on individual proteins, such as we can now accomplish, and the previous analytical protocols are not well suited for a routine clinical screening.

We developed a novel antibody that detected a specific protein modification and allowed us to assess airway inflammation in asthmatics. The goal was to assess further the study of the halotyrosine antibody to determine its ability to characterize asthma and thereby guide clinicians in the identification and treatment of this disease. We therefore examined sputum (airway fluid) samples from two sets of subjects. One sample set allowed us to characterize biomarker levels in asthmatics over time, and the other enabled us to assess differences between asthmatics and healthy controls. We also analyzed blood samples from asthmatics and controls. Obtaining the human samples for this research required a substantial effort. Transfer of both types of samples involved approvals and agreements, which took a considerable amount of time. After receiving both sets of blood and sputum samples, we performed and completed analysis. Specifically, we analyzed halogenation of 13 proteins in each sample. Currently, the data from the blood samples are being analyzed by the statistician. Preliminary examination results suggested that there were no major increases in protein halogenation in these samples.

For our focused work in FY 2014, we examined 25 human sputum samples from Hamilton University, 44 samples from the University of Washington, and 27 human serum samples from a commercial source. In these analyses, we used sandwich enzyme-linked immunosorbent analyses (ELISAs) to evaluate levels of halotyrosine modifications on specific proteins. The studies on sputum extended our previous results in that halogenated angiotensin was found to be associated with PC_{20}, a measure of airway hyper-responsiveness found in asthma patients. Additionally, there were three other proteins that had not been previously examined that were found to have greater levels of halotyrosine in this study. In the case of the blood plasma analyses, we did not find any increases in protein halogenation in asthma patients.

Overall, we confirmed that halotyrosine modifications of sputum proteins are associated with asthma symptoms consistent with these proteins being a marker of inflammatory disease. We have yet to demonstrate any relationship between halogenation of blood proteins and asthma. For future studies, we hope to extend our analysis to children, who are particularly susceptible to the adverse effects of asthma but are particularly difficult to diagnose using current methods.
Drugs of Abuse Retention and Degradation in Environmental Biofilms

Eric M. Winder

We are adding a new sampling and analytical capability to the forensic toolkit used to investigate crime scenes and suspect facilities.

Biofilms are found in most environments, particularly at the interfaces of solid, liquid, and atmospheric environments. The structure of a biofilm allows microorganisms to form a distinct microenvironment that is separate from yet interactive with the surrounding environment. A critical feature is the matrix of extracellular polymeric substances (EPS) secreted by cells that reside in the biofilm composed of a heterogeneous mixture of polysaccharides, lipids, nucleic acids, and proteins. Each EPS component plays a role in providing protection, sorption capabilities, nutrient/waste processing, and/or planktonic release of progeny cells. Of particular interest is the molecular sieve capability of an established biofilm that allows it to capture, sort, and sequester particular molecules from passing water, a sort of flypaper for passing cells, chemicals, biomolecules, and metals. This collection potential has several implications, including the extent to which biofilms may create and preserve a historical record of passing chemistry.

To accomplish our goals, we will be spiking established biofilms with drugs of abuse (heroin, methamphetamine, cocaine, γ-hydroxybutyrate, codeine, and methylone) at varying concentrations. Solid phase extraction (SPE) methodology will then be developed and utilized to extract these materials from the biofilm matrix, with the eluents subsequently tested utilizing an LC/MS to determine the presence or absence of the spiked material. The spectral data (peaks) obtained from blank media and biofilm samples will be compiled for background subtraction from the final data set, which will allow target and degradation product detection. Standard samples will be used to confirm molecular ion peaks and determine target analyte limits of detection (LOD) on the instrument.

Thus far, we have begun development of a solid phase extraction protocol for the drugs listed, utilizing C18 column packing material. The drug γ-hydroxybutyrate poses a unique challenge, as its molecular characteristics are much different from the other drugs. The biofilm and associated EPS is a complex environment, so any and all reduction to that complexity while maintaining our target analyte will be beneficial to increasing our analyte detection capability. Using an LTQ Orbitrap XLMS capillary liquid chromatography instrument, we have already seen a large reduction in the limit of detection of the drugs compared to values in literature (average LOD ~100 fg/mL c.f. 1 ng/mL).

In FY 2015, we will spike, test, and analyze results due to spiking of established biofilms for presence, degradation, and time stamping of the drug targets. From these results, we plan to submit manuscripts, present at a national conference, and integrate the sampling methodologies into a forensic toolkit that can be utilized by officers and first responders to determine if drugs are or were at a given location.
Elucidating the Natural Spore Phenotype

Marvin G. Warner

This project uses PNNL expertise in antibody evaluation to develop optimal methods for spore capture and retrieval from complex environmental samples (i.e., soil and blood soil mixtures) prior to proteomic analysis. Our process will enable direct mass spectrometric determination of the protein profile differences between natural vs. manmade organisms.

A persistent question in microbial forensics is whether there are methods to determine if a pathogen detected within or isolated from the environment is naturally occurring. The phenotypic (i.e., expressed trait) state of an organism is impacted by the environmental cues that it experiences, so assessing the phenotypic characteristics of an environmental pathogen may provide information about the environment in which it grew. The proteomic methods used have the potential to detect these characteristics; however, performing an analysis of environmental samples is challenging due to the microbial background and biochemical complexity.

Our project is evaluating optimal methods for Bacillus anthracis retrieval from a complex matrix such as soil with the goal of recovering sufficient spore cell mass for analysis and comparing to laboratory cultivated spores of the same strain. A laboratory mesocosm is used to simulate environmental factors that influence sporulation following death of a natural host. Spore mass retrieval occurs with state-of-the-art affinity reagents alone or in conjunction with cell sorting to reach a minimum estimate for proteomic analysis. A comparison of soil-produced spores with blood sporulation or the laboratory can provide useful insight into how these data are used to differentiate naturally and laboratory produced B. anthracis spores.

Methods to grow and prepare B. anthracis sterne spores were identified, tested, and optimized during FY 2013. Spores were prepared on either a solid agar surface such as tryptic soy agar (TSA) or brain heart infusion (BHI) agar plates. A liquid sporulation media (new sporulation medium [NSM]) produced the purist spore preparations (> 95% spores) free of vegetative cell mass. For spore purification, spores and cells are pelleted by centrifugation and resuspended in sterile water. Solution was stored for 7 days at 4°C to lyse any remaining vegetative cells, and spores were washed up to 6 times in sterile water prior to enumeration and characterization.

Evaluation of the affinity and specificity of the commercially available B. anthracis spore antibody was done by immunomagnetic separation. Antibody purchased from multiple commercial sources were coupled following manufacturer recommendations. Capture of 100 or 1000 colony-forming units spores or vegetative cells was performed in peptone buffered water. We determined that several available commercial antibodies bind to spores and vegetative cells with low specificity, with these antibodies not binding a high number of cells (low affinity). To improve capture efficiency, we are investigating additional antibodies and optimizing coupling and loading onto magnetic beads. The immunomagnetic approach should lead to capturing sufficient numbers of spores from complex environmental matrices for proteomic analysis without the need for a culturing step that could lead to increased microbial background.

In FY 2014, we completed our evaluation of the capture antibodies as well as completed development of our spore recovery and lysis protocols. We developed the proteomics tools as well as the methods needed to analyze the spore samples. Finally, we conducted preliminary analysis of the spore samples to determine the effects of culture conditions on the phenotypic profile of the organism.

We developed a spore lysis protocol with sodium dodecyl sulphate-compatible with mass spectrometry (MS) analysis that allows recovery of the captured spores from the beads. We also tested a flow cytometric assay that allows us to screen spores rapidly from complex samples. Initial results are promising and indicate that flow cytometry will be a valuable tool for screening spores from samples either directly on the capture bead or after separation and elution. We anticipate that this will provide a rapid method to prescreen sample prior to workup for MS analysis.

Bright field microscopy of (A) Bacillus anthracis sterne vegetative cells and (B) B. anthracis sterne spores. Vegetative cells were grown in tryptic soy broth, with spores were prepared in new sporulation medium. Scale bar is 10 µm.
Limited fossil fuel supply and environmental concern bring about urgent pressure to produce alternative fuel from renewable resources. Compared to ethanol, hydrocarbon is more promising because it has properties similar to gasoline or jet fuel. Oleaginous yeast has attracted attention recently because it accumulates lipid via de novo fatty acid biosynthesis using carbohydrates and could be a possible biofuel feedstock alternative. However, the lipids extracted from the biomass have to be treated by catalytic cracking or thermochemical liquefaction in order to convert to fuels such as gasoline and diesel.

It was recently discovered that cyanobacteria acyl-ACP reductases in combination with aldehyde decarboxylases is necessary and sufficient for converting fatty acid to alkanes or alkenes. *Lipomyces starkeyi* naturally produces high amounts of fatty acids; hence, it is a logical platform for engineering high rate alkane/alkene production. Our project is working to developing an innovative way to produce advanced biofuels (alkanes, alkenes) in vivo using a synthetic biology approach. Cyanobacteria acyl-ACP reductase and aldehyde decarboxylase will be engineered into *Lipomyces* and direct naturally synthesize fatty acid to make alkanes or alkenes. This work will provide extraordinary capabilities for advanced hydrocarbon biofuel development, which is expected to reduce petroleum usage significantly.

In FY 2013, we tested different antibiotic sensitivity for genetic screening in *L. starkeyi* and found that the hygromycin is the best selection marker. After we made several different transformation method attempts with *L. starkeyi*, including LiCl, protoplasting, and electroporation, we successfully developed the *Agrobacterium tumefaciens*-mediated transformation system that allows us to introduce genes into *L. starkeyi*. The transformation system is the foundation of this research. Also in FY 2013, different promoters from *L. starkeyi* were tested for their expression level by engineering a hygromycin selection marker under control of those promoters, respectively. Three promoters were chosen: the *pyrG* gene, the transcription elongation factor (*tef*) gene, and Glyceraldehyde 3-phosphate dehydrogenase (*gapdh*) gene. The *pyrG* promoter drove expression for the hygromycin selection marker.

Two genes from *S. elongatus PCC7942*, acyl reductase (orf1594) and aldehyde decarbonylase (orf1593), were the first codon-optimized for high expression in *L. starkeyi*. Next, acyl reductase was built under the control of the *tef* promoter, and aldehyde decarbonylase was driven by the *gapdh* promoter. All of these gene fragments were built together using yeast gap repair. Finally, the plasmid construct was isolated and cloned into an agrobacterium binary vector that carries cyanobacteria acyl-ACP reductase and aldehyde decarboxylase into *L. starkeyi*. By the end of FY 2013, the alkane biosynthetic pathway was reconstructed in *L. starkeyi*.

In FY 2014, the production of hydrocarbons in our genetically modified *L. starkeyi* system was analyzed by GC-MS. No hydrocarbon was detected. A reporter GUS gene was inserted under the control of *tef* promoter. The GUS activity results demonstrated the expression of *tef* promoter is depending on the insertion orientation. We redesigned an new expression platform, pRF-HU2-pte-f-intron-HpaI-term, using the intron-containing *tef* promoter and its terminator. GUS results showed very strong expression and gene expression is not affected by insertion orientation. This new expression platform will speed up our gene modification and strain development work.

Both acyl reductase and aldehyde decarboxylase were built into expression platform by Gibson Assembly. Both the alkane and aldehyde biosynthetic pathway were reconstructed in *L. starkeyi* using the new expression platform. By investigating the growth condition, different growth medium with different C/N ratio, the medium with C/N 100 is the best for lipid production; therefore, we used the same medium for alkane and aldehyde production. After 7 days of growth, a very small amount of alkane and aldehyde was detected by gas chromatography-mass spectrometry in engineered strains but not in the wild type strain.

The results demonstrated that a synthetic approach can be used to produce oleochemicals that are not naturally produced by the normal *L. starkeyi*. This research will place PNNL at the forefront of biological conversion of biomass to chemicals research using synthetic biology approaches.
We are improving PNNL’s software infrastructure to expedite the implementation and simulation of multi-scale biological system models. Once complete, the software technology will simulate important biological systems of DOE and NIH interests in an unprecedented level of complexity and scale.

Mathematical modeling and computer simulation are becoming an effective tool to understand, predict, and manipulate complex biological systems. Biocellion is a PNNL-owned software technology developed to accelerate large-scale simulation of high-fidelity biological system models using parallel computers. The version 1.0 software supports integrating various biological rules about individual cell behaviors and short-range interactions among cells and their micro-environments but does not support flow integration, which would facilitate long-distance communication and affects many biological system behaviors. Thus, we are extending Biocellion to support flow modeling in the context of large-scale biological system simulation.

Biological system behavior is the outcome of interactions among various biological processes at multiple scales ranging from subcellular molecular reactions to large-scale environmental processes (e.g., water flow). Predicting biological system behavior requires integrating all relevant biological processes and their interactions. Computational modeling is an essential tool in integrating multi-scale biological processes, but simulation of high-fidelity models is computationally expensive. This necessitates high-performance parallel computers and efficient software implementations. As noted, the most recent software version integrates user-provided rules to evaluate individual cell behaviors and local interactions among cells and their microenvironments (via physical contact and diffusion of molecules) but lacks support for water/blood flow modeling. This gap needs to be closed to cover important biological systems.

Modeling static water/blood flow requires solving advection-reaction-diffusion partial differential equations. If water/blood flow changes as the biological system evolves, we also need to solve Navier-Stokes equations (for incompressible flows) to compute flow rates. While Navier-Stokes equations may be used to describe both turbulent and non-turbulent flows, this work will focus on the latter: solving for turbulence demands much greater computational resources and is unnecessary, we believe, to predict biological outcomes of our interest. The CHOMBO package from Lawrence Berkeley National Laboratory has been integrated into Biocellion to solve reaction-diffusion equations. The CHOMBO package provides solvers for advection-reaction-diffusion equations and Navier-Stokes equations. We are extending and modifying Biocellion and CHOMBO to integrate flow modeling and simulation seamlessly with other computational modules at varying spatiotemporal scales.

With a mid-fiscal year start, we integrated CHOMBO’s advection-reaction-diffusion equation and incompressible Navier-Stokes equation solvers to Biocellion. This includes modifying the CHOMBO interface to work with the Biocellion framework, parallelizing CHOMBO solvers using Intel Thread Building Block to share multiple compute cores efficiently within a compute node with other computational modules in Biocellion, and extending the Biocellion API to allow users to set partial differential equation parameters and initial and boundary conditions for advection-reaction-diffusion and Navier-Stokes equations.

This accomplishment becomes the basis for the next release of this software package, Biocellion 2.0. We plan to extend an existing bacterial system model in complex soil structure to include water flow to test and verify the software extension. We expect that the new software release will expedite implementation and simulation of large-scale high-fidelity biological systems models that require flow modeling.
Exploring and Engineering Phototrophic-Heterotrophic Partnerships

Hans C. Bernstein

This project is identifying controllable, cooperative ecological phenomena employed by phototrophically driven microbial communities for conceptualizing and engineering multispecies biocatalytic platforms. The target application for this work is energy capture and transfer from renewable resources, light, and CO₂.

Microbial consortia engineering has become an established scientific discipline populated by interdisciplinary biologists, engineers, and ecologists. The methodology is based on assembling microbial communities through enabling, encouraging, or enforcing interactions between distinct cell populations and their environment. Applications have the widely accepted potential to contribute technology toward key social benefits such as biofuel production, carbon sequestration, and environmental remediation. The soundness of the consortia concept for biotechnology applications is supported by observations in nature. Naturally occurring ecosystems optimized by eons of evolution are almost ubiquitously organized as interacting mixed communities. Of these, photoautotrophic microbial consortia are of keen interest to chemical and biological engineers as promising catalytic systems capable of utilizing renewable resources light and CO₂.

The objective of this research is to dissect metabolically coupled interactions within naturally occurring biofilms from unique environments (i.e., high temperature and hypersaline) to discover ecological cooperation strategies to build engineered microbial consortia. The focus will be on identifying natural biological phenomena between photoautotrophic and heterotrophic microorganisms that can be controlled and harnessed. Our research differs from previously reported microbial community studies because it will advance technical understanding in the context of fundamental and applied science.

Phototrophic–heterotrophic communities were investigated in three separate experiments. The first study used data provided (partially) by external university collaborators and established that both photoautotrophic biofilm communities were capable of producing biofuel “precursors.” We also established the spatially resolved kinetics of photosynthesis and respiration in these systems, which was published in the Journal of Bioresource Technology. The second biofilm community study employed a novel flow-cell bioreactor designed and built for this project to culture and maintain benthic, hypersaline microbial mats. Advanced oxygen microsensor methods were combined with the novel PNNL technology laser ablation isotope ratio mass spectrometry (LA-IRMS) to resolve spatially photosynthetic oxygen evolution, heterotrophic respiration, and carbon fixation. The LA-IRMS methodology has already been published in Environmental Microbiology Reports, and the results portion of this experiment are expected to be published during FY 2015.

Finally, a high temperature “hot-spring” community was cultured in an advanced turbidostat bioreactor and tested for its capability to overcome light and oxygen stress as a community. Preliminary results suggest that the artificial phototroph-heterotroph community performs marginally better (in terms of measured specific growth rate) than the axenic, thermophilic cyanobacteria controls. The results from this portion of the project were presented at an international conference.

The physiology of marine cyanobacteria as potential drivers of synthetic photoautotrophic-heterotrophic consortia was investigated in greater detail by studying axenic growth and photosynthetic performance, for which two studies were completed. The first evaluated the growth and photosynthetic performance of Synechococcus sp. strain PCC 7002 under mono- and dichromatic light regimes, which found distinctions in photoautotrophic functional capacity based on the spectral quality of incident light. These findings were published in Frontiers in Microbiology. A second similar study employed an advanced feedback-controlled turbidostat photobioreactor to investigate/compare the growth and photosynthetic performance of Synechococcus sp. strain PCC 7002 to its transcriptional response during variable incident light intensities and oxygen tensions. This study found that Synechococcus sp. strain PCC 7002 is an extraordinarily robust organism that is more resistant to environmentally induced stress from light and oxygen than other “typical” unicellular cyanobacteria. The results from this work have been submitted for publication.

For FY 2015, we are performing sample and in situ ecophysiological data collection as well as ex situ bioreactor culturing and characterization of natural microbial consortia. We are also continuing the experimental design and stable isotope pulse-chase experiments.
Fungal Siderophore Production for Recognition of Uranium Compounds

David S. Wunschel

We are using fungal siderophores as adaptable metal recognition molecules that can be engineered to function as ligands for uranyl species. These ligands will enhance the selectivity of detection platforms and focus on the products of human enrichment activities.

Uranium is a natural element and, as the 49th most abundant element, is present in 5% of minerals at parts-per-million (ppm) levels. The chemical forms of uranium found in the environment are varied, complex, and impacted by biotic and abiotic factors. Anthropogenic enrichment of uranium usually involves uranium hexafluoride (UF₆), which degrades in contact with water, even atmospheric water vapor. Uranyl fluoride and hydrofluoric acid form during the addition of water, followed by degradation to varying types of uranium oxides and uranyl salts that depend on environmental conditions. The selective binding and immobilization of a broad selection of uranium containing compounds have been of interest for characterization and cleanup of contamination. Tools to extract anthropogenic forms of uranium selectively may also enhance analytical tools for treaty verification.

A number of mechanisms for binding metals, including techniques such as ion exchange resins and filtration, have been suggested for remediation. However, these approaches lack specificity for target metals. Organic synthesis of ligands has also been investigated as a solution for binding uranyl compounds, but this process is laborious, time-consuming, and expensive, making synthesis of a large compound library unsuitable for scale-up and testing. Naturally occurring mechanisms of metal immobilization provide an attractive alternative to this problem where organisms can be used to synthesize and secrete mg/L concentrations. Using biological pathways to perform multi-step synthesis is far faster and easier to scale up than purely synthetic routes.

For this project, we examined siderophores with hydroxamate and carboxylate functional groups as putative mechanisms of binding to understand which have a relatively greater binding affinity for UO₂ than for Fe at pH below 4. The first steps were to develop methods for detecting and characterizing the siderophores from fungal cultures. The tools included a colorimetric assay for siderophore binding to screen supernatants and purified fractions, an HPLC separation to create chemically pure fractions, and ESI-MS/MS for identification of the compounds based on the mass and fragmentation patterns. Having the siderophore production and characterization tools in place was vital to determine the binding specificity of different siderophores. We used ESI-MS as a tool to assay competitive binding experiments between uranyl acetate and varying concentrations of iron. The relative abundance of the Fe and UO₂ bound forms of each siderophore was observed over an iron concentration range and two pH values.

In FY 2013, the tools for performing the comparative analysis of siderophores were developed, including the fungal culture system, the iron binding activity assay, HPLC separation, and ESI-MS assay for UO₂ affinity. For this year, we focused on using these tools to understand the relative importance of different functional groups and UO₂ binding at decreasing pH. Specifically, one of the project goals was to compare the relative binding affinity of hydroxamate and carboxylate forms of siderophores for their UO₂ binding affinity relative to Fe at pH 5 and 3.5. A number of siderophores could be purchased, including the hydroxamates desferrioxamine and desferrichrome as well as the carboxylate desferrichrome A. A second carboxylate siderophore, malonichrome, was not available for purchase and was purified from Aspergillus oxyспорium cultures grown under Fe limiting conditions. A reverse phase HPLC separation was used to fractionate culture supernatants and a fraction having siderophore activity was isolated and analyzed by ESI-MS/MS. The mass and interpreted fragmentation data matched malonichrome.

The hydroxamate siderophores desferrioxamine and desferrichrome each showed decreasing affinity for UO₂ relative to Fe at pH 3.5. The two carboxylate siderophores desferrichrome A and malonichrome, showed similar affinity for UO₂ at both pH 5.0 and 3.5 with Fe displacing it equally well at each concentration and each pH. The siderophore malonichrome

Relative binding affinity for desferrichrome and desferrichrome A for UO₂ relative to Fe over a 0.065 to 0.1 mM Fe concentration, observed as the ratio of Fe to UO₂-bound form of each siderophore, which is lower for the carboxylate desferrichrome A at each concentration and pH.
showed the highest affinity for UO$_2$ (i.e., least displacement of UO$_2$ by Fe with increasing concentration) among the siderophores examined.

The position of UO$_2$ binding in the gas phase was examined for desferrichrome and desferrichrome A complexes by tandem mass spectrometry. Fragments associated with UO$_2$ following dissociation were identified as well as those portions of the molecule not associated with UO$_2$. The UO$_2$ ion was found associated most strongly with the carbonyl groups of desferrichrome than the hydroxamate groups. Analysis of the desferrichrome A showed that the carboxylate groups were, surprisingly, not the clear point of interaction with UO$_2$. This is despite the binding evidence illustrating a stronger affinity for UO$_2$ by desferrichrome A than desferrichrome.

The capabilities developed in this project allowed investigation of UO$_2$ binding by a variety of siderophores. Specifically, the impact of siderophore functional groups and pH on binding was examined. The results illustrated that the carboxylate siderophores have relatively stronger affinity for UO$_2$ at the lower pH values that are relevant for binding of soluble UO$_2$ species. The carboxylate siderophores need to be explored further as a class of compounds that offer increased affinity and selectivity for binding UO$_2$. These natural ligands can be used as tools to extract anthropogenic forms of uranium selectively in order to enhance analytical tools for treaty verification.
Genome-Enabled Systems Approach to Predict Immobilization of Technetium in the Subsurface

M. Hope Lee

Our research is an important first step for demonstrating the effectiveness of applying high throughput molecular techniques and metabolic models for monitoring and predicting technetium (99Tc) transformation. Data and modeling will provide important insights into coupling microbial activity to reactive transport and hydrological models currently used for remediation.

For the past three decades, 99Tc has been released into the subsurface through fallout from weapons tests and discharges from active nuclear processing plants and other facilities. 99Tc has a relatively long half-life, is soluble and mobile in groundwater, and can be absorbed by plants and animals. As such, if left untreated, 99Tc poses a risk to the environment and human health for thousands of years. Although much has been learned about the physiology and metabolic potential of single microbial species (pure cultures) that immobilize 99Tc, major gaps exist in our understanding of the function of these and other microorganisms in natural and contaminated ecosystems. Tools that integrate the chemical and biological reaction network influencing 99Tc mobility in the subsurface need to be developed and tested.

In this project, we are testing the utility of cultivation-independent molecular tools, such as high throughput sequencing techniques coupled to genome enabled community-level metabolic models, as a method for predicting and controlling the biotic component of 99Tc immobilization. While other metabolic models have been validated (some for contaminated subsurface environments), our stoichiometric metabolic modeling approach simplifies the microbial community into key or central metabolisms and is not based on cultured surrogates or well characterized single microbial members. This type of modeling has been used successfully to analyze natural and engineered microbial systems on a pure culture and community level and defines a network’s metabolic potential based on a complete listing of the simplest, non-divisible pathways.

Bioreactor experiments from FY 2013, where iron and lactate were monitored, provided a foundation for work conducted in FY 2014. Progress this year was established through compiling genome information from the literature and through sequencing of ES6 as well as growth information gained through batch studies of mixed communities. Metabolic models will bring all of these components together and provide a tool for predicting the impact of microbial systems on contaminants like 99Tc in the subsurface at the Hanford site and beyond.

Specifically during FY 2014, the project achieved the following accomplishments. First, cultures of dissimilatory metal reducing bacteria (DMRB) isolated from Oak Ridge Field Research Center (FRC) sediments (Geobacter sulfurreducens strain PCA, G. daltontii strain FRC-32, and Anaeromyxobacter dehalogenans sp. strain 2CP-C), from Hanford subsurface sediments (Cellulomonas sp. strain ES6), and from freshwater lake sediments (S. oneidensis MR-1), were obtained and cultured. These specific bacteria were chosen because they have been shown to reduce metals and radionuclides chemically. In addition, genome sequence information that will be used to inform the metabolic models is available for all species but the Cellulomonas sp. strain ES6; however, the genome of ES6 has been successfully sequenced and is currently being assembled and annotated. Information from the annotation will be used to complement and enhance our metabolic model of 99Tc reduction.

Initial experiments have been performed to look at metal reduction using ferric iron (Fe(III)) as a surrogate. All five metal reducing sediments were shown to reduce Fe(III) in SAG media. Batch experiments were conducted using axenic cultures of each organism to monitor 99Tc reduction. In addition, a combination of three (PCA, 2CP-C, and MR-1) and all five organisms were co-cultured to provide insight into community interaction during microbial 99Tc reduction in the subsurface. These experiments also used Hanford fine sands. Data from these batch experiments show biotic and/or abiotic 99Tc reduction in the presence of the mixed microbial combinations when compared to cell free controls and negative controls without Hanford fine sands.

Finally, metabolic models for individual species have been initiated using genome information available for the above cultures in DOE’s Joint Genome Institute (JGI). A community level metabolic model, which will provide knowledge on carbon and electron flow within the community and how that affects 99Tc reduction, has also been initiated. Growth information from the literature and experiments performed has also been used to estimate biomass production rates. This model is based on elementary mode analysis and different methods of combining each species metabolism are being performed. We are setting up advanced hardware and software for developing these metabolic models.
Global Forensic Chemical Exposure Assessment for the Environmental Exposome

Justin G. Teeguarden

We are developing technology that allows measurement of thousands of biomonitoring chemicals important to public and environmental health. These efforts will revolutionize the way in which chemical effects are studied, safer energy technologies are developed, and prediction of and response to global climate change effects.

Human and ecological health is widely recognized as the product of the genome and its environmental analogue the exposome: the comprehensive history of exposures to natural and manmade agents within individuals and populations. In the absence of corresponding knowledge regarding human chemical exposure and its interaction with the genome, however, information from the Human Genome Project has been insufficient for making these predictions. Advanced analytical PNNL-developed instruments offer the chance to provide missing information by performing measurements that were previously not possible. An example of this advancement is quantifying thousands of structurally diverse chemicals simultaneously within single samples of blood or other fluids used for biomonitoring of exposure. This project was initiated to perfect the application of PNNL’s advanced instruments in making these measurements with the analytical approach of ion mobility spectrometry-mass spectrometry (IMS-MS).

Developing a reference library of chemicals and their unique chemical signatures measured by IMS-MS was the overall objective during our FY 2014 project initiation. The chemical signatures included IMS drift times and accurate masses, which became the basis for the high throughput, accurate quantification of the chemicals. To date, we have developed a reference library and signatures for 300 chemicals. We discovered that by using two different methods of ionizing before analysis, chemicals with diverse physicochemical properties (e.g., hydrophobic, hydrophilic, with or without chlorines, acids) could be identified and quantified. This method is an important advancement over those that focus on one class of chemicals and supports our goal of developing a technology that works for most or all types of chemicals.

Mixtures of the chemicals were analyzed to determine sufficient resolve and instrument sensitivity to the chemicals. A key finding was that the IMS-MS platform provided extraordinary resolution and could detect chemicals down to the parts per trillion range in solvents, ideal for analyzing tissue and fluids for environmental chemicals. The technology separated all of a subset of chemicals we tested from thousands of endogenous chemicals in blood (e.g., lipids, metabolites). This finding demonstrated that the approach would allow simultaneous identification and quantification of chemicals normally in our body in addition to environmental or manmade chemicals introduced into the body. For blood, we achieved detection limits up to the parts per billion range.

To overcome a major obstacle in the field, advanced computational approaches were devised to enable the prediction of unique chemical signature for chemicals without the need for experiments. 3D simulations of chemical structures and quantitative structure-property models are used to assign the unique chemical signature to untested chemicals. Further, partnerships were developed with Oregon State University and the U.S. Environmental Protection Agency are advancing the application of technology to chemicals important for health and energy production: flame retardants, pesticides, herbicides, and plastic components, to name a few. We now have access to more than 1500 chemicals for testing.

In FY 2015, we will improve chemical detection limits in blood samples by one order of magnitude, adding a novel high pressure liquid chromatography separation dimension. We will extend the chemical reference/chemical identity library two- to three-fold as our partners provide additional chemicals. Finally, we will apply the technology to a relevant cohort of human chemical exposure(s), the first time that chemicals of such diversity will be quantified in human blood samples. Ultimately, we wish to achieve our ultimate objective of simultaneous measurement of chemical exposure – and response to that exposure – in single human blood samples.
Imaging and Monitoring the Initial Stages of Biofilm Formation

Raymond S. Addleman

The analytical capabilities developed in this project will enable unprecedented visualization, characterization, and understanding of the initial molecular and cellular processes involved in biofilm formation.

Systematic studies of the initial stages of biofilm formation – the conditioning film and primary colonizers – are lacking in literature largely due to the complex nature of the problem as well as the absence of available tools for studying the process. We are leveraging advanced chemical imaging techniques that have been recently developed at PNNL to improve the understanding of initial biofilm formation and subsequent surface biofouling. This interdisciplinary effort will provide better tools and a mechanistic understanding of the initial biofilm formation process on existing and novel material surfaces. Having new tools to study the processes that lead to biofilm formation will support the development of new, innovative, non-toxic means to combat fouling relevant to DOE missions in hydropower, efficient desalination, ship transport, bioremediation, and improved separations and catalysis as well as biomedical and other applications.

Key issues in our research include determining which new analytical methods are best suited to visualize and characterize the initial stages of biofilm formation. We will investigate how surface structure at the nanoscale and microscale affects the composition and structure of the initial biofilm and how surface chemistry and physical properties (e.g., hydrophobicity, hydrophilicity, surface roughness, surface patterning) affect the composition and structure of the initial biofilm and rate of formation. Another topic of consideration is whether the initial biofilm is deposited at random, as a uniform film, or is concentrated around identifiable nucleation points. We will also examine how the composition and structure of the resulting biochemical-organic layer affect the initial deposition of colonizing cellular organisms and consider how improved imaging data can provide a mechanistic understanding of how to construct multiscale materials to minimize and prevent biofouling.

A critical challenge for the study of biofilms has been the lack of methods and instrumentation that can perform detailed measurements and monitoring of wet surfaces. Our mid-year start in FY 2013 focused on evaluating recently developed techniques and developing new analytical methods. The imaging and analytical techniques explored in 2013 and into 2014 provide tools for fundamental science studies as well as new methods for quantitative and qualitative biofilm assays for a variety of applications. The specific imaging and analytical techniques in development include the following:

- MALDI-TOF has shown to be effective for biochemical characterization during biofilm formation
- X-ray microtomography has shown to be effective for structural characterization of biofilms
- Ultrasonic imaging has shown in situ monitoring of the growth of biofilms
- Digital quantification of biofouling has shown in situ monitoring of the growth of biofilms
- Optical Interferometry has shown in situ monitoring of the growth of biofilms.

The study of antifouling surfaces in FY 2014 resulted in the creation of a novel paintable superhydrophobic, ultralow surface energy, and self-healing surface that is nontoxic and has outstanding resistance to biofilm formation. Shown is the Chemical Imaging Initiative acronym painted in this water repellent coating, surrounded by water.

The study of antifouling surfaces has resulted in the creation of a novel paintable superhydrophobic, ultralow surface energy, and self-healing surface that has outstanding resistance to biofilm formation. The study of antifouling surfaces in FY 2014 resulted in the creation of a novel paintable, superhydrophobic, ultralow surface energy, and self-healing nontoxic surface that has outstanding resistance to biofilm formation.

For FY 2015, we will continue to explore new methods to monitor the composition of biofilms as they form. We will monitor the impact of surface composition (structure and chemistry) of the initial cellular settling and colonization processes and determine sequential dependencies of molecular deposition onto surfaces. With these demonstrated methods, this project will explore biofouling on selected materials in two focused, high impact areas: marine biofouling and biomedical-related biofilm formation. The biofouling processes as a function of time and surface composition will be studied quantitatively.
Multi-Scale Processes Controlling Spatial Variation in Greenhouse Gas Emissions in a Subarctic Watershed

James C. Stegen

This project combines field measurements with simulation modeling to deepen understanding of and reduce uncertainty in predicted greenhouse gas emissions across permafrost to non-permafrost transition zones.

Microbial communities play a central role in the functioning of natural ecosystems by heavily influencing biogeochemical cycles. A major scientific challenge is to use knowledge of those influences to improve the ability of Earth System Models to predict future climate change by incorporating feedbacks between environmental change and biogeochemical rates. Understanding how shifts in the environment are tied to those in biogeochemical rates via changes in microbial communities is relevant in high latitude terrestrial systems underlain by permafrost due to vast carbon stocks currently stored within (now thawing) permafrost.

As increased greenhouse gas emissions from thaws could produce positive feedbacks that accelerate the rate of climate change, there exists a high degree of uncertainty in model predictions because fundamental processes are poorly represented in climate models. Therefore, our research objective is to gain new knowledge of factors that govern observed patterns in the rates of greenhouse gas (CO\textsubscript{2} and CH\textsubscript{4}) emissions associated with permafrost to non-permafrost transition zones. We will use that knowledge to improve the representation of soil microbiology in the Community Land Model (CLM).

At project start-up, we used field studies to generate data needed to test CLM predictions and provide hypotheses for how the model may be improved through the inclusion of additional biotic (e.g., microbial community composition) and abiotic (e.g., organic carbon composition) features. Near Fairbanks, Alaska, the field site is characterized by spatial transitions in the presence/absence of permafrost and in active layer depth (soil overlaying the permafrost). Across these spatial transitions, greenhouse gas emission rates are being directly measured, and biotic/abiotic features of the associated soil environment are being characterized.

Results show a strong relationship between the active layer depth and CO\textsubscript{2} emission rates but only across the lowest elevation sites with the thinnest active layer depths. This result points to a highly non-linear influence of active layer depth on CO\textsubscript{2} emissions at the landscape scale. Field sampling designs have been implemented for the upcoming field season to characterize this non-linear relationship and understand how other environmental features contribute to the non-linear behavior. Beyond the active layer depth, soil cores were taken across the spatial gradients in the active layer depth. Soil core material was characterized by numerous biotic and abiotic characteristics, including microbial community and organic carbon compositions. Since mid-FY 2014, 28 samples have been analyzed.

In addition to the above activities, we completed initial Biome-BGC model runs. Field-observed non-linear relationship between respiration rate (i.e., CO\textsubscript{2} emissions) and soil depth did not emerge in the model predictions. This is an important outcome, as the project was formulated to leverage deviations between predicted and observed patterns to gain new insight into key features and processes currently missing from (and thus limiting the predictive ability of) ecosystem models. Focusing on the non-linear behavior of CO\textsubscript{2} emissions across active layer depths is therefore a prudent choice and is likely to generate fundamental knowledge relevant to ecosystem-scale modeling efforts.

We are pursuing additional simulations to determine the degree of correspondence between field-observed CO\textsubscript{2} emissions and CLM predictions. Current field efforts are generating direct estimates of CLM input parameters and quantifying how the parameter values change along active layer depth gradients. Going forward, these estimates will be used to run multiple instances of the CLM single-site version across active layer depth gradients. This approach takes CLM—a global-scale model often run on 10 km\textsuperscript{2} grid cells—down to the scale of field observation (~10 m\textsuperscript{2}), thereby reaching across an extreme disparity in scale. In addition to CLM parameter estimates, the project recently generated ~1000 point measurements of CO\textsubscript{2} emissions across active layer depth gradients for comparison to CLM predictions.
Optofluidics and Microfluidics for Exploring Biofuel Production at the Single Cell and Molecule Levels

Andreas E. Vasdekis

This project investigates biofuel production at the single cell level. By treating cells as a single biochemical factory, biofuel production efficiency and timing will be measured precisely, hence unmasking better performing traits.

Our society’s prosperity and growth is inevitably linked to reliable energy sources. Due to climate changes, increasing energy demands, and finite fossil fuel reserves, sustainable prosperity and growth necessitate the use of renewable energy sources such as solar, wind, or biofuel. These are of key importance due to their compatibility with our current transportation infrastructure. Despite substantial advancement during the past decades, there is still a plethora of unknowns related to such alternative energy sources, especially within the context of efficiency and species selection or design. In this project, we are addressing such challenges by directly imaging biofuel synthesis at a controlled cell and molecule density down to the single entity. At this level, the cell acts as an isolated chemical factory while its synthetic performance can be precisely characterized, unmasking invisible spatiotemporal phenomena and improved performance. The project’s methodology is based on cell handling microsystems, chemical imaging of biosynthesis, and ‘omic analyses (i.e., transcriptomics and proteomics) of such pre-analyzed microorganisms.

In FY 2014, we expanded on last years’ activities, reaching primarily two milestones: integration of 3D optical sensors in microbioreactors and investigation of microbial growth and cell biosynthesis in microfluidics. The work was collaborative, including academic partners at MIT (USA) and EPFL (Switzerland). For optical sensing, the focus was on oxygen, an element of significant implications, as it is one of the most important electron acceptors in bioprocessing. Unlike previous methods, we implemented solvent immersion imprint lithography, enabling imprinting of microfluidic systems and impregnation of microfluidic walls with an oxygen-sensing chemical moiety. This approach enabled two unique characteristics. The first was processing simplicity, requiring simple benchtop processing based on widely available organic solvents. The second unique element was the ability to impregnate all surfaces of the microfluidic channel uniquely enabled by solvent immersion lithography (SIL), giving rise to a 3D distribution of sensing moieties and thus to an enhanced overlap between sensor and analyte. We have shown that this approach leads to higher sensor sensitivity.

For cell physiology and growth in microfluidics, previously published single-cell isolation methods (from FYs 2012 and 2013) were implemented to demonstrate the applicability of such assays in single-cell immobilization for prolonged periods for exploring intracellular events and growth. Regarding the former, diatoms were selected (in collaboration with PNNL at Sequim) along with oleaginous yeast *Yarrowia lipolytica* (with MIT). Both cell types were successfully immobilized for over 12 h. Specific to diatoms, the biosynthetic properties were monitored via fluorescent imaging of intracellular protein kinetics. For cell growth, a proof-of-concept investigation involved *Shewanella* (p519nGFP strain). It was shown that such demanding strains grow under conditions of sub-microfluidic isolation, hence indicating that physiological conditions are characteristic of these assays.

In FY 2015, the project will expand upon the aforementioned deliverables to directly image the synthesis of biofuels at the single cell level. The focus will primarily be on the oleaginous yeast *Yarrowia lipolytica*. Microfluidic integration of ‘omic techniques will enable genome-wide analyses of pre-screened individuals.
Predicting the Response of Complex Biological Systems

Karin D. Rodland

This project integrates data from multiple imaging and mass spectrometry (MS)-based technologies to predict complex biological system response to external stressors. In addition to furthering PNNL’s capabilities in systems biology, we will explore applications relevant to human health.

Recent technical improvements in genomics, high-throughput proteomics and transcriptomics, and other analytical technologies provide biologists with powerful tools for describing the behavior of simple cellular systems. What has been missing are predictive capabilities that enable the manipulation of biological systems for desired outputs in bioenergy, bioremediation, and mitigation of harm in response to stressors such as ionizing radiation. Achieving this predictive capability requires continued technological improvements in both experimental systems and analytical tools, including imaging and developing new computational approaches and mathematical models that allow molecular-level data to be scaled to cells, cell communities, tissues, and organisms. The goal would allow us to predict, manipulate, and potentially design multi-cellular systems that contribute to DOE goals in bioenergy, contaminant fate and transport, carbon sequestration, and global climate change.

This project applies unique PNNL capabilities in ‘omics measurements, imaging, and computational modeling and simulation to promote the transition of biological science from merely describing biological phenomena to predicting – and eventually controlling – the response of complex biological systems to perturbation whether in the form of environmental stressors, changes in climate, or deliberate manipulation to enhance performance (e.g., biofuel production). Chief among the capabilities required are improved imaging systems that incorporate PNNL strengths in MS, nuclear magnetic resonance (NMR) spectroscopy, and emerging strengths in chemical imaging.

One of the specific subtasks in this project combines MS and NMR to provide a 2D image of biochemical changes in the brain. Integrating and interpreting data that arise from such combined imaging modalities requires the application of novel computational tools for registering and adjusting multiple inputs. While existing research has often focused on simple model systems consisting of one organism or cell type, it is increasingly clear that predicting the behavior of real biological systems requires model systems that incorporate realistic levels of cellular complexity while allowing accurate measurement of individual components. Application of systems biology tools to such complex model systems is another goal of this project. Finally, if the goal is prediction of response, then there is an urgent need to apply new computational tools that can simulate the behavior of complex biological systems accurately over time and space, and then extrapolate to predict the response to perturbation.

During FY 2014, predictive capabilities successfully developed under this project included panomic characterization of roles of Msx genes in development, quantitative nano-DESI imaging of neuroprotective metabolites, genetic analysis of Salmonella virulence, multiscale investigations of spatially heterogeneous alveolar stress, and the development of monoclonal antibodies to detect oxidative stress. The specific tasks undertaken this year, along with their outcomes, are described below.

Multi-modal imaging of complex biological systems. We applied unique PNNL capabilities in imaging MS (nanoDESI and MALDI) to identify the molecules responsible for protective responses to hypoxic stress.

Characterization of complex microbial communities. A combination of MS and NMR methods were developed for analyzing the metabolic activities of the human gut microbiome on host factors (bile acids) to characterize more precisely the interaction between the microbiome and its changing environment in addition to the host-microbiome interactions.

Characterize the protein modifications indicative of inflammatory responses. A combination of MS and antibody-based technologies was used to identify protein modifications induced by environmental stressors.

Development of advanced computational tools for the integration and interpretation of “big data” generated by ‘omic technologies. A variety of computational tools were developed to increase the utility of large datasets generated by PNNL’s ‘omic technologies. These included predictive models of genetic factors conveying virulence in Salmonella typhimurium, spatio-temporal models of spatially heterogeneous alveolar stress, and integration of multiple ‘omic measurements to describe the role of Msx genes in early development and implantation.

A total of four manuscripts were published, eight manuscripts have been submitted, and six grants or subcontracts have been funded based on the contributions as a direct result of work that has been completed under this project.
Catastrophic events such as that in Fukushima, Japan can result in significant radiation release and exposure to plant workers and large populations. Most studies of pulmonary radiation exposure effects have focused long-term cancer occurrence from low-dose medical exams or acute tissue damage from high-dose radiation oncology. Few studies have examined radiation exposure impact on whole-organ mechanical function, which is critical to gas exchange. Recent work at PNNL suggests that lung disease that is not detected by conventional imaging or histology can induce mechanical changes that may be detected using a new dynamic imaging approach.

The objective of this project is to develop an improved understanding of the fundamental pulmonary mechanical changes due to radiation exposure. By studying animal disease models, we can begin to recognize the effects of radiation on the lungs and develop a diagnostic approach translatable to humans critical to understanding the basic physiological response and disease course. We anticipate that our work will result in clinically translatable technical advances in dynamic pulmonary imaging and image analysis. This project will also develop a reliable animal model of lung radiation damage for future work of this nature.

In FY 2012, we standardized the radiation exposure protocol for rats, including development of contoured, rat-specific animal holders and a lead collimator to limit exposure to other organs. We developed and refined methods of the CT image analysis, including non-rigid registration of image data for ventilation map calculation, which was published in the international peer-reviewed journal PLOS ONE. By the end of the year, we found that pulmonary function tests and physiological measurements of body and lung weight and the like generally did not correlate with radiation dose. However, close inspection of the ventilation maps indicated differences in ventilation homogeneity between exposure groups.

Few (if any) standard methods of assessing image homogeneity currently exist. Therefore, during FY 2013, we developed a new method to compare the raw CT images and ventilation maps between exposure groups. This approach combines techniques octree decomposition (from computer science) and variogram analysis (from geostatistics). The application of this novel approach revealed differences between groups that were not obvious with other measurements. In particular, a dose-response relationship was discerned through subtle differences in image homogeneity as determined by the octree/variogram method, the results of which are published in the journal Academic Radiology. We successfully applied this technique to another animal model that was developed under a separate project.

In FY 2014, we developed and applied an automated method for detecting airway septal wall thickening. This work was done in collaboration with Oregon Health & Science University using an animal model developed in neonatal mice. The model of septal wall thickening is directly applicable to radiation exposure because it is often a direct consequence of radiation-induced lung damage. The well-developed model and available histology slides provided an ideal avenue for testing the automated program against the manual measurements. Results were presented at the American Thoracic Society (ATS) meeting in May. In addition, we performed an experiment to validate the 4DCT ventilation maps against particle deposition patterns in diseased rat lungs. This was important to validate the 4DCT approach to image analysis and disease detection. Results were presented at the Society of Toxicology and ATS meetings in 2014. A paper has also been submitted for publication detailing the results.

We continued to develop the 3D variogram approach to lung heterogeneity analysis, and we applied it to available human image sets in preparation for an National Institutes of Health submission. Additionally, we submitted a patent application related to this work.

<table>
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<th>Method</th>
<th>B6 (μm)</th>
<th>KO (μm)</th>
<th>Difference (μm)</th>
<th>P-value</th>
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<td>5.76</td>
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Results of septal wall thickness measurements, where the values represent the respective median for each sample. Both techniques showed that the B6 mice had a significantly smaller septal wall thickness than the TRAIL mice. For the selected threshold level, the median wall thicknesses measured manually and automatically were similar. The total number of manual measurements was 1060 (B6 = 609; TRAIL = 451) compared to 5035 data points from the automated approach (B6 = 2264; TRAIL = 2699).
Rapid Viability Assays for Biothreat Event Characterization

Janine R. Hutchison

This project uses PNNL’s expertise in bacterial detection and analysis to develop a field-based method to assess bacterial viability (is the sample alive or dead?) and the associated threat (will this cause disease?) of unknown environmental samples.

The identification of bacterial pathogens in environmental and clinical samples is important for a variety of environmental, national security, and medical applications. The response to a biological threat hinges largely on the knowledge of whether an identified organism can grow and subsequently cause disease (i.e., its viability status). As this information will guide the proper response and remediation, the time to detection and characterization is a critical parameter for protecting lives and containing exposure. While methods to detect and identify biological agents have been effective, significant challenges still exist in the follow-on determination of the biological threat agent’s viability. For example, detecting DNA in an unknown sample can reveal the identity of the organism (such as *Bacillus anthracis* vs. *Yersinia pestis*), yet this identification does not provide indication of the organism’s viability and therefore its potential to cause disease.

Rapid knowledge of the viability status of an unknown sample would greatly enhance downstream response and actions during remediation and recovery. Current viability methods rely on a laboratory-based cultivation step that takes hours delaying decisions made during a threat scenario. In this project, we will enable field-based detection for first responders and scientists to assess threats during a biological threat. Specifically, our project is focused on evaluating bacterial viability methods for *Bacillus anthracis* spores and *Yersinia pestis*. The aims of this effort include the development of rapid (<60 minutes) viability assays for bacterial cells (*Y. pestis*) and bacterial spores (*B. anthracis*) and the subsequent integration of these assays into biological detection technologies, with the end goal of rapidly characterizing biological threat events to inform both response and recovery.

To accomplish our goals, we are using three different approaches that can be coupled together. Our first approach is based on the premise that DNA within non-viable cells cannot be amplified, any DNA detected post-treatment must have originated in a viable cell. The second approach maximizes the differential permeability of live and dead cell membranes. We have coupled fluorescent cell staining with microscopy (traditional and cell phone-based) to identify organisms via specific molecular markers and differentiate live vs. dead cells. An unexpected outcome has been development of a 3D printable cell phone microscope. The PNNL design is unique in its low cost and disposable nature of the device. The final approach builds on our past work in the areas of rapid bacterial culturing. This experience enabled us to identify optimized growth and germination conditions to reduce overall detection time four fold.

We developed and optimized a biochemical approach to detect *Y. pestis* and *B. anthracis* samples in the presence of non-biological interferents (milk powder, baking powder, and coffee creamer). This assay is not only able to distinguish live from dead cells, but it also provides molecular-based detection, which provides DNA confirmation to identify the type of organism (e.g., *B. subtilis* vs. *B. anthracis*). We have also developed rapid growth conditions that germinate *B. anthracis* spores to the metabolically vegetative form in 4 h. This change can be monitored using the cell phone-based microscopy platform developed by our project team. Together, this method allows for the rapid detection and assessment of the bacterial viability.

In FY 2015, we will complete and be submitting our first manuscript describing our results of using biochemical assays to assess *Y. pestis* and *B. anthracis* viability. We will work toward integrating our viability methods with current detection technologies, which will provide additional methods for the detection and characterization community and enhance our ability to respond to a biological threat.
Rhizosphere Underground: Unraveling the Role of Microbes in Stabilizing Carbon Pools in Soils

Alice Dohnalkova

This project is developing a multi-capability platform for correlative imaging and analyses to investigate cellular and mineral association and interactions in the rhizosphere. This multi-modal, multi-scale imaging and analytical platform will be applicable to a variety of other biological systems that interact with minerals or other materials.

Microorganisms are fundamental to biogeochemical cycling, as microbial metabolism significantly contributes to the regulation of terrestrial carbon and nitrogen cycling. However, the impact of the community of soil microbes within the mycorrhizosphere has not been examined in detail due to the difficulty of tracking microscale processes in natural microbial communities in complex soil habitats.

This platform will be used on a model ecosystem to identify interactions of individual microcosm components: roots, fungi, microbial communities, and soil minerals. Special emphasis is given to formation of microbial extracellular polymeric substances (EPS) that may contribute to recalcitrant pools of microbial products with mineral surfaces and as organic matter (SOM). In particular, we will examine the current hypothesis that preferential association with mineral surfaces and soil pores is an important mechanism of carbon sequestration. Our imaging approach will provide fundamental high-resolution 3D information that will contribute to the better understanding of the factors influencing carbon flux and C sequestration and toward the scheme of microbial carbon pump in soils.

Seedlings of Pinus resinosa, a widespread North American pine forests ecosystem, was cultivated under experimental conditions in well-defined soil mineral mix (quartz, biotite, and anorthite) with bacterial and symbiotic fungal inoculum to develop biofilms and mycorrhizal associations. The mesocosms were destructively sampled at time points and investigated through the suite of imaging and analyses for extracted and fractionated labile and recalcitrant SOM. Datasets will be correlatively evaluated, and a mechanistic model will be created from the integrated databases that will connect microbial function to ecosystem processes.

We designed and are fine-tuning the multi-capability scheme of visualization and chemical imaging and analyses of system components: the top-down scheme implements instrumentation in the range of scales and resolutions, including X-ray tomography for overall root layout, confocal microscopy for identification of biofilm-rich areas to be sub-sampled for electron microscopy (EM), and high resolution EM for microbial-mineral interactions. We are coupling imaging with extractions of root microbial system for FTIR-mass spectroscopy to identify the carbon species involved in the process. In addition, we are building on EMSL’s state-of-the-art instrumentation and expertise to create a multi-modal, multi-scale imaging and analytical system to provide an integrated workflow with seamless consecutive steps in multi-scale investigations from micrometers-scale to atomic level in imaging or to the respective resolution limits of coupled chemical analyses.

Our work in FY 2014 applied this platform with addressing specific hypotheses in the model ecosystem: with the first FTICR results suggesting specific microbial roles in the soil systems, we added methods of DNA extraction and segmentation to address the structure to function question. The other hypotheses included 1) coexisting heterotrophic microbes as a part of the biofilm, seeking source of organic labile C; 2) anticipated pattern in preferential bacterial attachment to the mineral substrate, involving EPS as a surface adhesion agent; 3) organic hydrocarbons produced by microbes due to their viscoelastic properties would start filling the soil pore spaces, thus altering the system’s transport (possibly inducing soil material clustering); and 4) the formation of soil aggregates will physically shield otherwise labile SOM from microbial decomposition.

Multi-scale imaging: X-ray tomography visualized the designed root (yellow) and soil material (gray) components. Follow-up confocal microscopy shows the root (blue) and minerals and microbial community (red) correlated with SEM of bacterial cells and their extracellular polymeric substances. The FTICR-MS spectra show the labile carbohydrates produced by microbes.
Signatures of Environmental Perturbation – Microbial Community and Organic Matter Resilience

Vanessa L. Bailey

The overarching goal of this project is to use existing capabilities to discover one or more signatures that indicate impaired resilience of the soil carbon biogeochemical system following a system-wide perturbation such as simulated climate change.

The microbial metabolism of soil carbon leads to the release of the greenhouse gases into the atmosphere, which directly impact global climate by exerting a strong positive feedback effect on temperature (i.e., global warming). Currently, analytical tools do not assess the vulnerability of soil carbon reservoirs to changing climate conditions, but it is likely that microbial metabolism of soil carbon will increase with temperature, resulting in even greater gas emissions. The structure and function of the native microbial community is intimately linked to soil carbon by both the deposition of new soil carbon and respiration of existing soil carbon as part of the terrestrial ecosystem carbon cycle. By integrating key chemical and molecular signatures of the soil system, microbial community resilience and soil carbon reservoir vulnerability may be predicted with molecular resolution. Thus, the potential for more greenhouse gases to be released from native soil carbon can be better predicted as well under these changing environmental conditions.

The focus on ecosystem stress and climate change is currently relevant, as researchers and policymakers strive to understand the ecosystem consequences of climate change. Successful development of chemical/molecular profiles that link soil microbiology with soil carbon to ascertain soil vulnerability and resilience would have great impact on assessments of soil ecosystems in response to global climate change. These integrated signatures could be used to support the design of sustainable agricultural and food/energy crop security practices. In addition, these efforts align directly with research performed by DOE, USDA, and the National Science Foundation, and the ecosystem stress associated with pollution events may be of interest to multiple other federal agencies.

This project aims to move soil biogeochemistry and ecology toward a more informed understanding of the relationships between carbon chemistry, microbial community structure and function, and ecosystem perturbations. The demonstration that our analytical tools can be integrated to identify such signatures in a complex system such as soil has the potential to transform classical ecological research. To this end, we are leveraging an existing long-term experiment at the Arid Lands Ecology Reserve in Richland, WA in which soil cores were reciprocally transplanted between the cooler, moisture-filled upper slope position and the hotter, dryer lower slope position in 1994. This transplant was designed to mimic the stress of climate change with natural temperature and moisture gradients provided by elevation. A previous study of these soils suggested that one of these core soils lost robust microbial community function as a result of this transplant.

A new sample collection experiment was designed and performed in FY 2014. The chemical, molecular, and functional profiles for these samples were generated by Fourier transform ion cyclotron resonance mass spectrometry, Illumina HiSeq DNA sequencing, and targeted enzyme assays and respiration measurements, respectively. Analyses of data collected from the previous study combined with these new datasets have yielded several insights into the ecosystem response to the perturbation. The transplanted soils display less variation in water retention than native soils, prompting new hypotheses about the physical organization of the soil carbon system. Soils from the lower site exhibit fewer lipids and more condensed and unsaturated hydrocarbons than the upper site soils. The microbial community in the surface (at 0–5 cm depth) soils from soil transplanted to the lower (hotter) site exhibit increased respiration activity. A focused integration and analysis of these data will inform hypotheses about the complex interplay between the microbial community and the soil carbon reservoirs under changing climate conditions.

Variation in the hydrologic properties of the soil system. Native soil samples (blue) have high variability in water content relative to the transplanted soil samples (red).
Through this project, the ability to observe “live” biological systems across multiple platforms with various spatial, temporal, and chemical resolutions will provide unique insight for these model systems and validate the versatility of this combined approach.

As biological systems are highly complex, understanding how a single cell protein is related to the function of a whole organism requires spanning more than 10 orders of magnitude across spatial and temporal scales. This is a large feat on its own, but a complete picture is possible only if methods are added to probe the chemical and temporal evolution of the system to observe how it changes over time. Biologists have striven since the 1950s to link biological system structures to their physiological function, but countless details remain obscure from these systems intricacies and wide-ranging processes. Because no single instrument is currently capable of addressing structure, dynamics, and chemistry across these scales simultaneously, new methods integrating data from multiple instruments are required to achieve a clear understanding of biological processes relevant for the production of energy, cleanup of environment, and improvement of human health.

In this project, we are developing, adapting, and employing state-of-the-art approaches toward enabling a better understanding of biofilm organization, enzymatic energy transduction, and epithelial cell interactions with nanomaterial. The overall objective is to integrate six emerging technologies to enable multimodal and multiscale spatial, temporal, and chemical analysis of biofilm organization, enzymatic energy transduction, and nanotoxicology. We will combine dynamic transmission electron microscopy (DTEM) with femtosecond X-ray diffraction (XRD) at the linac coherent light source (LCLS), secondary ion mass spectrometry (SIMS), and atom probe tomography (APT) to interrogate the structure and dynamics of biological systems.

During FY 2013, significant progress was made with each of our specific project aims. Highlights included acquiring the first transmitted XRD patterns from 2D protein crystals using LCLS, nano-SIMS, and in situ time-of-flight (ToF)-SIMS to study biological samples with chemical sensitivity. We also developed novel methods for APT to detect the individual protein macromolecules embedded in a resin matrix. Both of the developments with biological APT and femtosecond XRD of 2D crystals were never before been demonstrated. Additionally, we developed a novel in situ liquid cell compatible with femtosecond XRD experiments to image the 2D protein crystals in a fully hydrated state in order to permit pump-probe dynamic observations.

Considerable achievements were made within this first year of the project. We had six published or in-press manuscripts, with two additional articles submitted for review. We also had eight invited presentations to domestic and international conferences, along with six contributed talks and posters. While the publications help with the dissemination of our work to the larger scientific field, the conference talks in particular helped to raise project visibility and foster new scientific collaborations.

In FY 2014, we continued to develop the multimodal and multiscale platform for interrogating biological systems. In particular, we implemented a more integrated approach by looking at the same sample but using multiple techniques. First, we designed and fabricated new in situ liquid cells for X-ray, electron, ion, and optical imaging to allow for a single sample to be transferred between each technique and the correlated images. We also demonstrated novel applications of in situ ToF-SIMS and structured illumination microscopy for multimodal imaging of hydrated biological samples, which yielded the first mass spectrometry identification of lipid content in live cells.

In FY 2015, we will extend our APT capabilities in by implementing a cryo-transfer system that will allow us to run samples in a room temperature embedded or cryogenic state. The benefit of running at low temperature is that the freezing process can be done strategically to prevent the crystallization of water and optimally preserve the sample in its native state. We will also evaluate the synergy of femtosecond X-rays and micro- to nanosecond electrons for acquiring movies of biological processes in real time, including conformational changes upon ligand binding and assembly mechanisms. This scenario will maximize the new methods that we developed with DTSM and at LCLS using femtosecond XRD. Finally, we will apply the novel in situ ToF-SIMS capabilities developed in FY 2014 toward imaging nanoparticle uptake and nanotoxicity in mammalian cells as well as observing lipid accumulation and other cellular responses by algal and yeast cells upon environmental changes. These focus areas will establish the interconnected framework to begin probing biological systems with high fidelity across multiple platforms.
Understanding the Processes that Govern Subsurface Microbial Communities

James C. Stegen

This project ultimately aims to develop the theoretical tools capable of predicting microbial community composition and function through space and in response to environmental change. The resulting tools will be crucial for improving environmental and human health through remediation of contaminated sites in the United States and beyond.

Microbial communities play a central role in the functioning of natural ecosystems by heavily influencing biogeochemical cycles. As such, it comes as no surprise that microbes can influence human-derived environmental contaminants and efforts to remediate contaminated locations. It has also been repeatedly demonstrated that the ecosystem function (e.g., elemental cycling) is strongly influenced by the composition of ecological communities. If we are to understand eventually how microbe-influenced contaminants move through ecosystems and how effectively to remove or stabilize contaminants, it is vital that we initially understand what governs the composition of those microbial communities.

Historically, ecological community research is descriptive (e.g., how many species are in a given area and how the number of species changes across locations). Current research focuses on the processes that govern observed patterns. Although useful, most contemporary studies unfortunately only infer the dominant class of process. This approach fails to describe the constituent processes quantitatively necessary to develop predictive models. This project fills that void by coupling observational, experimental, and stochastic simulation approaches using the Hanford 300 Area subsurface as a model system.

A new collaboration for FY 2014 applied the developed statistical methods to microbial communities distributed across a previously documented chronosequence that spans 105 years of ecosystem succession. In this work, the statistical methods were extended with a new simulation model that enabled deeper insights into underlying ecological processes. In addition, a new conceptual model was developed to link ecological processes to ecosystem succession both before and after environmental perturbations. As of FY 2014 end, a manuscript based on this work is under review and being revised for publication in the Proceedings of the National Academy of Sciences.

Another collaboration that spanned multiple fiscal years was one in which we developed a new simulation model that generates diagnostic fingerprints of ecological and evolutionary processes that govern spatial biodiversity gradients. This new model is general enough to be used across ecosystems and taxonomic groups. The details of this achievement were published as an invited paper for Ecology Letters and a published article in Frontiers in Genetics.

The design and execution of a field campaign across the river–groundwater interaction zone of the Hanford 300 Area has yielded substantial datasets on spatiotemporal dynamics of microbial communities, carbon composition, biogeochemical solutes, and hydrologic dynamics. These datasets are currently being integrated to understand how biological and physical processes jointly govern biogeochemical dynamics in the groundwater–river water interaction zone. These datasets will be expanded to include metagenomic and metaproteomic profiles through a supported joint Genome Institute–Environmental Molecular Sciences Laboratory user proposal. In addition, going forward within the context of PNNL’s subsurface biogeochemical research science focus area, ecological processes quantified through methods developed by this project will be integrated with mechanistic biogeochemical models to improve multi-scale predictions of hydro-biogeochemical models.
Atomic-Scale Chemical Imaging via Scanning Tunneling and Electron Energy Loss Vibrational Spectroscopies

Igor V. Lyubinetsky

This project will implement the inelastic electron tunneling spectroscopy (IETS) on the low temperature (LT) scanning tunneling microscope (STM) for measuring spatially resolved vibrational modes of single molecules, providing chemical specificity at the atomic level. The new capability will enable direct spatial and temporal visualization of chemical reaction pathways.

One of the ultimate challenges for surface microscopies is the ability to follow surface reactions with atomic resolution and chemical specificity. While the ultra-high vacuum (UHV) STM allows the imaging of individual atoms and molecules, it generally lacks the chemical sensitivity, which can be overcome through IETS implementation. Implementation of the IETS requires an STM operation at low temperatures to provide high mechanical stability, negligible thermal drift, and reduce thermal broadening, which improves the spectral resolution. Hence, the LT STM operated under UHV conditions and at temperatures down to 5K is a well suited instrumental base for developing IETS.

We have accomplished the combination of LT STM with the molecular beam instrument, which allows the preparation of chemically functionalized STM probes by placing of a well-defined atom and/or molecule (e.g., CO) on the tip. We will explore the effect of tip derivatization with specific chemical functional groups on the activity of various vibrational modes in the next stages of the project.

Because the selection rules for the active modes in IETS are not clearly established, it is useful to compare its results with complementary data from ultra-violet photoelectron spectroscopy (UPS), which provides ensemble-average information on filled state electronic structure of the surface. As a part of this project, we studied the reactions of O₂ with UPS and STM specifically with hydroxylated TiO₂(110), a model reducible metal oxide surface, a reduction that leads to the formation of point defects (surface O vacancies and/or subsurface Ti interstitials) and Ti³⁺ defect state in the band gap. We discovered that the resulting quasi-stoichiometric, O-vacancy-free TiO₂(110) surface was fully oxidized, as evidenced by a complete decay of both the OH 3σ and Ti³⁺ peaks in the UPS spectra. The latter indicates that the Ti interstitials are absent in the subsurface region, and thus O vacancies constitute major point-defects of reduced TiO₂(110) and dominate its redox chemistry. Further, observed adsorbates are well defined species for IETS studies and are comparable to ensemble-average high resolution electron energy loss spectroscopy.

To date, great progress has been reported in the literature on obtaining the IETS spectra for a number of molecules adsorbed on metal surfaces. However, the studies on metal oxide surfaces are absent because the oxides are often semiconductive and/or insulating in nature, which requires an application of high tunneling bias that may potentially disrupt the analyzed adsorbates. To overcome these issues, we prepared and characterized the single crystalline RuO₂(110), an oxide with metallic conductivity. We conducted the STM and density functional theory studies of the catalytically important system of water on RuO₂(110). The coverage-dependent water structures (monomers and dimers) were uncovered, which together with other H-containing species will be used in future IETS studies.

STM images (12 × 12 nm) of reduced TiO₂(110) surface hydroxylated by H₂O dosing and then exposed to an increasing amount of molecular O₂. Symbols indicate bridging hydroxyl groups (square), terminal hydroxyl groups (rhombus), and O adatoms (circle). In the middle, corresponding UPS He I (top) and He II (bottom) valence band (VB) spectra recorded during O₂ exposure. VB spectra are dominated by O 2p signal, while OH 3σ and Ti³⁺ peaks are observed outside of broad VB feature.
We are developing novel, more efficient strategies for selective separation to allow for better reprocessing of spent nuclear fuels that reduces the need for long-term waste storage.

Current techniques for the separation of transuranic actinides from lanthanides rely on multi-state liquid-liquid extraction. This approach is challenging due to the similar chemical properties of actinides and lanthanides: they are typically present under trivalent oxidation states in acidic solution. A fundamental understanding of the chemical and physical properties of actinide complexes is critical to designing chelating molecular systems rationally and with high selectivity. Nature demonstrates that it is possible to engineer systems with remarkable molecular recognition capabilities among metal ions (e.g., potassium channels show a selectivity factor for K+ over Na+ as high as 104:1). The possibility of mimicking such natural design to improve the selectivity to actinides collectively by incorporating multiple binding sites with O, N, and S remains to be explored.

In this project, we are observing the physico-chemical interactions of actinides binding motifs and designing chelating reagents with high selectivity to actinides. The research will be based on two main thrusts: the thermo-structural investigation of actinides-bio-ligands complexes and the tuning of redox potentials of actinides compounds through interactions with ligands. Specifically, we are studying interactions between actinides and binding sites in select biomolecules using first principle electronic structure methods that include relativistic effects and electron correlation to validate calculations via gas phase collision-induced dissociation experiments and solutions.

To study soft N-donor ligands in actinide bonding interactions, we focused on a bidentate chelating ligand with hard O- and soft N-donor heterocyclic groups: alpha and gamma-picoline carboxylates. These ligands bind to transoox complexes of An(VI) in different fashions as elucidated by our first-principle calculations using relativistic density functional theory (DFT) methods. We performed the analysis and computed binding/dissociative energies, including scalar and spinorbit coupling. The thermodynamically favorable structures of alpha picoline carboxylate actinyl complexes are O- and N-coordinated, in preference to bidentate binding with two oxygen atoms. The An-N distances are shorter compared with An-O bonds across the actinide series. In contrast, the stable configuration for gamma-picoline carboxylate is bidentate with the carboxylate group in the equatorial plane. Our DFT calculations show that the heterocyclic amine is a strong donor to the actinide center and more favorable compared to the hard O-donor. The calculated results were further verified by gas phase collision induced dissociation (CID) experiments from our Lawrence Berkeley National Laboratory collaborator.

A sulfur-sulfur (S-S) bond is postulated to reduce actinyl ions during the cellular biological remediation process. Therefore, we chose 2,2’-dithiodipyridine (DTDP), which contains one S-S bond that can reduce actinides under mild chemical conditions to study the role of soft S-donor ligands and the redox between actinyl ions and S-S. Relativistic DFT calculations showed strong interactions between actinyl ions (AnO22+, An=U, Np, Pu) and DTDP. We found that both N atoms and one S atom in DTDP coordinate to the actinide center, forming stable tridentate complexes and followed by S-S bond activation. Gas-phase CID experiments confirmed the dominant S-S bond cleavage in good agreement with theoretical calculations.

During FY 2014, this project supported an invited published chapter for a monumental book on computational lanthanides and actinides with the world-leading scientists in
the field. We also produced five manuscripts and attended four invited talks in international conferences. Additional progress is noted below.

**Redox Potentials of Actinide Complexes.** To predict the redox potentials reliably for actinide complexes is a great challenge to date. Scientists have been using empirical parameters to make corrections to predict the correct trend with increasing the Z number that was observed experimentally. We systemically investigated techniques and uncovered the method that can predict the redox potentials for these complicated systems without applying system-specific parameters for correction. Our calculations underpin the hypothesis that the redox potentials of actinide compounds can be tuned through the interactions with chelating ligands. This work is being submitted as a manuscript to *Physical Chemistry Chemical Physics*.

**S-S Bond Activation.** Further experiments based on free-electron lasers for infrared experiments verified the structures predicted by theory. These experiments were performed on FELIX at Radboud University Nijmegen, Netherlands. This is the first time that the N,S-coordination chemistry to actinide center has been firmly verified in gas phase. The manuscript in preparation will be submitted to *Angewandte Chemie International Edition*.

**N-donor ligands.** Based on the results from the previous fiscal year, we further verified the differences in binding between uranyl cation and alpha/gamma-picoline carboxylates in solution chemistry. The ultimate fluorescence spectra show distinct signature peaks for the two types of compounds. The manuscript related to these results is in preparation.
Biomass-Derived Acrylonitrile for Carbon Fiber Production

Michael A. Lilga

This project demonstrates a key catalytic step in the conversion of biomass-derived compounds to acrylonitrile, the precursor to carbon fibers used in numerous consumer products.

Developing new pathways for the production of biofuel and bioproducts from lignocellulosic feedstocks is a key objective of DOE EERE’s Bioenergy Technologies Office (BETO). There has been recent interest in routes to bio-based acrylonitrile as a precursor to carbon fiber. We are developing novel chemical catalysis pathways to acrylonitrile and acrylic acid (that can be converted to acrylonitrile via known chemistry) using olefin metathesis processes, which is the catalytic method of cleaving two alkenes (olefins) and recombing cleaved fragments to form new olefinic products.

Specifically, ethenolysis, a special type of olefin metathesis, is used in a process within which ethylene is the key reagent for metathesis. The ethenolysis transformation under study can be illustrated by the following equation, in which A=B represents a biomass-derived olefin.

$$A = B + CH_2 = CH_2 \rightarrow A = CH_2 + B = CH_2$$

This work will demonstrate for the first time the key process step of ethenolysis in the conversion of biomass-derived alkene compounds to acrylonitrile and acrylic acid. Successful implementation of this chemistry will improve biorefinery economics and support the production of cost-competitive biofuels and value-added bioproducts.

Compounds containing a –CH=CH$_2$CN or a –CH=CH$_2$CO$_2$R (R=H, alkyl) group were studied in proof-of-principle experiments designed to demonstrate feasibility. Compounds chosen derive from saccharide or lignin biomass fractions obtainable from biochemical (fermentation) or thermochemical processes. In addition, several carefully chosen compounds representing a variety of functional groups and structures were tested to determine reactivity with ethylene to form acrylic acid through ethenolysis with a commercial catalyst, which was relatively stable toward moisture and air. The compounds tested included fumaric acid (C$_4$ unsaturated dicarboxylic acid), fumaronitrile (C$_4$ unsaturated dinitrile), muconic acid (C$_6$ di-eno dicarboxylic acid), octatetraenoic acid (C$_8$ trieno carboxylic acid), and ρ-angelica lactone (C$_5$ cyclic unsaturated ketone). Reaction temperatures between 40–100°C and ethylene pressures between 100–200 psi were used. Owing to their low organic media solubility, dicarboxylic acids were converted to the corresponding methyl esters prior to conducting ethenolysis.

Results showed that ethenolysis is a promising pathway to the manufacture of acrylonitrile, acrylic acid, and/or methyl acrylate under mild conditions. Fumaronitrile gave a 30% yield of acrylonitrile; however, dimethyl fumarate provided less than a 5% yield of methyl acrylate. Dimethyl maleate gave a slightly higher yield of about 10%, possibly from higher energy of the cis-carboxylate arrangement. Trans-, trans- (30%) and cis-, cis- (36–54%) isomers of dimethyl muconate both gave good methyl acrylate yields. The cis-, cis- isomer is of interest because it can be obtained from lignin, which offers a potential route to a high value product from this major biomass component. The muconates also produce butadiene, another drop-in chemical product with high value. The octatetraenoic acid (tested in the acid form) gave detectable acrylic acid, but further research is needed with this substrate. This material is obtainable from sugar or hydrolyzate fermentation. The cyclic ketone ρ-angelica lactone remained unreactive to ethylene. Significant efforts were made to find an alternative ring-opening pathway without success.

Our work demonstrated a key step for converting biobased materials obtained from either thermochemical or fermentation routes to acrylonitrile, acrylic acid/methyl acrylate, and other value-added drop-in chemical products. Key findings are that open-chain olefins can be converted using ethenolysis to acrylics and acrylonitrile, cyclic olefinic lactones cannot be converted, and reaction conditions are very mild, suggesting low capital on scale-up.

For FY 2015, we will continue focusing on ethenolysis of dimethyl muconate and 2,4,6-octatetraenoic acid. Further process development with these substrates enables conversions of sugar and lignin feedstocks to bio-based fuels and value-added chemicals. We will work to optimize production conditions, modify the catalyst, and identify final product separation options. These results enhance PNNL core catalysis capabilities and support DOE BETO goals and cost targets for advanced fuels.
Characterization of Catalyst Materials in the Electron and Atom-Probe Microscopes

Ilke Arslan

With our current global business economy, fuel is essential for car, plane, and boat transportation. The catalytic materials and processes studied in this project provide renewable, conventional energy resource conversion for less expensive, more environmentally friendly fuel.

This project aims to advance and combine nanoscale techniques to further the examination of zeolite catalysts. The characterization-synthesis loop is an important aspect of designing and controllably synthesizing a material of industrial significance. Likewise, characterization on the atomic and nano scales allows for fundamental understanding of the catalytic processes that aids in designing a better catalyst. We employ atomic resolution, 3D imaging, and in situ fluid imaging in the scanning transmission electron microscope (STEM) combined with atom probe tomography (APT). Chemical information can be obtained in the STEM using electron energy loss spectroscopy.

In electron tomography (ET), images are taken at different tilt angles and combined using reconstruction algorithms to form a 3D representation of the nanomaterial. The application of ET to inorganic materials using STEM has developed rapidly. A fairly large range of volumes of material can be analyzed in 3D in configurations as small as 10 \( \times \) 10 \( \times \) 10 nm\(^3\) to as large as 300 \( \times \) 300 \( \times \) 300 nm\(^3\), with the 3D resolution varying from under 1 nm to nearly 5 nm depending on volume size, number of images acquired, tilt range achieved, and alignment and reconstruction methods.

APT is a controlled field evaporation technique that produces sub-nanoscale spatial and concurrent chemical resolutions. However, a number of artifacts can limit the overall resolution. Knowing the 3D structure of the material volume a priori by APT is therefore crucial. The most accurate way to accomplish this is by matching in 3D with a non-destructive technique such as ET.

The artifacts in APT and ET are in different directions; therefore, each method can be understood and compensated. These means are combined and applied to two sets of zeolite materials: MCM-22 (and related layered zeolites that can be delaminated) and ZSM-5. MCM-22 is used as a precursor material for delamination, with the goal of pulling apart the zeolite sheets to provide a higher surface area while keeping the active sites on the surface intact. The higher surface area allows access for larger bulky molecules to create reactions, opening the materials for new processes such as cracking, alkylation, and 3D delamination. ZSM-5 is studied as the acid catalyst for converting lignin-derived phenolic oil to produce gasoline range hydrocarbons and methanol. As this reaction occurs in water, it is important to understand the fundamental morphology and chemistry of zeolites in water. We are applying a fairly new technology of imaging through fluids in the electron microscope to understand the zeolites structure in its aqueous environment. High resolution imaging and 3D ET will be combined with APT to understand the location and density of acid sites with nanometer spatial resolution.

The ultimate goal of delaminating zeolites is to investigate the formation of bimetallic clusters on supports from complexes of metals that are chemically similar and have a strong tendency to form clusters. The support for the clusters will be zeolites because their support allows precise control as a consequence of the regularity of their surfaces and cages, and the opportunity to regulate the number of well-defined bonding sites (metal precursors tend to react with Al sites as evidenced by EXAFS spectra). One of the challenges of zeolites is determining the metal cluster structures throughout the samples. An appealing alternative is zeolites in the form of extremely thin layers as support for our clusters. We expect to obtain high quality 3D and atomic-resolution samples and cluster images (even of the zeolite frame), as all the

The resulting work of our efforts to show the visualization of delamination was chosen as the program cover at the 2013 North American Catalysis Society Meeting in Louisville, KY.
clusters will be located near surfaces. To realize this goal, the zeolite support must be fully characterized to understand the morphology and determine whether synthesis is successful.

To accomplish our objective, we performed a thorough analysis of the zeolite 3D morphology at three stages of chemical and heat treatment to understand the delamination mechanism. The starting material was the precursor MCM-22, after which STEM tomography was performed, which yielded many thin sheets of zeolite bound in large, flat clusters. The distance between sheets is the pore size, which limits larger bulky molecules from entering. The next step was chemical treatment, which in this case was performed at pH 9 using an aqueous solution at 353 K. This is a much lower pH than zeolite delamination in the literature, which yields no detectable amorphous areas that inhibit catalytic performance as those found in materials such as ITQ-2. The 3D imaging performed at this stage showed that the zeolitic layers were still flat and in clusters, but the distance between layers was slightly larger, suggesting swelling and breaking bonds.

At the final stage of synthesis, the material is calcined. The heat treatment does something phenomenal in that the zeolite sheets come apart in curvy layers and the surface area increases. The distance between clusters of the curvy sheets is larger (up to several hundred nm), thereby providing ample space for bulky molecule reactions. To date, there has been no published literature on a direct and 3D visualization of the delamination process. We performed the experiments and some reconstructions in FY 2012 and used the next year to focus on new reconstruction algorithms. Using the discrete algebraic reconstruction technique (DART), compressive sensing, and other conventional methods, we optimized the reconstruction procedure for the delaminated zeolites.

With zeolites for biomass conversion in FY 2012, we provided the first images of the ZSM-5 zeolite imaged in situ in water. We found that when suspended in water, particle cluster size was smaller than with dry material. Upon ZSM-5 analysis on a dry grid with different temperature treatments, the sample boiled to 250°C was more stable under the electron beam. The instability of zeolites under the electron beam was generally attributed either to the presence of trapped water in the pores or unstable cations in the structure, but this hypothesis was not proven.

During FY 2013, we continued imaging the zeolites in water and used heating elements with the liquid holder manufacturer to perform in situ leaching experiments. We imaged 50–100 nm ZSM-5 crystals in NaOH instead of a water solution, which should have initiated leaching when heated. We were hoping to image the process of desilication in real time to show how the zeolites progress from solid to hollow particles, which had never before been shown. Heating in solution is also new technology for the flow holders.

We worked with UOP and Utrecht University on studying features in ZSM-5 crystals with varying steam treatments to understand how the distribution of the acid sites changes with steaming. This was a challenging task that required chemical and 3D morphological information. We therefore correlated STEM tomography (morphological information) with APT (chemical information) to use each method to minimize the artifacts in the other and build an accurate representation of acid site distribution in these materials. We had already demonstrated the morphology and chemistry of the materials with each technique separately and focused on the analysis of the same sample with both methods. This correlation had never been done with any material other than metals and would provide much valuable information for the catalysis community.

In FY 2014, we accomplished all of the goals for which the research in FY 2013 proposed. We made excellent progress on electron tomography reconstruction algorithms by combining two advanced methods: total variation minimization within compressed sensing and discrete tomography methods. Currently, we have the only algorithm in the world capable of reconstructing high quality 3D data sets with only ~30 images in the field of electron microscopy. We were able to perform 3D reconstructions of a new set of delaminated zeolites, in which we showed an almost two-fold increase in surface area from our 3D quantification on the nanoscale, which correlated almost exactly with the results from the Katz group at the University of California-Berkeley on their bulk measurements of surface area. We were also able to run zeolites in the atom probe and correlate a defect structure between the STEM images and the APT data.
Design, Synthesis, and Activity Measurements of Monodispersed Multifunctional Catalysts for CO₂ Reduction

Roger J. Rousseau

We are developing technologies for efficient CO₂ conversion into various forms of energy carriers as a prerequisite to reducing the atmospheric carbon level.

With increasing energy needs and the potential long-term environmental effects from CO₂ emissions, carbon-neutral fuels are essential to the environmental sustainability of the U.S. energy supply and will contribute to energy independence from foreign sources. While sequestration may prove a viable short-term solution, the use of CO₂ as a renewable resource in a carbon-neutral economy is more desirable. As fuel consumption forms the major component of carbon utilization, CO₂ reduction to hydrocarbon fuels requires a substantial energy input, with most transformations being endothermic and posing formidable challenges for designing an efficient catalytic process.

CO₂ conversion is a strategy for the mitigation of greenhouse gas emissions: the process has the potential as a media for chemical energy storage and can be a renewable carbon source for fuels. CO₂ investigations provide fundamental insights into catalytic conversions of oxygenated organics relevant to other feedstocks. Although a high temperature and pressure CO₂ conversion process exists based on CuZnO catalysts, the extreme conditions needed to perform this synthesis necessitate large-scale conversions that are not commensurate with the distributed small-scale nature of CO₂ production.

This project was designed to synthesize and screen a series of catalysts based on a multifunctional motif as preliminary results for future fundamental or applied programs in CO₂ conversion. To contribute to solutions for the challenges of CO₂ conversion, we are developing novel catalysts that will activate and convert CO₂ into an energy rich species (i.e., methanol) at milder conditions (T<200°C P=1Bar). This is based on the recognition that CO₂ activation at low T can be achieved via a Lewis acid function and CO₂ reduction to hydrocarbons, a process that requires a low temperature hydrogenation functionality.

Our work in FY 2013 synthesized, characterized, and measured the activity of monodispersed model heterogeneous catalysts to find a correlation between catalyst activity and CO/CH₄ selectivity. We tuned the nuclearity of metal species in the PolyOligoSilSeOxiane framework systematically, identifying and developing synthetic protocols to stabilize mononuclear and dinuclear species as a fragment of the framework.

In FY 2014, we demonstrated that a multi-functional catalyst led to a low T CO₂ activation and conversion and also showed that carbonate activation can be achieved by the inclusion of an acid function in both the gas and vapor phase. Finally, we showed that conversion is a carbon capture solvent, which provides a low temperature/pressure route to methanol (two pots, not one).

Liquid phase catalysis. We demonstrated with homogeneous and heterogeneous Ru₂-based hydrogenation catalysts combined CO₂ capture and conversion (T=140°C, P=1 bar), with the synthetic approach as shown. The first three synthesis steps can be done in one pot, where the final step requires acid co-catalyst requires distillation.

Vapor phase catalysis. We synthesized well-defined, mono-dispersed Pd and Ru clusters supported on MWCNT and Al₂O₃ and shown reactivity below 250°C require a Lewis acid site. We found via in situ infrared (IR) spectroscopic studies that conversion is accompanied by the formation of carbonate species, as shown. Catalysis in both the vapor and liquid phases appears to go via a carbonate route at low temperature.

For FY 2014, work from our project resulted in two published articles in Physical Chemistry Chemical Physics, another in Inorganic Chemistry, and attendance at the 2014 American Chemical Society national meeting.
Development of a Novel Microscopy Platform for Fundamental Studies of Ice Nucleation on Atmospheric Particles

Alexander Laskin

We are using a novel experimental platform for fundamental molecular-level studies of atmospheric particle ice nucleation efficiency. These experimental data will be of critical importance to explain fundamental processes of aerosol-ice cloud interactions.

Our present understanding of the role that atmospheric particles play in the formation of ice clouds is limited to the extent that their impact on the environment and climate cannot be predicted accurately by models. Atmospheric particles are complex in nature (multicomponent and multiphase) and exhibit different ice nucleation efficiencies that need to be probed with individual particle specificity. This project focuses on the development and applications of a novel experimental platform for fundamental studies of ice nucleation efficiency of atmospheric particles with microscopic determination of physicochemical properties of individual particles. This knowledge will help elucidate aerosol-ice cloud interactions, one of the most challenging problems for understanding the earth’s climate change.

The formation of atmospheric ice in clouds can proceed by homogeneous and heterogeneous nucleation. For homogeneous nucleation, ice forms when a supercooled aqueous droplet freezes. Heterogeneous ice nucleation is initiated by an ice nuclei (IN) and can be subdivided into immersion freezing (i.e., ice forms on IN suspended in a supercooled droplet), deposition nucleation (i.e., ice nucleates onto a solid IN surface), and contact nucleation (i.e., ice forms in a supercooled droplet when impacted by IN).

Our project focuses on heterogeneous ice nucleation, which is governed by the physical and chemical properties of particles that can vary from particle to particle. Previous studies suggested that the following properties may control a particle’s ice nucleation efficiency: 1) insolubility, solid particles such as mineral dust; 2) size, a higher nucleation probability for a larger surface area; 3) chemical bonds and their crystallographic arrangement on particle surface, ability to form hydrogen bonds; and 4) active sites, characteristic locations initiate nucleation such as cleavage and growth steps, crack, cavities, inclusions, and defect sites. Although these guidelines aid in identifying which materials are likely to act as IN, they cannot explain the contradicting results observed for real-world atmospheric particles. This is because a microscopic understanding of the nature and location of ice nucleation events on the particles is lacking. The lack of these microscopic observations severely limits our understanding of the atmospheric glaciation processes and calls for systematic studies to unravel physicochemical properties of individual IN at microscopic level of detail.

In collaboration with the State University of New York and Lawrence Berkeley National Laboratory, our research efforts were performed under two primary tasks: first, the development of a new capability to allow experimental observation of ice nucleation over individual IN at temperatures (T) as low as 180K and relative humidity (RH) typical for the upper troposphere/lower stratosphere inside of an environmental scanning electron microscope (ESEM); and second, the application of the IN-ESEM platform to investigate ice nucleation of complex atmospheric particles relevant to anthropogenic and biogenic emissions. Combined with theoretical chemistry calculations, the experimental data will be analyzed to gain a better understanding of ice nucleation and parameterizations for cloud models.

During the first 6 months of the project, we designed, fabricated, and assembled all basic parts of the cryogenically cooled ice nucleation cell, a core part of the IN-ESEM experimental platform illustrated in the figure.

The image shows an individual ice nucleation event observed in our first IN-ESEM experiments and confirms the ability to create a freezing environment confined to a very small
(~0.4 mm²) circular sample area as shown. Our ongoing efforts are focused on the precise temperature control and testing of the cell and will be followed by the first set of ice nucleation measurements over chemical standard particles with known IN efficiencies. This scenario will allow for evaluation of the performance of the platform and demonstrate its applicability for systematic studies of ice nucleation with precise control of T and RH.

During FY 2015, we will utilize this platform to study ice nucleation efficiencies of ambient particles collected in different atmospheric environments (anthropogenic and biogenic particles). Spectro-microscopy analyses of individual IN will assess particle chemical composition, the presence of inclusions or surface features that most efficiently induce formation of ice. Complementary theoretical chemistry and molecular dynamics modeling of selected systems will be used to further understand experimental results and relate them to fundamental macroscopic and molecular level properties of particle surfaces.
Increased Sensitivity and Improved Quantification of Th and U in Particles by SIMS

David G. Willingham

This project seeks to develop state-of-the-art SIMS capabilities for addressing national security concerns related to nuclear forensics and nuclear archaeology applications.

SIMS is a surface/depth analytical technique that has been around for nearly 70 years and has had many bright minds applied to its advancement. A quantitative understanding of the useful yield from radionuclide-containing samples, however, has been relatively unexplored. This limitation in previous research mainly arises from the difficulty of accurately measuring ion generated crater volumes, the inability to handle radionuclide containing samples safely, and an inaccessibility of real-world nuclear forensics and nuclear archaeology materials.

This project focuses on SIMS signature discovery and a quantitative determination of the ultimate sensitivity of SIMS measurements. With the bridge between fundamentals of SIMS analysis of actinide-containing materials and the application of a standard analytical methodology being relatively unexplored, our work aims to strengthen this connection and increase the utility of SIMS measurements for nuclear forensics and nuclear archaeology applications. Specifically, we are developing a robust method for quantitatively determining the SIMS useful yield of U and UO\textsubscript{x} species, identifying real-world SIMS signatures relevant to nuclear archeology samples, and determining the analytical SIMS methodologies needed to perform isotopic depth analysis on uranium enrichment facility components and implement these methodologies accurately for real-world sample analysis.

A combination of secondary ion mass spectrometry, optical profilometry, and a statistically driven algorithm was used to develop a non-contact volume analysis method to validate the useful yields of nuclear materials. The volume analysis methodology was applied to ion sputter craters created in silicon and uranium substrates sputtered by 18.5 keV O\textsuperscript{-} and 6.0 keV Ar\textsuperscript{+} ions. Sputter yield measurements were determined from the volume calculations comparable to Monte Carlo calculations and previously reported experimental observations. The volume calculations were also used to determine useful yields of Si\textsuperscript{+}, SiO\textsuperscript{-}, and SiO\textsubscript{2}\textsuperscript{+} ions from the silicon substrate and U\textsuperscript{+}, UO\textsuperscript{+}, and UO\textsubscript{2}\textsuperscript{+} ions from the uranium substrate under 18.5 keV O\textsuperscript{-} and 6.0 keV Ar\textsuperscript{+} ion bombardment.

SIMS depth analyses of a uranium enrichment facility component have been reported for the first time. A standard operating procedure was developed to enable preparation of SIMS samples from a corroded pipe piece without disturbing the corrosion layer. Unique uranium, oxygen, and fluorine containing signatures were discovered in the corrosion layer by performing a mass scan of the region of interest from 230–280 amu. These signatures identified the source of the corrosion layer as uranium hexafluoride (UF\textsubscript{6}) or an associated hydrolysis product. Isotopic analysis of the corrosion layer revealed that it was enriched in $^{235}\text{U}$ to a value of 1.164 ± 0.019 for $^{235}\text{U}/^{238}\text{U}$.

The initial SIMS analyses of the pipe piece focused on obtaining mass spectra from the corrosion layer in order to determine the presence of any unique nuclear archeology signatures. Spectra were obtained by scanning the magnet and measuring the ion counts as a function of mass-to-charge ratio. The first observation to note is that although initial radiometric counting did not yield a detectable result, there are ion signals from uranium isotopes ($^{235}\text{U}^+$, $^{238}\text{U}^+$) and uranium-containing compounds (UO\textsuperscript{2+}, UF\textsuperscript{-}, UF\textsubscript{2}\textsuperscript{-}, and UOF\textsuperscript{2+}). It
is also well known that UF₆ reacts with metals to form uranium sub-fluorides (UF₄, U₂F₈, UF₅, etc.) that deposit as constituents of a corrosion layer. Additionally, if exposed to water vapor, these sub-fluorides will hydrolyze to form hydrofluoric acid and oxygen- and fluorine-containing compounds.

The most important findings consist of development of a method for quantitatively determining the useful yield of radionuclide containing materials aimed toward validating the inter-laboratory and cross-platform performance of mass spectrometry for the analysis of nuclear materials. Another milestone was providing data that are conclusive evidence that SIMS depth analyses can be used to identify novel nuclear archeology signatures from uranium enrichment components and perform meaningful isotopic analysis of these signatures.

This year’s activities have resulted in two-peer reviewed publications in the open literature and a presentation at an international conference.
Localized Surface Plasmon Resonance Spectroscopy, Microscopy, and Sensing

Patrick Z. El-Khoury

This project combines nanoscopic (surface- and tip-enhanced Raman) and theoretical (static and dynamic quantum chemical simulations) tools to probe the interplay between a single molecule and its local environment.

Efforts to reach the ultimate detection limit (i.e., the sensitivity required to probe 1.66 yoctomoles \([1/N_s]\)) of a substance-rendered the art and science of engineering plasmonic nanojunctions popular over the past few years. This is a consequence of the extreme localization of electromagnetic fields between plasmonic nanostructures, whereby the detection of the feeble optical response of a single scatterer is feasible. The effect is most evident in surface- and tip-enhanced Raman scattering (SERS and TERS) from molecules coaxed into plasmonic junctions. Through this project, a combination of experiment and theory is aimed at understanding the operative mechanisms that govern optical spectroscopy at plasmonic nanojunctions and applying the knowledge to designing and constructing ultrasensitive plasmonic sensors.

Our FY 2013 work revealed that inelastic photon scattering at plasmonic junctions not only retrieves molecular polarizabilities but also broadcasts intimate details about the environments in which the scatterers reside as well as the interplay between molecule and plasmon. Through TERS trajectories recorded at a nanojunction formed by a gold atomic force microscopy (AFM) tip in contact with a silver surface coated with biphenyl-4,4'-dithiol (BPDT), we established in an article published in *Nano Letters* that junction plasmons can tunnel through conductive molecules that bridge the nanogap through chemical bonds. In the aforementioned study, the change in scattering activity associated with shorting the junction plasmon served as a method for monitoring the breaking and making of single chemical bonds.

In a separate report published in *Chemical Physics Letters*, we employed tools of density functional theory to compute the Raman spectra of 1,3-propanedithiol (PDT) molecules in various media. The derived polarizability tensors were used to simulate molecular orientation-dependent Raman scattering. Our derived single molecule framework was weighed against AFM/SERS experiments that probe the optical response at a plasmonic junction formed by an Ag surface coated with PDT and a single 60-nm Ag nanosphere. A remarkable agreement between experiment and theory not only allowed for reliable spectral assignments but also provided an intuitive theoretical framework which accounts for commonly observed phenomena in the single molecule realm (i.e., spectral fluctuations).

During FY 2014, we built on and expanded the concepts set forth during the previous year. Four key reports were published in *The Journal of Physical Chemistry Letters, The Journal of Chemical Physics, The Journal of Physical Chemistry A*, and *Nano Letters*. In particular, the first and last reports are of particular relevance to the directions that will be undertaken in this project during FY 2015. In the former, we combined AFM-based TERS point spectroscopy, within which the AFM is operated in non-contact mode, with the single molecule framework developed in FY 2013. Through Raman trajectories recorded at a nanojunction formed between the silver AFM tip and a corrugated silver surface coated with BPDT, we illustrated how time and frequency-dependent intensity variations in TERS can be uniquely assigned to molecular reorientation.

In the latter study, we recorded sequences of Raman spectra at a plasmonic junction formed by a gold AFM tip in contact with a silver surface coated with 4,4'-dimercaptostilbene (DMS). Besides the choice of molecular reporter, the experiment is similar to our work in FY 2013 and makes use of the assignments made therein. A 2D correlation analysis of the recorded trajectories revealed that the observable vibrational states can be divided into subsets by virtue of the symmetry of DMS (C\(_{2h}\)). Our findings were rationalized on the basis of the charge-transfer theory of Raman scattering and density functional theory calculations, and illustrated how current carrying plasmons modulate the vibronic coupling terms from which the intensities of the bu states are derived. In effect, we identified gateway molecular modes for mediating charge shuttling across a plasmonic gap. In the near future, these concepts will be rigorously accounted for TERS images recorded by taking advantage of plasmonic tip-sample nanojunctions. Moreover, lessons learned from these studies allowed us to design and construct a first generation uniform SERS sensor, which has already been characterized using the wealth of microscopic and spectroscopic tools housed within EMSL at PNNL.

In addition to the several aforementioned publications, our work on this project resulted in an appearance at a research conference and at two invited university department seminars.
In this project, we are understanding and controlling radiochemical separations as key to characterizing current nuclear materials and processes and developing the next generation of nuclear characterization technologies.

The goal of this project is to develop advanced capabilities in radiochemical separations both during fuel irradiation for sequestration purposes and after environmental dispersal for monitoring and remediation. Our efforts are divided into three tasks that are described in detail below.

**Marine Detection of $^{231}$Th.** Suspended particles are a large carrier of radionuclides in oceanic systems. Uranium and thorium display unique interactions with particles in ocean environments, with uranium remaining dissolved as a carbonate complex and thorium adsorbing to any available particle. This behavior allows uranium/thorium parent/daughter ratios to be useful for tracking the lifetime and motion of particulates suspended in ocean currents by establishing the deviations from secular equilibrium as the loss to particles moving through the system. However, this ability is limited by the time necessary to establish secular equilibrium between parent and daughter. Processes occurring faster than equilibrium are not observable. Our efforts in this project are aimed at extending these capabilities by performing the first measurements of $^{231}$Th, daughter of $^{235}$U, in seawater for tracing rapid particle motions in seawater. Although the short half-life of 25.5 hours for $^{231}$Th is extremely desirable for such measurements, the small abundance and rapid decay of the isotope previously prevented its use as a tracer.

We evaluated the various techniques for separating thorium from seawater and selected a method based on the coprecipitation of thorium with MnO$_2$ followed by filtration and washing to remove other species. This produces a filter pad containing the precipitated thorium that can be directly used in counting techniques. The method was tested with a $^{234}$Th tracer at the expected levels of $^{231}$Th in seawater that was capable of collecting high yields. In addition, measurement techniques suitable to an in situ measurement that could also collect data rapidly enough to utilize $^{231}$Th were evaluated, and beta-gamma coincidence counting was chosen for its ability to discriminate the signal relative to contaminants and for a simple, robust design for the moving platform of a ship at sea. Detector components were purchased this year, with construction of the detector planned for FY 2015. In addition, we will construct and test the beta-gamma detector and test the combined chemistry/detection with seawater simulants of controlled concentration and natural waters to obtain the first natural $^{231}$Th direct measurement.

**Development of NF$_3$ Mass Spectrometry.** Traditional extraction of actinides from environmental samples for mass spectrometry can involve multiple radiochemical separations and require considerable time, facilities, and expertise to obtain suitable sample purity. Our objective is to reduce the preparation time for actinide mass spectrometry by utilizing unique fluorination techniques developed at PNNL with milder NF$_3$ as the fluorinating agent to separate actinides from solids selectively and rapidly for direct insertion into the mass spectrometer. To support this effort, a quadrupole mass spectrometer (QMS) with an electron impact ionization source was constructed and directly coupled to the gas outlet of a thermogravimetric analyzer (TGA) used to perform fluorination reactions between NF$_3$ and solid materials. Non-radioactive transition metal species were reacted with NF$_3$ to serve as cold analogs of fission products. As pictured, the first known mass spectrum of gaseous tellurium fluorides was obtained from this instrument and, as of FY 2014 end, a manuscript based on these results will be submitted for publication.

Mass spectrum of evolved species from the reaction of TeO$_2$ with NF$_3$. Multiple TeFx species are present due to electron impact ionization induced fragmentation. Isotopic resolution was obtained and corresponds to the correct natural abundance ratios for tellurium.
In FY 2015, we will explore the use of a negative ion source in an effort to obtain improvements in ionization efficiency (and thus sensitivity) of metal fluorides. In addition, this task will prepare and perform NF$_3$ fluorination/mass spectrum coupled experiments of uranium to demonstrate the ability of NF$_3$ to separation uranium hexafluoride selectively from a mixed actinide sample for mass spectrometry.

**Advanced Fuel Development.** During fuel reprocessing, volatile radioactive fission products are released into the environment, creating high levels of localized contamination and increasing the global background. “Smart” fuels designed for end-of-life reprocessing would ideally incorporate additives to capture these products, preventing their release to the environment and maintaining them for incorporation in secured radioactive waste repositories. These designer fuels would have significant impact on facility designs and decisions for long-term used fuel disposition. Our efforts in this task are aimed at using a recently discovered property of silver (Ag) found in used fuel white inclusions to retain iodine during reprocessing. Silver-containing inclusions have been found to hold up to 50% of the fission product iodine during alkaline reprocessing activities, making silver-doping a viable candidate for retention of halides during these processes. Our efforts have been evaluating the viability of incorporating additional silver into the fuel matrix at the fuel formation stage to capture iodine during irradiation for retention later during reprocessing.

Throughout this past year, three methods designed to incorporate silver into the uranium system were investigated: direct recrystallization of UO$_2$(NO$_3$)$_2$•AgNO$_3$ from solution, precipitation of UO$_2$C$_2$O$_4$•Ag$_2$C$_2$O$_4$ by addition of oxalic acid to the dilute nitrate solution, and precipitation of UO$_2$CO$_3$•Ag$_2$CO$_3$ at a 2:1 and 4:1 uranium-to-silver molar ratios. All methods were found to retain silver as small inclusions in the fuel matrix up to 1200°C under air for up to 24 h without loss of silver. SEM/EDS analysis was performed on the resulting oxides from each method and found that different morphologies result for each species, forming cylinders (method 1), platelets (method 2), or spheres (method 3), depending on the processing conditions used. The results of these experiments led to the submission of an open journal article for publication as of FY 2014 end.

In FY 2015, our efforts will continue to investigate the Ag-U-O system, and samples will be prepared for potential neutron irradiation to investigate the retention of reactor-produced iodine. This retention will be evaluated as a function of burn-up to address nuclear forensics issues, fuel reprocessing by ammonium carbonate peroxide, and fuel disposition concerns. In addition, the morphological properties of the fired uranium oxides will be further investigated in FY 2015 for potentially useful signatures of advanced fuels for nuclear forensics.
Novel Alloy Nanoparticle Materials for Catalysis and Energy Storage

Grant E. Johnson

This project is developing one-of-a-kind capabilities for the controlled preparation and characterization of alloy nanoparticles (NPs) of precise composition for applications in fuel cell catalysis and energy storage. The emerging capabilities are being applied to establish structure-reactivity relationships for alloy NPs.

We are focused on understanding how the size, elemental composition, surface density, and support-interaction of alloy NPs may be tuned to improve catalytic activity, selectivity, and durability toward the oxygen reduction reaction (ORR). Custom modifications are underway on a unique nanocluster deposition system that will enable atomically-precise control of the size and elemental composition of alloy NPs soft landed onto surfaces. A non-thermal physical synthesis technique is being developed to produce binary and ternary alloy NPs across a range of sizes and compositions that cannot be prepared using traditional solution-phase methods. New nanomaterials with promising catalytic properties are being discovered using this approach. A highly sensitive surface analysis technique is also being developed to screen the catalytic activity of NPs supported on surfaces at ambient conditions with minimal sample preparation. Achieving precise control of NP surface coverage and size is necessary to enable catalytic activity to be measured and calculated accurately as a function of metal loading and exposed surface area.

Employing simultaneous direct current magnetron sputtering of up to three independent metal targets in a single region of inert gas-aggregation, we produced anionic binary and ternary alloy NPs that contain a variety of transition metals (e.g., Fe, Co, Ni, V, Cu, and Pt). Mass-selected NPs were soft landed onto conductive glassy carbon (GC), highly-oriented-pyrolitic graphite (HOPG), and indium-tin-oxide (ITO) coated glass surfaces that are compatible with electrochemical analysis in solution using cyclic voltammetry (CV). We controlled NP coverage soft-landed onto substrates by measuring the ion current at the surface and adjusting the length of deposition. The NP surface coverage was determined by screening the surfaces with atomic force microscopy (AFM) following deposition. Using this approach, we demonstrated that on flat substrates such as GC, NPs locate randomly on the surface at low coverage. In comparison, on stepped surfaces such as HOPG, NPs nucleate preferentially along step edges, forming extended linear chains and leaving the terraces unoccupied.

With increasing coverage, we observed with AFM that terrace sites fill until a dense layer of NPs is present across the HOPG surface. We also determined the size and size distribution of deposited NPs from the height measured frequency distribution. To validate the AFM observations, we analyzed the surfaces using scanning electron microscopy (SEM), which confirmed that at low coverage, the soft landed NPs are separated and located randomly on the flat GC surface. SEM results also verified that NPs line up at step edges at low coverage on stepped HOPG surfaces.

Left: AFM image of 8 nm diameter Cu NPs soft landed onto graphite; right: height profile across rows of Cu NPs aligned at step edges.

In addition to controlling the size and surface coverage of soft landed NPs, it is desirable to tune their morphology and elemental composition. Elemental composition may be adjusted to reduce the loading of expensive precious metals (e.g., Pt and Au) and bring about physical lattice compression and strain as well as electronic structure effects that improve catalytic activity and selectivity. We employed systematic adjustments to the sputtering power applied to each of the three metal targets, the flow of sputtering (Ar) and buffer (He) gas, and the length of the gas-aggregation region to tune the morphology and elemental composition of NPs formed by magnetron sputtering and deposited them onto surfaces.

While the majority of NPs produced using this physical synthesis approach are spherical, we demonstrated that in the case of vanadium (V), it is possible to produce highly monodisperse nanocubes and soft land them onto carbon surfaces for subsequent atomic-level characterization using scanning transmission electron microscopy (STEM) at EMSL. As shown, the wide-field STEM images established the cubic shape and similar size of the individual NPs on the surface. Atomically resolved near-field STEM images revealed sharp differences in contrast at the center and edges of the V NPs, indicating the presence of metallic V cores surrounded by V\(_2\)O\(_7\) shells. In addition, we achieved control of the elemental composition of alloy NPs. X-ray photoelectron spectroscopy (XPS) was used to confirm the incorporation of multiple metals into
size-selected alloy NPs soft landed onto surfaces. A multimodal approach involving analysis by medium energy ion scattering (TOF-MEIS) and STEM confirmed the controlled creation of Pt-M (M = V and Cu) NPs with homogeneous alloy compositions and core-shell morphologies. In particular, STEM combined with elemental line scans using electron energy loss spectroscopy (EELS) demonstrated the formation of V-core Pt-shell NPs. These particles will make efficient use of a limited loading of precious Pt metal by concentrating it in the NP shell, not in the inaccessible NP core. The catalytic activity and stability of alloy NPs on GC was evaluated using CV under acidic solution conditions. A promising trend of increasing activity toward the ORR with incorporation of early 3D transition metals into the Pt-alloy was observed for NPs of similar size and surface coverage.

In FY 2014, an invited article was published in a special issue of the *International Journal of Mass Spectrometry* on the synthesis and characterization of metal oxide NPs that are promising candidates for applications in oxidation catalysis and electrochemical capacitors. A second invited paper was published in a Festschrift issue of the *Journal of Physical Chemistry* A describing the use of a flow reactor to control the distribution of metal NPs and to access reaction intermediates for soft landing and dissociation experiments. An invited comprehensive review article was published in *Mass Spectrometry Reviews* that highlights several aspects of this work. The technical accomplishments summarized in the preceding paragraphs were presented at the 2014 TechConnect World Conference in Washington, DC. Finally, our work was showcased in two invited university departmental seminars.

We are continuing our fruitful international collaboration with the Daegu Gyeongbuk Institute of Science and Technology (DGIST) in Korea, where they are analyzing supported NPs using TOF-MEIS. Two white papers regarding this work were submitted and an EMSL user proposal was awarded in collaboration with Purdue University that will utilize the novel capabilities developed in this project. The capabilities, publications, presentations, and collaborations resulting from this project are also providing the foundation necessary to compete for funding through DOE’s Basic Energy Sciences.
The long half-life, complex chemical behavior in tank waste, limited incorporation in mid- to high-temperature immobilization processes, and high mobility in subsurface environments make technetium-99 (Tc) one of the most problematic long-lived contaminants at DOE’s Hanford Site. This project investigates new technologies for the separation of Tc from the low activity waste (LAW).

In the strongly alkaline environments typical for Hanford tank waste, Tc exists predominantly in the liquid tank waste phase as Tc(VII) in the form of pertechnetate $\text{TcO}_4^{-}$ as well as low oxidation-state Tc(I) tricarbonyl $[\text{Tc(CO)}_3]^+$ species. While $\text{TcO}_4^{-}$ can be removed from LAW by the commercial ion exchange materials, they are not effective for the separation of the $[\text{Tc(CO)}_3]^+$ species from the tank supernatants. The objective of this project is to achieve better understanding and control of the redox behavior of both Tc(VII) and Tc(I) tricarbonyl species under conditions relevant to the tank waste needed to enable separation and long-term disposition of Tc. This acquired knowledge was applied for developing novel inorganic materials that can selectively separate total Tc from LAW and consequently convert it to Tc(IV), potentially allowing Tc immobilization in low-temperature waste forms.

Our focus was the design and testing of new inorganic materials for Tc(VII) removal from LAW. A series of inorganic composite materials of the general formulae were chosen. We found that the inorganic composites doped in Sn$^{2+}$ exhibited the highest $\text{TcO}_4^{-}$ uptake capacity and conversion of Tc(VII) to Tc(IV). In FY 2014, this methodology was extended to design hybrid redox-active inorganic sorbents that will remove $[\text{Tc(CO)}_3]^+$ from the waste supernatant and simultaneously oxidize Tc(I) compounds to Tc(IV). In addition, the library of inorganic composite materials was significantly extended, specifically tailoring the composition of materials with high affinity for $[\text{Tc(CO)}_3]^+$ attributed to the high complementarity between sorbent and guest species. The incorporation of the $[\text{Tc(CO)}_3]^+$ species within the sorbent lattice occurs when such an uptake results in an energetically more stable sorbent structure or lattice.

To increase immobilization of Tc within the sorbent matrix, we designed novel composites containing redox active centers that convert mobile Tc(VII) or Tc(I) species to significantly less mobile oxidation states through appropriate redox reaction and enhance their immobilization by suppressing the reverse reaction. The choice of the appropriate redox center was guided by electrochemical studies, and the Tc redox behavior was investigated using spectro- and electrochemical and techniques providing to the simultaneous quantification of the redox potentials and identification of transient reaction species and final products. This experimentation was performed using aqueous solutions containing high sodium nitrate and variable sodium hydroxide concentrations comparable with the Hanford tank waste supernatants. In FY 2014, the formation of Tc(IV) upon $\text{TcO}_4^{-}$ by the Sn$^{2+}$-based composites was confirmed by the X-ray photoelectron spectroscopy (XPS). The potential required for the oxidation of Tc(I) $[\text{Tc(CO)}_3]^+$ was estimated $+1.33V$ suggesting that incorporation of such oxidants as Bi$^{3+}$, Co$^{3+}$, and Mn$^{4+}$ in the composite matrix should result in the oxidative sorption of the $[\text{Tc(CO)}_3]^+$ species. Indeed, the synthesized Bi$^{3+}$ sorbents exhibited efficient removal of $[\text{Tc(CO)}_3]^+$.

Finally during this past year, we expanded the range of spectroscopic techniques for the characterization of Tc in different oxidation states. The inorganic composite materials were characterized by x-ray diffraction (XRD), XPS, scanning electron microscopy, Raman spectroscopy, $^{99}$Tc nuclear magnetic resonance (NMR), and electron paramagnetic resonance (EPR) spectroscopies prior and post exposure to Tc solution. The Tc solutions subjected to the electrochemical testing were monitored by the $^{99}$Tc NMR and EPR to evaluate the reaction products. Integration of the computational and experimental approaches were necessary because lack of the experimental data for some Tc oxidation states was initiated. This significantly contributed to the understanding of Tc redox behavior in the solution and composite matrices.

The mechanism of Tc sorption using inorganic composite materials and representative examples of $\text{TcO}_4^{-}$ removal from 1M NaOH/1M NaNO$_3$ and Tc(I) removal from 5M NaNO$_3$ by the selected composites.

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<th>Representative $\text{TcO}_4^{-}$ sorption</th>
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<tr>
<td><strong>Composite</strong></td>
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<tr>
<td>Sn(II)-Al(III)-Zr(IV) oxide</td>
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<tr>
<td>Sn(III) phosphate</td>
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<tr>
<td>Snciflyroxaciurite</td>
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<tr>
<td>Fe(III)-XO$_3^-$ (K-Mo, W)</td>
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<tr>
<th>Representative $\text{Tc(I)}$ sorption</th>
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<tr>
<td><strong>Composite</strong></td>
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<tr>
<td>Bi(III)-Co(III)-Al(III) hydroxide</td>
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<tr>
<td>Bi(III)-Co(III)-Al(III) hydroxide</td>
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<td>Ni(II)-Al(III) hydroxide</td>
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<td>Bi(III)-Ni(II)-Al(III)</td>
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Predictive Understanding of Self-Assembly: Particle-Mediated Growth

Kevin M. Rosso

We are developing a fundamental understanding of particle-mediated growth of crystalline materials from aqueous solution. The primary goal is to develop appropriate new theory that identifies and encompasses the relevant chemical physics and couples length and time scales through appropriate projection schemes.

Despite its widespread importance in the precipitation and properties of earth materials and its prospect as a new synthesis pathway to tailored functional materials, there presently is no predictive modeling capability in mesoscale science space. This project will ultimately provide a foundation for predictive simulations on particle-mediated growth systems for comparison with self-assembly outcomes at various scales. An existing popular theory to describe energetics between two surfaces considers a simple balance between attractive and repulsive electrical double-layer forces, where parameters are strongly correlated with microscopic features like molecular structure and electron distribution. However, a complete understanding requires correlations over differing length scales in the energetics between two charged surfaces in aqueous electrolytes.

In FY 2014, our theoretical effort was developing an approach for modeling solvent controlled interactions between nanoparticles that reaches into the mesoscale while retaining molecular details of the interacting particle surfaces and intervening solvent. We constructed the total Hamiltonian of the system, which includes contributions from long-range particle-particle dispersion interactions across solvent that accounts for the influence of solvent structuring on high frequency dielectric and ion screening of the static response as well as contributions from ion-mediated interactions. We pursued two directions: first, developing the molecular Lifshitz theory of dispersion forces between two flat surfaces across solvent, which takes into account solvent structuring at solid/liquid interface. Second, we worked on developing classical density functional model (cDFT) of ion-mediated interactions between two surfaces across electrolyte solutions. The use of the explicit coarse-grained water model with experimental density ensures that all contributions of the free energy account for solvent structuring and its static and dynamic dielectric properties.

The model was validated against its ability to reproduce ion activity in varying electrolyte solutions in the 0–2 M concentration range and its ability to capture the qualitative ion-specific effect in 1:1 electrolytes at the air-water interface. Simulations of activity coefficients in 2:1 electrolytes revealed the importance of ion-water attractive interactions for reproducing the chemical potential of ions with high hydration energy such as Mg$^{2+}$. These results led to including hydration interactions into the total free energy function.

We applied various approaches to understand the influence of pH on facet-dependent interactions between anatase TiO$_2$ nanoparticles. Simulations revealed that \{112\} surfaces have a close-packed hexagonal arrangements of oxygens that are partially hydrogenated at the studied pHs of 3, 2.1, and 1.2. The resulting close-packed regular arrangement of charges on these surfaces gives rise to strong attractive ion-correlation interactions favoring attraction between these facets. In contrast, oxygen (and therefore charge distribution) is much more sparse on the \{101\} surface leading to weak ion-correlation interactions between these anatase faces. These findings are in good agreement with qualitative experimental observations of high frequency oriented attachment along \{112\} facets, less frequent attachment along \{001\} facets, and rare attachment along \{101\} facets of anatase.

Experimental work in FY 2014 focused on developing strategies for fabricating crystallographically-oriented face-specific probes. In our initial approach, focused ion beam (FIB) milling and nanomanipulation were used to create hybrid tip systems. For the second approach, EMSL capabilities were used to deposit or synthesize thin films via molecular beam epitaxy starting with metal oxide systems of interest. Under deposition, thin films were directly deposited onto AFM tips. For FY 2015, we will assess and mitigate surface roughness and microtopography in developing our thin film growth protocols. We will also investigate attaching FIB-excised nanoslabs or nanoplatelets with oriented crystal faces to tipless cantilevers. All face-specific fabricated tips are subject to a detailed characterization protocol to determine the spring constant of the cantilever and new tip, shape, radius and morphology, and composition to obtain a 3D image of the chemical composition via micro-X-ray diffraction for crystallinity.

Dynamic force spectroscopy (DFS) was used to measure the force between crystal faces vs. the rate at which the crystals are pulled apart. DFS can be used to determine free energies of binding, which can in turn be fed back into predictive crystal growth models. Experiments will focus on force as a function of pulling rate that can yield free energies of attachment. We performed preliminary DFS measurements of force-curves for the interaction between two ZnO \{001\} surfaces. In FY 2015, we will continue refining the experimental protocol and perform a direct comparison of experimental data with simulated force-curves.
We are combining PNNL’s advanced measurement, computational, and chemical synthesis capabilities to describe and understand the title catalysts and their interaction with the reactants and products of biomass conversion.

The process of converting biomass into liquid fuel requires the use of catalysts to accelerate and direct chemical reactions from original plant material to transportation fuels (or precursors of) that can be further processed in existing refineries. This project provides a way to quantify the molecular scale composition and structure of liquid reactants and products in contact with a catalyst. The research will help understand one aspect of how the catalysts work and identify ways in which they can be improved. While there has been considerable research of the molecular structure of the catalysts themselves, much less is known about their interaction with the immediate environment. Because rates of chemical reactions depend on concentrations of reactants and products, it is necessary to measure those concentrations as locally as possible, preferably at catalytic sites so we can learn how to guide molecules to and from the sites. This project is yielding information about the composition of the reaction medium that can affect the catalyzed conversion of biomass into fuels.

We adapted Stokes shift spectroscopy (measurement of light absorbed and emitted) of catalysts to study the immediate solution environment of the catalyst site. The technique is generalizable because even apparently clear materials absorb light, at least in ultraviolet and infrared ranges. Light emission is familiar to anyone who has pasted glow-in-the-dark “stars” to the ceiling of a child’s bedroom. We measure changes in spectra, particularly shifts in energies of spectral features (color), and changes in relaxation times on a scale comparable to molecule movements (millions to billions of seconds; glow-in-the-dark stickers relax more slowly, typically over several minutes).

During FY 2014, we tested the photoactivity of one of our model compounds that resembles isolated sites of metal oxides supported on silica. The test reaction was hydrogenation of cyclohexene dissolved in reaction mixtures that ranged from neat cyclohexene through 5 vol% cyclohexene in heptane (nonpolar case) or tetrahydrofuran (polar case) to probe the effect of solvent polarizability on a biomass upgrading reaction where there was the possibility for a heterolytic activation of H₂. We found a striking difference between the two cases: the results are not consistent with previous rationalizations of solvent effects in heterogeneous catalysis, rather with a new hypothesis that the rate constant itself may depend on the nature of the reaction medium. Thus, there is reason to suspect that solvent effects may complicate the interpretation of rates of reaction involved in upgrading of biomass.

In FY 2014, we started to attach the well-characterized chromophores to the walls of mesoporous supports to probe how a constrained geometry would affect the ephihlicity of solvent molecules. We also took a “flyer” and tried to photo-activate methane, neither of which yielded definitive results.

The mesoporous support fluoresced so strongly that we could not discern the solvatochromism; the methane did not show noticeable conversion at the low pressures attempted. We will thus perform the experiments using a different emission mechanism that employs photons energetic enough to penetrate dense reaction mixtures and robust cell windows. We will also generalize the research in FY 2015, replacing the UV-visible spectroscopy that was conveniently available in our labs with resonant inelastic X-ray spectroscopy, which requires access to a synchrotron.

As of FY 2014 end, a manuscript describing last year’s results has been revised and is pending at ACS Catalysis, and a manuscript on this year’s results is being prepared for an invitational volume of Topics in Catalysis.
We are developing a fundamental understanding of materials dynamics (from microseconds to nanoseconds) in systems where the required combination of spatial and temporal resolution can be reached only by the dynamic transmission electron microscope (DTEM).

This research will develop the DTEM capability to perform single-shot in situ measurements in liquid and gas stages with a combined spatio-temporal resolution at least four orders of magnitude faster than any other competing technique (including aberration corrected STEM/TEM). In this temporal regime, the DTEM is expected to have atomic spatial resolution, providing an in situ TEM capable of studying nanoscale dynamic phenomena with several orders of magnitude time resolution advantage over any existing in situ TEM. In addition to providing unique insights into the inorganic and organic systems studied, this research will test the limits of temporal resolution and define electron optics and alignment for the next generation of truly ultrafast TEM (i.e., sub-ns). For nanoclusters in fluid around an electrode, interactions between the particles leading to the nucleation and growth of thin films will be examined for the first time. The ability to observe “live” biological systems will provide unique insights into biological systems.

The primary goal accomplished in the first year of the project (FY 2012) was to move the DTEM from the University of California-Davis to PNNL and install the microscope in the EMSL Q-wing. We finished the year with the instrument performing up to factory specifications, providing the platform for work in FY 2013. During this year, two laser systems were needed to convert from a field emission microscope to a DTEM. The first laser system uses a UV pulse used to create the photoemission pulse of electrons (this defines the DTEM resolution), while the second system creates an optical pulse to stimulate the specimen (i.e., creates the reaction in the DTEM). The final part of the DTEM was modification of the electron gun. Working with JEOL, Energy Beam Sciences, and consultants from the University of Michigan and University of Illinois at Chicago, the gun was designed and assembled.

In FY 2014, testing of the complete system began. During this process, several issues with the manufacture and supply of parts to the DTEM were identified (all third-party vendor issues not associated with the DTEM design). First, the alignment of the mirror in the gun was offset during the final stages of the installation. This was rectified by the design and implementation of alignment jigs to align the mirror precisely within the design tolerances. The second issue concerned the cleanliness of the photoemission tip used to create the beam. Oil introduced during the fabrication of the emitter led to the instrument being unable to reach its 200 kV operating voltage. New protocols introduced for the fabrication and installation of the emitter rectified this problem. Diagnosis of these issues required a significant improvement in the alignment protocols for the laser system on the DTEM, resulting in vastly improved testing and operating procedures for the instrument. The improved gun is now on the microscope column and undergoing initial tests with the expectation that operation of the microscope will begin in early FY 2015.

Work commenced in FY 2014 to develop new technologies for implementation of fast imaging within the DTEM framework. The first of these involved collaboration with the National Center for Microscopy and Imaging Research at the University of California, San Diego. The goal was to determine the ability of direct electron detectors to provide increase in the signal-to-noise over conventional CCDs and thereby increase the overall spatio-temporal resolution of the DTEM. Work showed that a simple frame shifting device plus detector should be able to generate a frame interval of ~50 µs. The first direct electron camera capable of 100 Hz continual acquisition movies will be loaned to PNNL in FY 2015.

To overcome data issues associated with imaging at the frame rate that the DTEM will produce, work was initiated to develop a compressive sensing approach to image acquisition. Initial designs for this approach have been made and will be implemented on microscopes in EMSL in early FY 2015.
**Quantitative Imaging of Atomic Scale Chemistry Changes at Interfaces**

*Nigel D. Browning*

This research will develop the statistical methods necessary to quantify changes in the atomic structure and the chemistry that occurs at interfaces and in nanoparticles.

Interfaces (including surfaces) control many of the structural, electronic, and chemical processes that take place in materials and in the properties of a device or system. Using new imaging technologies, critical fluctuations in structure and composition controlling these properties can be observed and quantified, leading to a new level of understanding and control. In this project, we will provide statistical validity to the presence of a particular structure, the number of impurities/vacancies present, and the effect they have on the structure, thereby extending atomic scale analyses to the micro to macro scale that are important in real systems. Application of an *in situ* gas stage and environmental transmission electron microscopy will allow the stability of interfaces/nanoparticles to be quantified as a function of environmental conditions and identify likely pathways for structural instability. Such measurements applied together will significantly improve our understanding of the functionality of materials under real working conditions. The specific aim is to develop the framework for quantitative chemical imaging of interface/nanoparticle structures under environmental conditions (specifically under different ambient gas conditions). Quantitative chemical imaging has been applied ad-hoc and has not been used for detailed comparisons between experimental results and first principles simulations. A quantitative framework for image interpretation is the only way to compare atomic-scale determination of interface structure and composition with larger scale property measurements.

In FY 2012, our analysis focused on grain boundaries in oxides as a model system that has potential to create a set of crystallographic rules for interfaces. The synthesis of new materials through crystallographic rules for specific applications to proceed at a more rapid rate allowed the defect properties to be predicted from the bulk structure. During FY 2013, our work investigated the effect of cation doping on the grain boundary plane structure. Initial results from SrTiO$_3$ grain boundaries prepared to be doped intentionally with Pr and Eu suggested that dopants affect more than just chemistry: Pr in the structure seemed to limit the grain boundary plane to one particular structural variant, which means that composition fluctuations in the nominally undoped grain boundary plane caused two equal energy structures to form. The Eu doping had the opposite effect and pushed structural stability in the other direction.

Our work in FY 2014 extended the analysis of interfaces to a study of catalytic systems, particularly the active site distribution within MoVTeNb oxide catalyst systems. Using atomic resolution Z-contrast imaging and electron energy loss spectroscopy, a direct determination of the atomistic surface termination layer was obtained. This layer is essential in catalytic processes because it is the place where reactions actually take place. The particular advance achieved in this case was that because of the direct visualization methods, a quantitative analysis of the active sites at the surface was obtained. Using the average particle size determined for a range of sample morphologies by helium ion microscopy, a statistical analysis of facet exposure distribution was performed, which permits the atomistic scale analysis of the scanning transmission electron microscopy (STEM) to be translated into a mesoscale distribution of active sites. The density of active sites determined in this way correlated directly with the catalytic activity of the system, allowing the overall response of a catalyst to be built up one atom at a time.
time. These results provide new insights for the design and optimization of synthetic methods, leading to more efficient materials.

In addition to our work on the complex oxides, aberration-corrected Z-contrast imaging in STEM was used to characterize zeolite and oxide supported metal clusters and single-atom complexes. Atomic scale images are the first showing direct visualization of site isolated Pt, Rh, and La complexes supported on zeolites at the atomic scale with single atom sensitivity. The data illustrates how Z-contrast imaging can be used to quantify accurately the size (mononuclear or clusters), locations of metal atoms in the zeolite pore structure, and distribution of metal species (mononuclear or clusters) in crystalline and amorphous regions of dealuminated zeolites. In addition, sequential images nanostructures taken at the same location of the specimen allowed dynamic structural changes caused by the electron beam to be observed. With the influence of electron beam carefully elucidated, the results were used to accurately correlate the catalytic performance to the structure.

The above results also demonstrated that STEM complemented by extended X-ray absorption fine structure and infrared spectroscopies, permits an atomic to macroscopic level of analysis. A combination of these methods can provide unprecedented fundamental insights into the functionality of supported metal catalysts. The experimental setup and capabilities are not limited to highly uniform catalysts and can be extended to more complicated catalysts with non-uniform structure (like those typically used in industrial applications). The methods developed as part of this project can therefore be expected to offer great opportunities for providing insights into the design, synthesis, and characterization of catalysts.
We are providing a reagent free ultrasensitive contaminant analysis technique for the semiconductor and other high purity materials industries. This project has relevance to the trace level detection and measurement of elements that are important to non-proliferation efforts.

The shrinking size, increasing speed, and complexity of semiconductor integrated circuits requires advanced processes that place extreme constraints on the level of metal contamination allowed on silicon wafer surfaces. Such contamination degrades the performance of ultra-thin SiO$_2$ gate dielectrics (< 4 nm), for example, that form the heart of individual transistors. Ultimately, reliability and yield are reduced to levels that must be improved before new processes can be put into production. Much of this metal contamination occurs during the wet chemical etching and rinsing steps required for the manufacture of the integrated circuits. Industry is actively developing new fabrication methods that have already brought the metal contamination to levels that challenge detection capabilities of conventional analytical techniques, but further progress requires improved methods. In addition, a need exists to detect and measure trace level radioactive and chemical agents with ever smaller detection limits.

Through this project, we are developing a new reagent-free sample preparation technique using mass selective ion implantation to concentrate impurities of interest from the bulk matrix material to improve the sensitivity of existing mass spectrometry analytical techniques. This approach removes the single greatest impediment to improved analytical methods for trace element detection and measurement; namely, the process of blank limitations that originate from impurities in the reagents and/or from the leaching of impurities from the labware by reagents. The semiconductor industry has a target sensitivity of < 10$^7$ atoms/cm$^2$ for surface impurities in silicon wafers, while their current analytical techniques can achieve only < 10$^9$ atoms/cm$^2$. Coupled to a high efficiency elemental mass spectrometer, our method should be able to achieve sensitivities at 2–3 orders of magnitude below the current semiconductor industry goals. Our technique also offers the opportunity to advance the detection of $^{40}$K, $^{232}$Th, and $^{238}$U in ultra-pure metals and plastics that contribute a significant radiation background from these materials in detectors used for the faintest nuclear radiation signatures related to questions in particle physics and treaty verification.

In FY 2014, we designed experiments that investigate implant hardware design, including macro- (30 mm$^2$) and micro- (< 1 mm$^2$) sized implants, along with differing sized quad exit lens apertures that influence implant dimensions. Actual implant atom collection efficiency was evaluated along with quantification of the method detection and instrument detection limits. Our work on the tandem mass spectrometry analysis concept showed considerable promise, with detection limits in the low femtogram range achieved in a number of experiments using a fairly contaminated copper substrate with background trace levels of the elements under investigation. Switching to a very clean substrate (such as semiconductor grade silicon) should drop the detection limits considerably (probably 2–3 orders of magnitude), allowing attogram detection to be attained.

Our work highlighted the need for careful sample handling to avoid analyte loss; additionally, the effort indicated that some of the work aimed at shrinking the ion implanted area from > 10 mm$^2$ to < 1 mm$^2$ would be highly beneficial. The use of piezo electrically driven translation stage to position the substrate for multiple implants without breaking vacuum looks to be an important next step development to expedite the process to broaden the commercialization potential of the concept. With the acquisition of the high mass resolution (and higher sensitivity) ICP-MS next year's work looks well positioned to tackle a challenging analysis of more commercially important elements like the low mass alkali, alkaline earth and transition metals of particular interest to the semiconductor industry.
Understanding the microscale chemical gradients in electricity-producing biofilms and the ability of these microorganisms to use extracellular electron transfer can lead to novel applications in bioremediation, alternative energy production, and electrochemically stimulated synthetic biology to produce high value products.

Previous studies demonstrated that some bacteria are capable of transferring electrons derived from respiration to solid extracellular electron-accepting materials. Termed extracellular electron transfer (EET), this ability allows bacterial biofilms to use solid conductive substrata as a sole electron sink. The electrochemically active biofilms have numerous implications in biogeochemistry and microbial ecology, and they have been used in practical applications such as in marine-based microbial fuel cells to power oceanographic sensors and monitoring devices to extract energy and enhance chemical oxygen demand removal during wastewater treatment; to act as biosensors for nitrate/nitrite, glucose, and other chemicals; to desalinate water while simultaneously generating electricity; and for producing hydrogen gas via microbial-driven electrolysis. Understanding EET mechanisms will allow us to exploit and engineer this process for several beneficial applications, many of which are of interest to DOE, such as heavy metal and radionuclide bioremediation and electrochemically stimulated synthetic biology.

It is not known how microenvironments inside electrochemically active biofilms affect electron transfer mechanisms or if it is possible for a biofilm to use multiple electron transfer strategies simultaneously. We are addressing the role of microenvironments on electron transfer at a basic level leading to enhanced applications of electricity producing biofilms. Combining nuclear magnetic resonance (NMR) with electrochemical techniques, we can explore electricity-producing microorganisms non-invasively at the microscale.

To reach our project goals, an electrochemical (EC)-NMR biofilm reactor was designed and optimized to allow simultaneous NMR and electrochemical techniques at high resolution and quick scan rates. To fulfill our project objectives, we created a reactor with built-in reference and counter electrodes, improved the radio frequency coil, and incorporated electromagnetically shielded wire to minimize noise on the potentiostat lines. We formed a new reactor design using 3D printing technology that eliminates the optical window and has a ~60% smaller cross-sectional area (~40% smaller perimeter) with 50% less internal volume. A custom Faraday cage was built to enclose the potentiostats used for electrochemical techniques, improving the signal-to-noise ratio.

During FY 2014, two new NMR methods were developed that have significantly expanded the capability the EC-NMR setup. The point-resolved spectroscopy (PRESS) method enables up to second order shimming on a localized voxel, which increases the signal by 40% while improving the spectral resolution by improving peak resolution from between 14% and 24%. Second, a chemical shift selective imaging method was developed that enables 1D chemical shift selective imaging using slice selective excitation to choose a 1.5 mm thick plane centered on the explant that allowed rapid depth profiling of quantitative porosity. This method is an order of magnitude faster than previous depth profiling methods, though the spectroscopic dimension is not collected and the signal intensity is quantitatively proportional to excited nuclei concentration. These two methods were used to study several microbial mat and biofilm systems and are currently interrogating Geobacter biofilms.

During the past fiscal year, work from this project has yielded five published journal articles and presentations at four conferences, two of which were invited international appearances.
This project will develop new research capabilities for simulation of reactivity and structure in complex heterogeneous and homogeneous environments.

A significant issue in basic energy sciences is understanding and characterizing the novel chemistry that takes place at interfaces. This requires the use of molecular simulation with interaction potentials that contain charge transfer, polarization, and the ability to make and break chemical bonds (i.e., chemistry). The development of novel simulation protocols to probe differences between bulk and interfacial environments is a crucial component to making quantitative predictions about reaction thermodynamics, selectivity, and activity. Understanding the nature of ion solvation at interfaces can change how we conduct basic energy research; however, fundamentals of an ion’s propensity to be present at an interface and the important interactions are still not fully understood.

In recent years, theoretical and experimental studies have presented a picture of the aqueous interface, wherein hard and/or multiply charged ions are excluded from the interface, but large polarizable anions show interfacial enhancement relative to the bulk. Thus, a fundamental understanding of ions in solution is an important step toward controlling matter. Surface sensitive spectroscopy and current and next-generation x-ray absorption experiments require high quality simulations in order to interpret observation. Thus, there is a unique opportunity to use and develop molecular simulation methodology based in quantum mechanics to advance our understanding of these important systems and provide sorely needed data to aid in the interpretation of experiments. To this end, the air-water interface serves as a model interface where much of the important phenomena regarding ions and proton transfer are an active area of research.

In FY 2011, a joint experimental and theoretical study revealed the remarkable differences in the solvation structure around molecular HNO3 under bulk and interfacial solvation, suggesting that hydrogen bonds between HNO3 and water molecules at the solution surface stabilize the molecular form at low concentration. The same mechanism was postulated for the stabilization of molecular HNO3 that occurs in bulk solution at high concentration. During the next two years of the project, the first solvation shell structure about the polyoxoanion, iodate (IO₃⁻), under bulk conditions as measured by extended X-ray absorption spectroscopy (EXAFS) was investigated. The region of IO₃⁻ behaves like cation wherein the iodine atom has a formally positive charge while the other region behaves like an anion wherein the iodate oxygen atoms have formally negative charge.

In FY 2014, we further expanded the above concept of the first solvation shell in determining/predicting interfacial propensity. We investigated three ions (iodide, iodate and thiocyanate) with similar polarizabilities but significantly different surface propensities. Their hydration structure under both bulk and interfacial conditions suggest that it is indeed the characterization of the hydration structure rather than the underlying polarizability is a strong indicator of surface propensity. These results were published in the Journal of Physical Chemistry Letters and Faraday Discussions.

Through the use of EXAFS measurements in conjunction with state-of-the-art density functional theory simulations, we obtained an unprecedented view into the molecular structure of medium to high concentrated electrolytes. Especially, we find a Cl—H₃O⁺ contact ion pair that persists throughout the entire concentration range studied that depicts a significantly different structure from moieties studied in micro-solvated hydrochloric acid clusters. These results were published in a frontiers article in the Journal of Physical Chemistry B.

Consistent with our previous studies on nitric acid, it is indeed the preponderance of the contracted contact ion-pair between chorine and H₃O⁺ in high concentration HCl, which is also observed at low concentrations of HCl in the vicinity of the air-water interface. The abundance of this contracted ion pair preconditions the likelihood for fast proton exchange as observed in molecular beam studies. These results were published in the Journal of Physical Chemistry B.
Upgrading of Bio-Oils by Selective Ring-Opening of the Oxygenated Cyclic Compounds

Vanessa Dagle

We developed a two-step ring-opening process to maximize the yield of high molecular weight paraffins products. This effort will lead to the efficient upgrading of (hydroprocessed) bio-oils and be applicable to upgrading any bio-oil or fuel-containing cyclic compounds through ring opening catalysis.

Bio-diesel represents less than 1% of the total U.S. diesel market, and all aviation fuels are currently derived from fossil fuel sources. Fast pyrolysis and subsequent catalytic hydro-processing is one of the most viable technologies to produce liquid biofuels. However, bio-fuels obtained from direct liquefaction routes have limited use due to the high cyclic nature of the carbon chains produced. Efficient upgrading of these aromatics and cycloparaffins into (iso)-paraffinic compounds that are highly valuable for diesel and jet markets will support the U.S. economy. Heavy transportation consuming 70 billion gal/yr of diesel + jet fuels is a future probable target industry for biomass-derived diesel and jet fuels.

Hydrotreated bio-oils contain up to 90% of cyclic hydrocarbons that could be converted into high molecular weight paraffins via ring-opening technology. This process is conventionally conducted in a single step over a bifunctional catalyst containing a metal and an acid function. The efficiency is limited for C₇ rings from the production of a large amount of cracked products. When metal and acid are mixed, multiple reactions take place simultaneously leading to undesired products. Our hypothesis is that to solve this issue, acid and metal functions must be separated into two catalysts loaded in two separate reactors. Hence, we developed a two-step process consisting of a ring contraction catalyst reactor for selective production of C₅-ring compounds and a hydrogenolysis catalyst reactor active for C₅ ring-opening to maximize the yield of high molecular weight paraffins.

First, we studied process conditions and screened catalysts for the two-step ring-opening of methycyclohexane (MCH), which is one of the major compounds of hydrotreated pyrolysis bio-oils. For the “ring-contraction” step, parametric tests have shown that the selectivity toward the desired alkylcyclopentanes (C₅-ring compounds) decreases with the increase of the conversion. Thus, lower temperature (250–320°C) and higher space velocity (GHSV=10,000-23,000 h⁻¹) are preferred. The pressure (15–45 bar) has little effect on catalytic performance. At moderate temperature and pressure, a remarkably high yield of alkylcyclopentanes (65%) can be obtained.

We demonstrated that the nature of zeolite support significantly affects catalytic performance. Indeed, the 1% Pt/H-ZSM22 catalyst was selective to the desired alkylcyclopentanes compared with the 1% Pt/H-ZSM5 catalyst, especially at high conversion. For example, for conversion equal to 70%, the alkylcyclopentanes selectivity was high and equal to 95% for 1%Pt/H-ZSM22 and only 60% for 1%Pt/HZSM5. The undesired cracking reactions leading to the formation of unwanted C₅-C₇ products are more facile over the 1%Pt/HZSM5 from higher concentration of acid sites. For the 1%Pt/HZSM22 catalyst, exceptionally high selectivity (> 90%) toward desired products was obtained over a wide range of conversions studied (0% conversion ≤ 70%). Because the 1% Pt/HZSM22 catalyst appeared promising, we investigated the effect of metal loading (0–3% Pt) for the supported HZSM22. Results have shown that Pt is necessary to produce olefins that are readily transformed into ionic intermediates leading to C₅ ring formation. However, Pt dispersion does not significantly affect the activity, with only small quantities of Pt (≤ 1%) required.

For the hydrogenolysis step, we examined the effect of the process conditions using a 1% Ir/Al₂O₃, as this catalyst is known to be efficient for C₅ ring-opening/hydrogenolysis. The products and unconverted MCH of the ring-contraction step were used as feedstock. The results have shown that the selectivity toward the n and iso C₇ paraffins is higher at lower temperature (300°C) and pressure (15–20 bar). Cracking reactions were indeed favored when temperature and pressure increased from 300 to 360°C and 15 to 30 bar, respectively. For T=320°C and P=21 bar, up to 67% selectivity of n and iso C₇ paraffins was obtained.

Next, we compared the efficiency of this novel two-step process with the one-step. For the one-step, we studied two configurations: a “mixed bed” configuration where the 1%Pt/ ZSM22 catalyst was mixed with the 1% Ir/Al₂O₃ catalyst and a “cigarette bed” configuration with the 1%Pt/ZSM22 catalyst loaded on top of the 1% Ir/Al₂O₃ catalyst. For comparison purposes, the catalytic performance of the “mixed bed” and the “cigarette-bed” was evaluated at 320°C and 21 bars. For conversion to equal 30%, the selectivity toward n and iso C₇ paraffins was equal to 26% for the mixed bed configuration, 35% for the cigarette bed configuration and 41% for the two-step process. These results demonstrate that it is preferred to separate the ring-contraction catalyst and the hydrogenolysis catalyst to avoid multiple reactions leading to carbon loss to take place simultaneously. Another important finding is that...
optimal \( n \) and iso \( C_7 \) paraffins selectivity is obtained when the two catalytic functions are loaded into two different reactors rather than on top of each other in one reactor. For the two-step process, the hydrogelenolysis step can be conducted at higher throughput, which limits cracking and thus favors formation of the desired products.

The successful proof-of-concept principles demonstrated during the FY 2013 work provided reason to extend this research to the selective ring-opening of oxygenated cyclic compounds of bio-oils. Bio-oils contain a large fraction of oxygenated cyclic compounds (e.g., phenol) difficult to hydrotreat and thus requiring higher hydrotreating temperatures and \( H_2 \) excess. A preferred solution would be to convert these oxygenated cyclic compounds into linear (oxygenated) carbon chains before hydrotreating. This would prevent the “over hydrogenation” that currently occurs with phenolics bio-oils.

In FY 2014, we thus evaluated the efficiency of the process for the conversion of 2-methylcyclohexanol and 2-methylphenol (oxygenated cyclic compounds) into long chain paraffins (\( n \) and iso) under similar conditions as those for methylcyclohexane. For both 2-methylcyclohexanol and 2-methylphenol, the ring-contraction step conducted over the 1\% Pt/HZSM-22 catalyst lead to the formation of desired methylcyclohexane, ethylcyclopentane, and dimethylcyclopentane and small amount of “unwanted” toluene (as shown in the graphic) for 2-methylphenol.

The liquid product from the ring-contraction step was then used as feedstock for hydrogenolysis conducted over the 1\% Ir/Al\(_2\)O\(_3\) catalyst under similar conditions as those for methylcyclohexane model compound (from FY 2013) to convert the cyclic compounds into long-chain paraffins (i.e., \( C_7 \)). Then, we compared the efficiency of the two-step process with the one for the conventional one-step where the 1\% Pt/HZSM-22 was physically mixed with the 1\% Ir/Al\(_2\)O\(_3\) using both 2-methylcyclohexanol and 2-methylphenol as model compounds. Interestingly, for a given conversion and under similar temperature and pressure, the selectivity toward the desired \( C_7 \) paraffins was comparable for both processes. However, higher contact time is required to convert the oxygenated cyclic compounds into paraffins using the one-step process compared with the two-step.

Hence, we successfully demonstrated that (oxygenated) cyclic compounds (e.g., methylcyclohexane, 2-methylphenol) can be converted into long chain hydrocarbons via this novel two-step ring-opening process minimizing cracking while operating at mild conditions.

![Graph showing the evolution of the conversion of 2-Methylphenol as a function of the GHSV over 1\% Pt/HZSM-22. T = 320°C, P = 20 bar, H\(_2\): 2-methylphenol/Heptane (50/50 wt %) = 10:1 molar.](attachment:image.png)
Earth and Space Sciences
Determining Groundwater Residence Time Through Ultra-Low Measurements of $^{39}\text{Ar}$ and Other Radiotracers

Jill M. Brandenberger

We are leveraging PNNL’s ultra-low background proportional counting (ULBPC) capability to develop, optimize, and validate ultra-sensitive measurements of the noble gas radioisotope Argon-39 as a radiotracer that constrains the age of groundwater in the intermediate timescale range of 50–1000 years.

Quantifying the mean residence time (MRT) or age distribution of groundwater is important for determining surface-groundwater interaction (recharge rates) critical to refining future water budgets (e.g., drinking water supplies). MRT supports estimating the recovery time of contaminated groundwater aquifers by verifying numerical groundwater flow models, evaluating connectivity of aquifers in hydraulic fracking regions, and defining “drinking water protection areas” under forecasted climate change scenarios. Estimates of the MRT are possible by using multiple environmental radiotracers that currently cover age ranges of under 50 ($^{3}\text{H}/^{3}\text{He}, ^{85}\text{Kr}$) and over 1000 years ($^{14}\text{C}$), but there is a gap in the 50- to 1000-year age range. Established tracers would not adequately define the age of a groundwater aquifer where recharge was occurring at intermediate time scales of 50–1000 years. The outcomes of this project will significantly advance PNNL as a national leader in the ultra-sensitive detection of radioactive tracer and provide significant scientific contributions in both environmental and national security applications.

Progress on this project during the last fiscal year is listed and explained categorically below.

High recovery $^{39}\text{Ar}$ separation chemistry. The existing argon separation and purification system developed by PNNL uses a commercial pressure swing adsorption (PSA) oxygen generator to remove nitrogen and oxygen from gas samples prior to argon analysis. The limitation to this system is that the argon recovery efficiency is just 20–30%. The ultra-trace measurement of $^{39}\text{Ar}$ (half-life of 269 years) extracted from groundwater requires more volume and subsequently the existing methods greatly increase the costs. This project developed two new processes to increase the argon purification recovery: a calcium carbide reactor and a high recovery dual reflux PSA process. The calcium carbide reactor coverts nitrogen and oxygen in the sample gas into solid compounds and gas species that are easily separated from argon, providing a means of separating nitrogen and oxygen from argon with close to 100% recovery. To this end, a high recovery dual reflux PSA system was developed as a part of an $^{37}\text{Ar}$ measurement system (see photo). We tested the nitrogen separation process to ascertain the recovery efficiency for $^{39}\text{Ar}$ measurements. The dual reflux PSA system provides up to 80% argon recovery from sample gas similar in composition to air.

A groundwater well located in Coyote Canyon, Kennewick, WA was selected for a site to demonstrate the ability to effectively degas groundwater at the well site, transport the gas sample back to the lab, purify it using the dual reflux PSA system, and count the $^{39}\text{Ar}$ in the shallow underground laboratory. We successfully collected the groundwater demonstration sample and conducted an end to end analysis that decreased the required sample size by a factor of two. In addition, PNNL and the U.S. Geological Survey (USGS) National Water Quality Assessment Program collaboratively sampled a series of nested groundwater wells in Fresno, CA. This collaboration provides a direct comparison between the radiotracers that USGS uses for determining MRT ($^{3}\text{H}/^{3}\text{He}$ and $^{14}\text{C}$) and our $^{39}\text{Ar}$ measurements. This will demonstrate the utility of the intermediate age modeling that $^{39}\text{Ar}$ can provide. The samples will be counted in FY 2015 and a joint publication produced.
The age modeling of the Coyote Canyon groundwater aquifer near Kennewick, WA is established at 133–222 years old.

Absolute gas counting. The development of accurate, low-level calibration standards improves the measurement accuracy of $^{39}$Ar and other isotopes such as $^{37}$Ar and radio Xe. The absolute gas counting capability employed is term length-compensated, internal source proportional counting. This method has been used for decades, but PNNL is the first to adapt and utilize this method in the measurement of very low-level background materials and new detector fabrication techniques. Sets of detectors have been fabricated and a system built and tested for careful, quantitative gas transfer of samples into the detectors, which significantly improves the efficiency of making low-level measurements. For FY 2015, the system will be used for measurements of standard materials as part of international intercomparisons or “round-robin campaigns.” With this participation, PNNL will gain international visibility in the area of low-level calibration of $^{39}$Ar, $^{37}$Ar, and radio Xe standards that will lead the way for further measurement campaigns.

Ultra-sensitive $^{39}$Ar measurements. This capability leveraged the shallow underground laboratory and other research to develop low background materials and proportional counters. This project specifically provided optimized operating parameters and analysis packages for ultra-sensitive measurements of $^{39}$Ar extracted from groundwater using ultra-low background proportional counters. Three detectors have undergone characterizations with modern and ancient sources of Ar to determine sensitivities and baseline reference performance. The project successfully conducted the first U.S. measurement of $^{39}$Ar degased from $^{39}$Ar degased from groundwater, purified, and counted to determine the age of the groundwater at Coyote Canyon. The groundwater in this region has not been at the surface for more than 133–222 years (see images).

Our project accomplished a significant milestone by demonstrating the first U.S. measurement of $^{39}$Ar from groundwater to provide the MRT or age modeling of the aquifer. This measurement required increasing the efficiency of the argon purification, enhancing our absolute gas counting method for providing argon standards, and optimizing the proportional counters to provide low-level detection of $^{39}$Ar. The joint publication of this technique with the USGS Climate Response Network and execution of the international intercomparison will provide key information regarding the U.S. water budget in sensitive regions.
Development of a Method to Calculate Force of Storm Surge and Wind-Wave on Energy Infrastructure Under Extreme Climate Conditions

Zhaoqing Yang

We are developing a method to calculate the combined forces induced by storm surge and large waves on offshore structures to understand their impacts on energy infrastructure under extreme climate conditions.

Coastal zones are home to more than half of the U.S. population and a wealth of natural and economic resources. These areas include some of the most important energy and transportation infrastructures, ports and pipeline systems, offshore oil and gas platforms, and prestigious ecosystems. About 30% of the U.S. oil supply and 20% of the natural gas supply is produced in the Gulf of Mexico region alone. Storm surge and oversized waves induced by hurricanes pose significant threats to the onshore and offshore energy infrastructures. Impacts of extreme waves on offshore oil and gas platforms can be exacerbated by the nonlinear wave-current interaction and additional force induced by storm surge under extreme climate conditions. Extended pounding by large waves and storm surge can demolish offshore structures that are not specifically designed to withstand such forces. Based on global climate model predictions, the intensity of tropical cycles is expected to increase under future climate change conditions. Although some studies have considered the effects of currents on wave dispersion relation and force, the calculation of combined forces from storm surges and large waves on offshore structures is routinely excluded in impact assessments. Therefore, a need exists for an efficient method of calculating the combined force induced by waves and storm surges under extreme climate conditions, especially in large coastal regions.

In this study, a method with a combination of higher-order wave theory, wave model, and storm surge model outputs was developed to calculate the horizontal drag and inertia forces induced by extreme waves and storm surge. The method was applied to determine wave force distributions during Hurricane Katrina in the northern coast of Gulf of Mexico, where approximately 7,000 oil and gas offshore platforms are located. To explore the effects of future climate change on extreme waves and storm surge, the correlation of wind shear and accumulated cyclone energy (ACE) with significant wave height was briefly evaluated using long-term wave model outputs in the Gulf of Mexico. Wave force on structures can be calculated based on wave parameters such as significant wave height, period, length, velocity, acceleration, and other environment parameters including water depth and currents.

In this study, the fifth-order dispersion relation was used to determine the wavelength using significant wave height and period from the National Oceanic and Atmospheric Administration’s regional WaveWatchIII model as well as storm surge height and velocity from PNNL’s high-resolution coastal storm surge model. Once the wavelength was determined, velocity and acceleration were calculated based on the higher-order Stokes wave theory. The horizontal drag and inertia forces, which

Distributions of wave and storm surge model outputs and calculated wave forces in the northern coast of the Gulf of Mexico during Hurricane Katrina: (a) storm surge level, (b) significant wave height, (c) storm-surge velocity, (d) wave velocity, (e) drag force, (f) inertia force.
depend on the wave and storm surge velocities and accelerations respectively, were calculated based on the modified Morrison equation.

Model results showed that significant wave heights reached as high as 15 m near the center-core of the hurricane track. Storm surge velocities exceeded 5 m/s in the shallow water region, although they were generally small in the deep continental shelf. A sensitivity analysis indicated that impacts of storm surge and wave nonlinear effects on wavelength and drag force are significant in the near-shore region during hurricane events. In areas where storm surge velocities are extremely high, storm surge-induced drag force can be as large as wave-induced drag force. However, storm surge-induced acceleration in the entire domain is at least one order of magnitude smaller than the magnitude of wave acceleration. Therefore, the effect of storm surge on inertia force is negligible compared to wave-induced inertia force.

Analysis with 16-year WaveWatchIII model outputs indicated that even though the wave height is maximum during winter, the maximum interannual variability occurs during the peak hurricane months of August and September. Consistent with this, the scatter of ACE and wave height shows that ACE explains about 40% of the total interannual variability in wave height.
Enhanced Sediment Geochronology Achieved Using Ultra-Low Background Materials and Ultra-Sensitive Detection Capability

Gary A. Gill

New, enhanced capabilities developed by this project will have a significant impact on environmental geochronology and other low-background radiation measurement applications, significantly advancing PNNL as a national leader in new geochronology capability and radioactive signals ultra-sensitive detection.

A gap exists in age dating of environmental systems (e.g., sediment, trees, groundwater) between 100 and 1,000 years, limiting our ability to understand the ecosystem changes as a function of both climate and human drivers. Thus, the objectives of this project are to produce a new sediment geochronology tool based on highly sensitive radiometric dating using 32-Si (half-life of ~140 years); develop the world’s lowest-background beta detectors using new low-background plastics to enable the 32-Si age dating method; demonstrate 32-Si age dating with Puget Sound sediment cores from the 100- to 1000-year age bracket; and create a new, high-precision measurement of the 32-Si half-life.

Sediment geochemistry. A major effort in FY 2014 involved the processing of enriched sediments from Sequim Bay using optimized chemistry procedures and measuring chemical yields and radiogenic decontamination at each step. The final phosphorous yield was 66% with no measureable Si based on ICP-OES analysis. The final P solution was prepped for a final CASCADES measurement, with the results indicating a weak positive for thorium decay chain isotopes (Ac-228, Pb-212, and Ti-208). Efforts are ongoing for interpreting these values against critical limits for CASCADES. However, the associated background from the sample may still be unacceptably high and will be determined using the BIDS detector when operational in 3425/B124. In the meantime, additional chemical steps will be evaluated to further reduce both the current radiogenic background and the final volume of the P fraction for easier BIDS detector sample preparation.

Ultra-sensitive BIDS detector development. The design of a prototype low-background counter was completed in FY 2013. The detector is a variable-length pressurizable single-wire counter that can be paired with an identical counter to provide 4 Pi solid angle coverage of the source. Two of the prototype low-background detectors were assembled and tested during FY 2014. The initial tests indicate good spectroscopic performance of the detectors. Initial measurement of the detection efficiency is ~40% for two detectors, which is lower than desired. Materials have been received to optimize the sample geometry, with a significant detection efficiency boost anticipated. Preparations are underway to measure the detector background in an existing shield, and shielding materials and active anti-cosmic detectors have been received to prepare a small shield system. After gathering additional data, an article related to this work will be presented at an international conference and submitted for publication.

Great strides have been made with the physical and chemical separations to isolate the biogenic silica for extraction. Samples are being prepared that will be ready for beta counting for the start of FY 2015, along with the completion of detector configuration and cave preparations so that counting can begin as soon as the samples are prepared. Finally, alternative options for establishing the 32-Si half-life are being researched using multi-collector thermal ionization and multi-collector inductively coupled plasma mass spectrometries, where these results will be reviewed in the next fiscal year for their viability.
Enhancing EMSL Mass Spectrometry Capabilities for Characterization of Soil Organic Matter

Nancy J. Hess

We are developing experimental capabilities to allow molecular characterization of organic molecules in soil, leading to harnessing chemical reactions that impact C cycle dynamics in response to climate change, land use and agricultural practices, and extreme weather events.

In standard practice, analytical capabilities to characterize soil C provide a broad description of classes of organic components based on chemical solubility in extractants under laboratory conditions or total elemental composition from pyrolysis. These explanations are inadequate for development of mechanistic functional models of carbon allocation in soils in terrestrial ecosystems by plant, microbe, and fungal metabolism. The lack of chemical and molecular detail also makes assessing the vulnerability of soil C to global climate change and its incorporation of potential feedbacks in global climate models equally unobtainable. This technical gap can be addressed by leveraging EMSL’s recognized expertise and capabilities in high resolution mass spectrometry (MS), imaging, and automated data analysis capabilities and developing novel separations and ionization approaches for the characterization of soil C, thereby providing the chemical and structural detail needed to develop mechanistic descriptions of soil carbon flow processes.

Our research is developing high throughput, high resolution MS capabilities for the characterization of organic matter contained in mineral-and organic-rich soils. In FY 2014, we focused on two issues: addressing the data analysis bottleneck for high-throughput soil organic matter (SOM) characterization and development of extraction protocols for Fourier transform ion cyclotron resonance (FT ICR)/MS characterization of SOM from wide variety of soils.

Workflows for data analysis of high resolution-MS from SOM. We are creating user friendly data analysis tools for rapid assignment of thousands of peaks in SOM spectra via a toolkit that enables user-defined workflows in high-resolution MS data. The uniqueness of our approach is that peak classification and assignment relies on the high-order mass defect algorithm used in the toolkit for classification and identification of molecules based on mass defects. As a classification technique, the algorithm reduces the number of features by clustering peaks with similar first- and second-order mass defects into classes of molecules that vary only by the number of functional groups for the mass defect calculation. This powerful method efficiently reduces the number of features for identification and enables assignment of elemental formulas to higher m/z species that cannot be unambiguously assigned based on the accurate mass alone. We implemented post-peak assignment validation tools so that cross-correlation of peaks across multiple datasets is possible and added agile error handling features.

Development of extraction protocols for FT ICR/MS. The use of ultra-high resolution (UHR) MS enabled the examination of organic molecules directly from mixtures with ultra-high resolution and sub-ppm mass accuracy. We leveraged EMSL’s extensive expertise and capabilities in UHR MS proteomics to develop soft extraction protocols for the characterization of carbon compounds in SOM, providing the detail needed to develop mechanistic descriptions of soil carbon flow processes. Using a variety of solvents, we identified thousands of intact compounds in complex soil mixtures with a wide range of C content representing diverse ecosystems. The yield of the chemical extraction was dependent on the type of solvent and its polarity, sample-to-solvent ratios, and the chemical and physical nature of the samples. We found that hexane, a non-polar organic solvent, was efficient in extracting lipid-like compounds regardless of soil origin or organic carbon %. For samples with high organic carbon %, acetonitrile extracted a wide range of compounds characterized with high O/C ratios identified as polyphenolic compounds that were not observed with methanol extraction. The extraction followed by UHR MS is a promising tool to understand the dynamics of soil organic matter. Information gained from this study has been used to assess the sensitivity of soil carbon decomposition and feedbacks to climate change.

To complement the organic solvent-based extraction protocol, we developed a super critical fluid extraction (SCFE) method to characterize the organic molecules that constitute SOM. Online SCFE methods were developed to deliver highly concentrated products onto chromatography columns for easy coupling of the extraction product to a liquid chromatography (LC) system and subsequently MS analysis. The extracts and spent soil sample were solvent free, creating a robust/powerful alternative approach to solvent-based methods. In addition, the SCFE LC-FT ICR/MS identified nearly twice the number of peaks and used nearly an order of magnitude less soil sample. This on-column SCFE system was compared to a commercially available SCFE system to determine the advantages of collecting extracts directly on column and sensitivity of the systems with varying sample sizes.
Cloud feedbacks remain one of the greatest uncertainties in climate models. A more quantitatively rigorous identification of cloud phase from remote sensors can improve understanding of cloud processes, leading to better accuracy of cloud predictions from global climate models.

Between atmospheric temperatures of 0 and −40° C, clouds can contain ice crystals, super-cooled liquid droplets, or a mixture of both, impacting how clouds influence the energy budget of the atmosphere. DOE’s Atmospheric Radiation Measurement (ARM) Climate Research Facility makes multiple remote sensing measurements capable of providing information about the vertical distribution of cloud phase, though each is more effective in particular conditions. Current operational phase identification algorithms exist in the literature; however, they do not use all the available information from ARM remote sensors that has shown to be useful, nor do they give quantitative assessments of the uncertainty of the phase determination in given conditions. In this project, we are leveraging statistical and big data tools developed at PNNL to identify data signatures to formulate a phase detection algorithm that includes additional information from radar Doppler spectra and a more rigorous assessment of algorithm fidelity in a given situation using Bayesian networks.

In the initial seed-phase of this project, we created a merged dataset from the Barrow, Alaska ARM site that puts measurements from multiple remote sensing instruments (lidar, cloud radar, balloon-sonde, etc.) into a common temporal and spatial resolution. This scenario allows us to compare the information content from multiple remote sensing instruments during a field campaign that also has in situ validation data of cloud phase gathered from aircraft flights through clouds.

We applied the current best operational phase classification algorithm from the literature to this data to use as our control algorithm. This phase classification is based on only three moments of the radar Doppler spectra (reflectivity, mean Doppler velocity, spectral width) but can miss information from Doppler spectra with multiple peaks, an indicator of mixed-phase conditions. We examined this initial phase detection method with a more detailed radar measurement dataset and found indications of phase misclassification. For example, only 2/3 of cases with multiple peaks in the radar Doppler spectra were classified as mixed-phase instead of all cases, as we would expect. Also, some liquid-identified cloud cases gave radar reflectivity values that were too high, another likely indication of phase misclassification. These preliminary results were presented at the American Meteorological Society Cloud Physics meeting in mid-summer.

In FY 2015, we plan to develop an improved cloud phase algorithm using a Bayesian net framework that gives an indication of the signature quality for a given set of available measurements. For example, lidar depolarization ratio can be used to determine cases of super-cooled liquid water with high confidence. However, the lidar is attenuated quickly in clouds that contain water, so is not always available to help determine cloud phase. Currently, we are exploring statistical relationships between new moments of the radar Doppler spectra using a combination of clustering algorithms and big data visualization tools. We plan to use the results of this analysis to identify which radar Doppler spectral variables will be most useful in the new algorithm.

One of the difficulties of this problem is the lack of a “truth” dataset with which to validate remote sensing retrievals. We will validate our retrieval using the field campaign data currently available but also develop a framework so that we can easily continue to improve retrievals when additional aircraft in situ data becomes available. In particular, a field campaign planned at the ARM site in Alaska for summer 2015 will be ideal for further validation and improvement of the algorithm.
Measuring and Modeling the Climatic Effects of Brown Carbon Atmospheric Aerosols: Developing an Integrated Capability

John E. Shilling

This project is leading to new insights into the conditions under which brown carbon aerosols form; the processes that govern time-evolving chemical, physical, and optical properties; new methods for representing the processes and properties in climate models efficiently; and an evaluation of the impact particles have on climate.

Aerosols represent one of the greatest sources of uncertainty in understanding and simulating future changes in the earth’s climate. Aerosols affect the climate system by scattering and absorbing radiation, thereby affecting regional and global energy balances, and indirectly by altering cloud properties and lifetimes. It is commonly assumed that organic aerosols contain only non-absorbing materials and therefore have a predominantly cooling effect on climate. However, increasing evidence suggests aerosol aging may lead to the formation of light-absorbing organic compounds (i.e., brown carbon), which could exert a significant climatic impact currently not captured in climate models.

Unraveling the chemical composition, physical properties, and potential climatic effects of brown carbon aerosols is a multidisciplinary challenge that spans spatial scales ranging from individual molecules to the entire globe. We are developing a fundamental, molecular-level understanding of the chemical and physical processes governing the growth and aging of brown carbon aerosols in the atmosphere; determining how the resulting chemical and physical transformations affect the radiative properties of the species involved; and evaluating the significance of these processes for global and regional climate by developing parameterizations that encapsulate this new understanding and testing these parameterizations in climate models. Incorporating brown carbon formation processes will improve the accuracy of climate models, leading to better predictions of future climate.

In FY 2013, we found that aerosol particles were white (non-absorbing) when produced under low-NOx conditions and brown (absorbing) when produced under high-NOx conditions. Aerosol samples were collected on filters, and the samples from experiments were collected and analyzed using nanospray desorption electrospray ionization (nano-DESI) coupled to a high-resolution mass spectrometer at EMSL. These results indicate the incorporation of NO and potentially NO2 with concomitant loss of one water molecule into the primary oxidation products of trimethylbenzene.

Several advances in the modeling of brown carbon aerosol were achieved in FY 2013. On the molecular modeling scale, we explored aliphatic and aromatic compounds with and without carboxyl and nitro groups attached to these species to understand their absorptive properties, based on the preliminary results of laboratory molecular analysis. We performed an exploratory scoping exercise using the Community Earth System Model (CAM5) global climate model to estimate atmospheric and surface forcing that would arise if organic aerosol were much more absorbing than usually assumed by climate models. “Tags” were implemented that allow us to identify contributions from various precursors of organic aerosol and to assess the forcing associated with aerosol originating from those precursors. Finally, we performed multi-year simulations with a climate model in which we varied the aerosol optical properties and yields.

In FY 2014, we extended our laboratory studies to a wider range of precursors and photochemical conditions. We investigated the optical properties of organic aerosol produced from the photooxidation of toluene under high-NOx conditions. Liquid chromatography separation followed by UV-VIS detection and mass spectrometric detection is used to identify specific molecular products responsible for aerosol absorption (browning).
alpha-pinene, toluene, and isoprene under high- and low-NO\textsubscript{x} conditions. Optical absorption for all precursors is enhanced under high-NO\textsubscript{x} conditions; however, aerosol produced from isoprene and alpha-pinene showed little absorption even under high-NO\textsubscript{x} conditions. Aerosol formed from toluene under high-NO\textsubscript{x} photochemical conditions showed the largest absorption with a four-fold increase relative to trimethylbenzene aerosol produced under similar conditions. The use of acidic sulfate particles did not significantly enhance absorption of SOA produced from any precursor.

Because the high-NO\textsubscript{x} toluene SOA produced the largest absorption values, samples were collected for detailed molecular analysis to determine the specific molecules responsible for light absorption (chromophores). The aerosol chemical composition was analyzed with nanospray desorption electrospray ionization (nano-DESI) coupled to a high-resolution mass spectrometer and at EMSL. To identify the chromophores more readily, samples were analyzed with liquid chromatography instruments equipped with UV-Vis and mass spectrometry detection at EMSL. The combination of these techniques allowed us to identify the specific molecules responsible for light absorption that include nitro-aromatic species substituted with acid or phenol groups. The results again indicate that incorporation of nitro groups during toluene oxidation are the key to producing chromophores.

The objectives of the molecular modeling task of this project are to use quantum mechanical methods to understand and quantify the UV/Vis absorption spectra of potential organic chromophores. From these calculations, we can obtain wavelength-dependent optical constants from the absorption spectra. In turn, the optical constants are used in the global climate model calculations to determine the extent of radiative adsorption of aerosols in the atmosphere. We have benchmarked the level of electronic structure theory and basis sets needed in our calculations to yield results in excellent agreement with experimental absorption spectra for several compounds. This provides us with the computational fidelity required to investigate the various compounds identified as potential chromophores from our laboratory studies.

Finally, we have been exploring the role of brown carbon aerosol on climate by implementing a simple treatment for these aerosols in the CAM5 model framework. Primary and secondary aerosols were tagged by the source precursor to the secondary aerosols (isoprene, alkenes, alkanes, etc.), and changes were made to the complex index of refraction to make them absorb more strongly than the standard treatment in the visible and UV wavelengths. Forcing estimates were made of this aerosol, with attribution to the source precursor. A paper is planned describing these results, with an extension reformulate the optics to use a shell core Mie calculation rather than the current homogeneous mixing rule.

In FY 2015, we plan on integrating the finding of the laboratory experiments into the global climate models. First, the conditions which produce brown SOA will be parameterized and implemented in CAM5. The optical properties of the SOA samples will be input into the model and an estimate of the climate effects of these particles will be calculated. We will complete several manuscripts in FY 2015, two describing the laboratory results and one describing our initial climate simulations. A final manuscript integrating all the results will then be prepared.
Microscale Reconstruction of Biogeochemical Substrates Using Combined X-ray Tomography and Scanning Electron Microscopy

James P. McKinley

We are combining and examining microscale images across multiple physical and chemical domains. This ability to combine images across imaging techniques and across imaging scales would represent a scientific tool that is more valuable than its individual parts.

Data collection in the form of sample imagery is a powerful tool used in many scientific investigations. A family of scientific imaging tools is available to collect complimentary images of solid samples. Microscale imaging is ubiquitous in the sciences, and scientific images are common in the popular press such as magazines and newspapers. The best known and most common images are photomicrographs, particularly scanning electron micrographs that show the invisible details of scientific samples. Many of us have seen the scanning electron image of a fly’s eye, for example. More specialized imagery includes representations of the composition of the sample, including variations in composition; the visualization of 2D spatial relationships among sample parts or subregions; the distribution of different crystalline properties within the sample; and the distribution of void space within a natural or manufactured material.

More recently, the ability to produce X-ray tomograms (3D images that are analogous to CAT scans) has emerged as a significant useful tool. Tomography relies on the differential ability of physical substances to absorb X-rays analogous to a medical X-ray, which maps absorption in two dimensions, with the additional computational reconstruction of absorption in three dimensions using multiple X-ray collections. The resultant images can be viewed either as rotatable solids or slices through the sample but do not include information on the specific compositions that are responsible for the absorption. This project combines different types of electron microscope images, including compositional and crystal-phase information, with X-ray tomography images to provide a detailed 3D image of solid samples that includes chemical data.

Our approach is to collect X-ray and chemical data, assimilate the data using software we develop and adapt, and progress to more complex volumetric, multi-scale data as our experience and abilities evolve. We initially assembled intact sediment and soil samples, and began synthesizing artificial analogues using metal, mineral, and organic substances at different length scales. Tomographic images of the samples were collected, then physically sectioned and analyzed via electron microscopy methods; and the compositional data were propagated into the tomographic solid using project-developed algorithms.

The first year of work on this project was limited to collection of tomographic images and optimizing the resolution of those images across imaging modes: high and low resolution tomographic images from both the EMSL instrument and the Argonne National Laboratory X-ray beamline with and without phase contrast. That work provided the preliminary data needed to begin including compositional imaging from electron microscopy.

In FY 2014, we investigated the combination of compositional and tomographic data, using environmental samples from a microbially reduced fine-grained sediment and from sites with anthropogenic glass. We evaluated the results using commercial and purpose-written software and were able to identify specific solid-phase species within the tomography volume. In the image, a 3D reconstruction of heterogeneous glass shows the inclusion of relatively dense solid-phase materials that formed within the originally molten amorphous material. In FY 2015, we will conduct and present the results of a limited number of ongoing experiments.
Numerically Robust Climate Simulation Through Improved Interaction between Model Components

Hui Wan

This project will provide new methods for representing the interactions between atmospheric processes in numerical models and develop more robust and reliable tools for understanding and predicting climate change.

General circulation models (GCMs) that numerically solve the evolution equations of atmospheric motion have been used as a fundamental tool in climate research for more than five decades. Recent progresses in process studies, the fast growth of computing power, and the decision-makers’ need for detailed information of regional climate change have motivated the current emphasis on high-resolution modeling. Complex processes such as aerosol lifecycle and cloud microphysics have been incorporated into global models, which dramatically broadens the spectrum of spatio-temporal scales that are explicitly represented by numerical methods. Although these processes interact strongly with each other and with the rest of a model, there is not yet an established theory or standard practice regarding the coupling technique. In contrast, a number of studies have shown disconcerting sensitivities of model behavior to numerical details. The symptoms reveal a major weakness in current climate models, which implies that large structural uncertainties exist in the simulated climate responses to anthropogenic forcing.

The objective of our work is to reduce numerical errors associated with component coupling in climate models. Through the development of new coupling methods, we aim toward achieving a higher level of numerical and physical consistency between different processes and constraining artificial sensitivities in climate predictions. In previous years of the project, we used a toy model to demonstrate that the widely used operator splitting technique can cause severe problems when applied to strongly competing or compensating processes. Substantial improvement in numerical accuracy can be achieved by solving multiple processes simultaneously. For the Community Atmosphere Model (CAM) version 5, we performed an atmospheric water budget analysis and found that complex process interactions are ubiquitous in cloud regimes of important climate impact. The analysis also revealed that the process coupling technique currently used in the model leads to artificial sensitivities to model time step in terms of the simulated mean climate and process rates.

In FY 2014, our investigation focused on pinpointing the source of numerical artifacts in CAM5. A new strategy was developed for the numerical experimentation, which replaces the traditional serial-in-time, multi-year climate integrations by representative ensembles of short simulations that are a few days in length. Validation tests showed that the new method typically helps to reduce the total computational cost by a factor of 15 and the experiment turnaround time by a factor of several hundred, allowing for the efficient use of leadership computing facilities for numerical experiments that would otherwise be prohibitively expensive. The new strategy was published in the peer-reviewed journal Geoscientific Model Development.

Using the ensemble approach, numerical simulations were performed to characterize CAM5’s time step sensitivity. The simulations revealed that the model’s convergence rate with respect to time step from theoretical arguments is substantially lower than that expected. Sensitivity experiments showed without ambiguity that the time stepping errors are dominated by those from the stratiform cloud parameterizations, especially the representation of water vapor condensation and cloud/precipitation formation. This work provides a clear guidance for our tasks in FY 2015, during which time we will revise the parameterization of the stratiform cloud macro- and microphysics, improve the convergence rate, and develop a solver that provides higher accuracy.

Time step convergence test quantifies the numerical error associated with various components of a climate model.
The Platform for Regional Integrated Modeling and Analysis (PRIMA) demonstration project explored and compared the impact of climate and climate policy on energy-water-land interactions in the eastern United States. The experiments represent a major first for the global change science community: 100-year simulations of integrated energy-water-land impacts at the regional scale forced by dynamically down-scaled regional climate, including regional stakeholder input regarding the analyzed scenarios. This project was the culminating demonstration effort for the five-year PRIMA initiative.

Global climate and integrated assessment models typically address large-scale questions such as the geophysical consequences of greenhouse gas emissions (e.g., global warming and attendant changes in the global hydrological cycle) and the socioeconomic dimensions of climate change (e.g., the consequences of policy assumptions on economic and energy systems). These models are not designed to resolve human and environmental system interactions at finer spatial scales. Local to regional climate changes are generally obtained by downscaling global climate model projections, while sector-specific models are used to assess climate impacts on particular systems (e.g., water resource management, energy production and transmission, etc.). There have been few attempts, however, to include multiple human and natural systems in a single integrated regional modeling framework. This shortcoming means that existing models of regional systems are inherently limited in their ability to resolve interactions and feedbacks among different processes that can significantly influence the evolution of the coupled system; e.g., how land use patterns and crop prices might be affected by the combined effects of changes in air temperature, fluctuations in water availability, competition for water resources, changes in energy prices, and increasing demand for biofuels.

The Platform for Regional Integrated Modeling and Analysis (PRIMA) provides an integrated framework and explicitly includes stakeholder input to guide development and demonstration to help ensure that the research is “used and usable.” The PRIMA FY 2014 demonstration project explored the evolution of the future energy technology mix and climate-energy-water-land interactions for a greenhouse gas mitigation scenario (global carbon price) as well as a “business as usual case.” These scenarios were selected in consultation with regional stakeholders to provide additional insights into previous analyses for the energy sector without consideration of natural system interactions. PRIMA’s unique capabilities were demonstrated by coupling a regional climate model with a regional integrated assessment model and more highly resolved sector models addressing building energy demand, electricity infrastructure siting and operations, hydrology and water management, and land use/land cover, where all models are forced by a consistent set of regional climate information.

The framework demonstration consisted of a series of one-way coupled simulations for two overarching experiments representing the mitigation and business as usual scenarios. Each of the simulations is summarized below.

**Regional climate modeling.** These simulations produced regional climate information for the historical (1975–2004) and future (2005–2100) time periods generated by a regional earth system model consisting of the regional atmosphere model Weather Research and Forecasting (WRF) coupled to the land surface model Community Land Model (CLM), along with prescribed boundary conditions from the Community Earth System Model (CESM). Two scenarios corresponding to the Representative Concentration Pathways (RCP) for RCP 4.5 (mitigation) and RCP 8.5 (business as usual; no mitigation) are available. Data are available as raw model outputs defined on a domain covering the conterminous United States at 20 km grid resolution and bias-corrected model outputs on a 1/8 degree grid. Surface variables such as temperature, precipitation, winds, humidity, pressure, and shortwave and longwave radiation are available at hourly and daily temporal frequency. The data can be used for analysis of regional climate change and to generate climate forcing for impact assessments using sectoral models such as hydrologic and crop. Future changes of water availability and wet/dry trends have been analyzed and summarized. The data in netCDF format are availability upon request, and limited spatial maps and time series plots are also available for seasonal/annual changes of temperature and precipitation over the United States and a few specific states.
Land surface and hydrologic modeling. The meteorological variables from the bias-corrected, downscaled regional climate simulations, including precipitation, air temperature, specific humidity, surface air pressure, wind speed, and incoming solar and longwave radiation, were converted to the CLM input format and drove the simulations at hourly time steps. The model was spun up by recycling the meteorological forcing over the historical period (i.e., 1975–2004) until all state variables, including soil moisture, soil temperature, and groundwater table depth, reached equilibrium. The spun-up state variables were then used as initial conditions for a historical simulation, followed by two future simulations under scenarios RCP4.5 and RCP8.5 to simulate terrestrial hydrological states and fluxes from 2005–2100 driven by the bias-corrected regional climate model outputs.

Consistent with the regional climate model’s forcing data, the Model for Scale Adaptive River Transport (MOSART) was coupled to CLM to generate hourly natural streamflow at 1/8th degree resolution in the United States (same domain as CLM) under the historical (1975–2008) and future (2005–2100) time periods. For the latter, both RCM4.5 and 8.5 scenarios are simulated. All the streamflow simulations are stored in netCDF format, or one file for each calendar year.

Water management modeling. A regional scale water management model (WM) was coupled to the river routing model (MOSART) to simulate reservoir operations for the historical (1985–2004) and future (2005–2095) time periods. The model is driven by runoff generated by CLM, and the consumptive irrigation and non-irrigation water demands were generated by the regional version of the Global Change Assessment Model (GCAM-USA) and downscaled to the temporal and spatial scales of CLM-MOSART-WM. These simulations were executed for the RCP 4.5 and RCP 8.5 scenarios. Data are available as raw model outputs defined on a domain covering the conterminous United States on a 1/8th degree grid (≈12 km). Variables such as water demand, water deficits, and regulated flow are available at each grid cell at a daily time step. In addition, storage and releases are available for all 1848 reservoirs simulated over the domain at the same temporal frequency. The results indicate that the combination of the impacts of regional climate and higher water demands under RCP4.5 (due to higher water demands for agriculture) increase water stress in most basins in the United States. The data can be used for analysis of water resources vulnerabilities to regional climate change and to generate forcing for impact assessments using sectoral models such as Capacity Expansion Regional Feasibility. Limited spatial maps and time series plots are also available for seasonal/annual changes of regulated flow, supply deficit, elasticity of supply deficit to drivers of change (i.e., runoff and demand).

Regional integrated assessment modeling. For both RCP4.5 and 8.5, the GCAM-USA model simulated the evolution of the energy-economy across the country at the state, national, and global levels and the evolution of the agricultural sector, land use change, and water demands across the energy and agricultural sectors. GCAM-USA incorporates a carbon price to achieve the necessary emissions reductions required by RCP4.5. GCAM-USA is coupled to the output of the regional climate model so that future climate affects building energy demands. The GCAM-USA results reveal that the RCP4.5 future is vastly different from the RCP8.5 scenario within the United States. Under RCP4.5, the electricity generation mix switches completely away from conventional coal- and gas-fired technologies toward solar, wind, nuclear, biomass, and carbon capture and sequestration. Due to the increased demand for biofuels, agricultural demands for water increase dramatically.

Electricity system modeling. The GCAM-USA results were further explored in more highly resolved sector models of building energy demand, electricity operations, and power plant siting. The building energy demand model was coupled with the hourly regional climate model results to simulate hourly building energy demand under RCP8.5 for the future building stock simulated by GCAM-USA. The geospatial power plant siting model was coupled to GCAM-USA output as well as to the WM streamflow results to explore possible constraints on power plant siting under the future scenarios and to provide feedback for the GCAM-USA modeling team. The siting analysis showed that GCAM’s results for the RCP4.5 scenario require a level of new wind and nuclear capacity that goes beyond the resources available in certain states (for wind) and would require certain state moratoria on new nuclear power to be lifted.
This project is evaluating the Platform for Regional Integrated Modeling and Analysis (PRIMA) models for their ability to simulate extreme climatic events, their impacts on energy demand and water resources, and potential interactions among various systems.

Changes in climate extremes present important challenges for climate mitigation and adaptation because many human systems are already vulnerable to extreme events. The 2012 central U.S. drought is a good example of an extreme event that stressed multiple human systems. This project designed and executed a suite of numerical simulations to evaluate how well the PRIMA models capture the anomalous climate, hydrology, water resources, and energy demands associated with the aforementioned drought compared to more normal conditions of 2009. Evaluating model skill is important in documenting the validity of numerical models used to project regional climate change and assess climate mitigation and adaptation options. Through PRIMA, a suite of numerical models have been developed/refined and coupled to represent the integrated human-earth system that controls climate and its interactions with human systems and the environment.

The following simulations were performed using individual/coupled models:

- The Regional Earth System Model (RESM) was used at 20 km grid resolution over North America with large-scale circulation provided by a global reanalysis to produce an ensemble of four climate simulations with different combinations of convection and cloud microphysics parameterizations for 2009 and 2012.
- Meteorological outputs from the ensemble RESM simulations were used to drive the Community Land Model (CLM) and Model for Scale Adaptive River Transport (MOSART) to simulate natural streamflow at 1/8 degree resolution over the conterminous United States for 2012 and 2009.
- Daily temperature simulated by RESM was used to provide heating and cooling degree days as inputs to the Global Change Assessment Model for the United States (GCAM-USA) to simulate drought impacts on the building energy sector and changes in heating and cooling requirements under the contrasting conditions.
- Using the GCAM-USA simulated water demand and MOSART simulated natural streamflow, a water management (WM) model was used to simulate regulated flows at major stream gauges and storage in reservoirs in the United States.
- The meteorological outputs from RESM were also used to drive the Building Energy Demand (BEND) model to simulate building energy demand in the Electricity Reliability Council of Texas (ERCOT) region during the summer of 2012 and 2009 using building stock adjusted for population for the 2005 to 2010 timeframe.
- Using the GCAM-simulated state-level industrial and transportation values and the BEND-simulated hourly load profiles for residential and commercial, the Model of Electricity Demand (MELD) was used to simulate hourly electricity demand profiles for each PROMOD region.

To evaluate model performance in capturing the difference between 2012 and 2009, observation data were compiled and used for comparison with the simulations from the various models. From the regulated flow in the Mississippi River simulated by the coupled CLM-MOSART-WM driven by the RESM simulated climate conditions and GCAM-USA simulated water demand for 2012 and 2009, the central U.S. drought had significant impacts on regulated flow in the western and southeast part of the basin. Reduced streamflow in the west was primarily driven by reduced precipitation in 2012 compared to 2009, but reduced streamflow in the southeast was mainly associated with warmer (but not dryer) conditions in the prior winter that affect streamflow in the following spring and summer.

Comparing observed and simulated regulated flows at various stream gauges, models captured broad changes in total amount and seasonality of flow between 2012 and 2009. Most notably during 2009 corresponding to a typical year, streamflow peaks between May and June, but in 2012, streamflow was higher than 2009 between December and March and was significantly reduced between May and July when the drought peaked. There were large spreads among the ensemble members driven by the ensemble RESM simulations for each year, but the difference between 2012 and 2009 is clear despite the ensemble spread. The model simulated flows were higher than observed, but observed differences in seasonal flow between 2012 and 2009 are well simulated by the model.

Impacts of the 2012 drought on building energy use was evaluated using a detailed service-based buildings energy model at the 50 U.S. states level nested in the GCAM-USA modeling.
framework. The model was calibrated in 2005 using energy consumption data by sector, service, and fuels in each of the 50 states. The evolution of energy demand in building sector and its interactions with climate change were explored by constructing estimates of heating and cooling degree days (HDD/CDDs) for the two scenarios built from RESM model output. Results showed that the percent change in electricity requirement between 2012 and 2009 for buildings varies across states but generally exhibited an increase under the warmer climate of 2012. In turn, this resulted in similar increases in total electricity generation and the total water demand for electricity generation.

To evaluate BEND and MELD, hourly electricity demand profiles simulated by MELD are being compared to the actual electric demand that occurred in each PROMOD region in 2009 and 2012 to demonstrate the models ability to accurately capture the impact of climate on aggregate regional electricity demand.

As of FY 2014 end, a manuscript is in preparation for submission to a peer-reviewed journal documenting the skill of various PRIMA model components in simulating the central U.S. drought conditions of 2012 and their impacts on streamflow, building energy demand, and electricity demand. Such documentation is important for establishing the validity of the PRIMA models for addressing climate impacts, adaptation, and mitigation, and understanding model limitations to guide future development.
We are using and developing a coupled land-atmosphere carbon data assimilation system that will simultaneously handle multiple modeling components and multiple streams of data.

Current coupled carbon-climate models have uncertainties in their projected future atmospheric CO₂ concentration in a changing climate. Based on recent reports, these concerns have not narrowed, especially for terrestrial ecosystems. In the meantime, observations of the carbon cycle in the atmosphere for land and oceans have intensified dramatically. Together with site observations and in situ atmospheric CO₂ network, carbon cycle observations are poised to play a major role in constraining carbon cycle simulations and their representation in climate models. Present approaches, however, remain limited to an isolated use of such information.

The data assimilation approach we propose in this study is intended to overcome such limitations by taking full advantage all available data sets. The system we create will be used specifically with Orbiting Carbon Observatory 2 and 3 (OCO2/OCO3) and Greenhouse Gases Observing SATellite (GOSAT) observations. We will also use other datasets in this study, including CO₂ measurements from flask sampling network, remotely sensed vegetation indices and fraction of Absorbed Photosynthetically Active Radiation, FLUXNET measurements of surface-atmosphere CO₂, water and heat fluxes, vegetation and soil biometrics, and land use history.

Our project plan is as follows: first, we are quantifying improvement to near-surface CO₂ flux estimates based on OCO2 and GOSAT measurements and delineating the contributions from different data streams from remote and in situ platforms. Second, we are combining the measurements of XCO₂ and the sun-induced chlorophyll fluorescence (SIF) in the same data assimilation framework to assess the value and uncertainty of using the novel SIF as an indicator of GPP both with and without other land based measurements. Next, we are providing a flux product constrained by both atmosphere and land observations, which enables the depiction of uncertainties due to underlying terrestrial processes and parameter choices. Finally, we are assessing current and future requirements for measurements of XCO₂ in terms of sensor/mission characteristics to meet the required accuracy, spatial, and temporal coverage for different biotic and abiotic conditions affecting terrestrial ecosystems.

In FY 2014, we recruited a post-doctoral fellow to join the project to work on coupling of the terrestrial ecosystem model VEGAS with the atmospheric carbon transport GEOS-Chem model in “assimilation mode.” We also recruited a University of Maryland graduate student to begin assembling the required atmospheric CO₂ and other Tier 1 data sets. These team members are working together to develop the methodology for scaling spatially the in situ CO₂ flux measurements to the CO₂ observations obtained by remote sensing satellites at the scale(s) they represented in the models.

Activities planned for FY 2015 include a series of coupled carbon assimilation experiments to understand and quantify a number of issues. First, we wish to understand the complimentary features of the CO₂ measurements by different methods. Next, we will explore the limits to quantifying seasonal and interannual variability in CO₂ exchange between atmosphere and terrestrial ecosystems. Finally, we will perform coupled CO₂ assimilation experiments to understand and quantify the decadal variability in sources and sinks of CO₂ for major biomes and ecoregions globally. We will also commence work on developing indicators on terrestrial ecosystems phonological and physiological parameters based on remotely sensed observations that can be used in the terrestrial ecosystem models such as VEGAS. The initial focus of this task will be the United States, and we will subsequently explore the applicability of this approach to other select ecoregions worldwide.
Regional-Scale Measurement and Modeling of Biogenic Organic Fluxes: Bridging the Gap Between Process Studies and Climate Models

Alex B. Guenther

We are transforming emission measurements of chemicals that drive climate change and air pollution.

Climate and air quality models that have been used to make policy decisions previously relied on indirect, highly uncertain emissions data. With positive results from our current project, data can now be based on direct, more accurate measurements on relevant regional scales. Specifically, an airborne capability utilizing the PNNL AAF G1 aircraft for measuring regional scale fluxes of chemical species is being developed to provide observations that can inform and constrain climate and air quality models. This scenario goes beyond existing capabilities by using techniques that enable emission measurements on much higher spatial scales than previously has been possible. In addition, we are integrating the high spatial resolution and accuracy of aircraft flux measurements with satellite observations to enable global continuous coverage of emission measurements. The approach is being demonstrated using observations from the DOE GoAmazon study and will be used to enhance future aircraft and modeling studies. This capability can then be extended to other important chemical constituents (e.g., aerosols and greenhouse gases) and other sources (e.g., urban and industrial facilities).

Techniques for calculating and evaluating high spatial resolution aircraft flux measurements have been refined and evaluated using available observations from three past field studies and campaigns: the CARB-sponsored CABERNET, the NSF-sponsored NOMADSS, and the NOAA-sponsored SENEX. The flux calculation approach is based on the wavelet technique which enables relatively high spatial resolution flux measurements. An approach for integrating aircraft observations with satellite data has been formulated, and preliminary tests have been initiated using these past data sets. In addition to the three aircraft campaigns, satellite data-derived estimates cover terrestrial ecosystem emissions, canopy coverage, photosynthetic activity, and environmental conditions including soil moisture, solar radiation, and canopy temperature. An approach for analyzing and comparing satellite data and direct flux measurements was developed to identify the cause of disagreement between "bottom-up" (earth system model) and "top-down" (e.g., satellite atmospheric data derived) emission estimates.

MATLAB software was created to process PNNL G1 aircraft VOC and wind data and to calculate eddy covariance fluxes using the wavelet technique. An approach was also developed to calculate the vertical change in isoprene fluxes (flux divergence) to estimate regional OH concentrations.

Input was provided for flight planning for the 2014 DOE-sponsored GoAmazon study to optimize flux measurements from the PNNL G1 aircraft. An initial assessment of the potential for using PNNL G1 aircraft for flux measurements has been accomplished using observations from the initial campaign of the GoAmazon study. Results indicate that fluxes of most compounds are relatively low and near or below the detection limit. However, emissions of at least some compounds including isoprene can be estimated using the G1 aircraft observations. In addition, models predict that the second campaign (during the September to October dry season in the Amazon) will have considerably higher fluxes; therefore there may be opportunity to observe fluxes of additional compounds.

Project activities for FY 2015 will be focused on demonstrating the accuracy of aircraft flux measurements and reconciling discrepancies between direct aircraft measurements, earth system model predictions, and estimates based on satellite atmospheric data. This process will involve examining not only the total fluxes but also investigating the individual components that contribute to the total flux. Our focus will be on using observations from the 2014 DOE GoAmazon study, which will provide the comprehensive measurements required for this effort. The improved emission estimates expected from this activity will be integrated into the DOE climate modeling studies conducted for GoAmazon.
Simultaneous $^{14}$C and T Dating of Environmental Organic Matter

Jim Moran

We are developing high sensitivity methods for tritium-age dating of organic compounds. Once complete, this advanced technique can be coupled with other approaches (including 14-carbon [14C] analysis) to provide a powerful tool for detailed analysis of C cycling through environmental systems.

A well-established method, $^{14}$C age dating enables research investigations in areas as varied as microbial substrate tracking, carbon cycling, dating anthropological samples, atmospheric chemistry, and biomarker sourcing. By definition, however, organic molecules also contain hydrogen which can be independently age dated using tritium (T) analysis. Tritium has a much shorter half-life than $^{13}$C and thus can be used to track different processes and different aged materials than $^{14}$C. While T has widespread applications in hydrologic, limnologic, oceanographic, and other investigations, current measurement approaches are made difficult to apply to organic molecules by the large sample sizes required for analysis. The primary technological goal of this project is to improve the measurement sensitivity of T such that modest amounts of organic samples can be prepared for and undergo accurate measurement for T dating. Once developed, this approach may be used to better understand the molecular stability of environmental organic compounds and refine our understanding of chemical recalcitrance with respect to the C cycle.

In this project, we are testing the applicability of this new capability by characterizing the relative $^{14}$C and T ages of soil organic C fractions. Worldwide, soil stores a tremendous amount of carbon, yet key characteristics governing its stability remain undefined. For example, some C fractions appear nominally passive but may actually be very dynamic. $^{14}$C measurements can offer an understanding of the age of the carbon stored in these compounds; $^{14}$C is limited in determining the stability of these fractions because C could be turned over and incorporated into different organic materials without altering the $^{14}$C content. Tritium measurements applied to these organic fractions will provide added resolution into the stability of soil organic carbon and help assess the degree to which this stability is controlled by molecular structures of the organic fraction vs. physical organization of the soil (i.e., proximity to surface or ground waters and the dynamics of those water fluxes. At shallow depths, surface water percolates more quickly through a soil profile than organic carbon accumulates, resulting in younger water ages (meaning it has been in contact with the atmosphere more recently) relative to the retained soil organic carbon. When bonds within soil organic compounds are hydrolyzed, they incorporate the relatively young hydrogen atoms from the surrounding pore water. Thus, we expect hydrolysis of organic compounds more susceptible to degradation to impart a divergence between $^{14}$C and T dates in the residual organic structure. This approach allows us to assess compound degradation at an early stage. Less hydrologically dynamic systems associated with long-lived soil C such as permafrost soil layers are hypothesized to have similarly "old" C and H in their soil C fractions.

To date, this project focused on developing measurement and sample preparation systems needed for making sensitive T assessment of organic samples. By basing T measurement on an ultra-low background proportional counting of hydrogen present in methane molecules, we anticipate enhanced measurement sensitivity and reduced measurement times over the traditional approaches. To this end, we measured the T content of methane samples from different environmental sites using a fraction of methane needed for commercially available analysis. We are employing modeling techniques to understand analyte behavior in these counters, which is guiding further improvements in measurement sensitivity. In parallel, we are developing the sample handling techniques needed to convert organic compounds to methane (for analysis) while preserving the T content. Specifically, we are exploring various materials and heating options to produce a final system having optimal reaction yields, no sample carryover between runs, and producing high purity methane without altering the T content. Once this analytical approach is verified, we will commence measurement of environmental samples. We collected a series of samples from northern permafrost and southern wetland soils on which to demonstrate this measurement capability. These samples will be separated into water soluble and humic acid fractions for T analysis that will enable a stronger interpretation of $^{14}$C data collected on the same samples.

Electrical field models have been developed to understand the internal workings of the proportional counters used as a basis for making T measurements. The electron avalanche modeled here replicates detector pulse formation from experimental results and will be used to develop modified detectors to enhance further sensitivity gains.
Simultaneous $^{14}$C and T Dating: A Case Study Using Soil Organic Matter

Jim Moran

We are developing high sensitivity methods for performing simultaneous carbon ($^{14}$C) and hydrogen ($^{3}$H) age dating of organic compounds. These unique techniques will be powerful tools for understanding carbon cycling through environmental systems.

Simultaneous $^{14}$C and $^{3}$H age dating of organic samples is a technique with promise for environmental-based applications but also a technique not currently provided in the greater isotopic community. Current approaches require dividing a sample and processing it independently for each individual isotope, a method neither consistent with small sample sizes nor streamlined for sample preparation. In this project, we are developing a robust sample preparation system that will allow simultaneous dating of $^{14}$C and $^{3}$H by proportional counting. Applying a dual-isotope method permits evaluation of specific carbon to hydrogen bonds within a chemical compound rather than the ages of specific atoms within the structure. These measurements will provide us enhanced resolution for exploring the stability of organic compounds within the environment that will have direct implications on our understanding of global carbon cycling.

Fixation of atmospheric CO$_2$ by land plants results in organic carbon introduction into soils. The balance of this accumulation rate with organic matter decomposition controls the amount of carbon stored in soils and its role in the global carbon cycle.

We are developing isotope methods to explore the controls on organic matter decomposition and thereby inform how changing conditions can influence the overall soil carbon budget. Specifically, we are demonstrating this new capability using soil organic carbon as a representative case study. Worldwide, soil stores a tremendous amount of carbon, yet key characteristics governing its stability remain undefined. The dual isotope approach that we are developing will offer added resolution to help understand what governs stability of soil organic carbon, such as whether stability is inherent of a compound’s molecular structure or rather controlled by its physical location (and susceptibility to decomposition) within a soil. At shallow depths, surface water generally percolates through a soil faster than organic carbon accumulates resulting in younger water age in age: it has been in contact with the atmosphere more recently) than soil organic carbon. When bonds within these organic compounds are hydrolyzed, they incorporate relatively young hydrogen atoms from this surrounding pore water. Thus, we expect hydrolysis to produce a divergence between $^{14}$C and $^{3}$H dates in the residual organic structure and indicating compound instability under those conditions. This approach will allow us to assess compound degradation at a very early stage.

The main objective of this project was to develop the sample conversion techniques and hardware to convert organic compounds to methane in preparation for dual isotope analysis. To this end, we constructed a combustion system to convert organic carbon to carbon dioxide and water. These products are used as starting material to synthesize methane over a heated metal catalyst. Both of these systems are assembled and have been demonstrated to result in methane production.

A second aim of the project was to refine proportional counting to permit the required dual isotope measurements. The overlapping decay energies of $^{14}$C and $^{3}$H required optimization of measurement techniques to permit accurate decay counting. We tested measurement accuracy over a range of fill conditions and compared these measured values to those figures obtained by traditional, individual measurement approaches. Finally, we collected highly productive soil samples from the Palouse region in eastern Washington. These samples were separated into water soluble, humic acid, and fulvic acid components and await isotope analysis.
The Integration of Water in iRESM

Mohamad I. Hejazi

We are advancing the integrated regional modeling framework in the Platform for Regional Integrated Modeling and Analysis (PRIMA, previously known as iRESM) by improving spatial representations of water demands in the Global Change Assessment Model (GCAM) and reconciling water modeling components to establish inter-linkages that will yield consistent modeling in the water system.

The integration of water representations in integrated assessment and earth system models at the regional scale is an important step toward improving our understanding of the interactions between human activities, terrestrial system, and water cycle and evaluating how system interactions are affected by a changing climate. Additionally, this integration is critical to enable the PRIMA framework to investigate the implications of climate change impacts and adaptation and mitigation options on water resources (e.g., balances between water demand and supply) in the United States and determine how water constraints can influence other human decisions and physical processes.

Our project focused on developing a regional representation of water demands and allocation framework in the GCAM and creating a linkage between GCAM and the land surface component of Regional Earth System Model (RESM) — including the Community Land Model (CLM), the MOdel for Scale Adaptive River Transport (MOSART), and the Water Management (WM) components — to propagate decisions about water demand per sector and technology from GCAM to RESM at the appropriate temporal and spatial scales. These goals required a careful effort in representing the interaction pathways in the integrated water cycle among GCAM and RESM (i.e., CLM-MOSART-WM) and addressing any inconsistency in representing the integrated water cycle. Our work constitutes a key step in advancing PRIMA toward a consistent, integrated framework of water modeling that is portable (consistent with global modeling and analyses) and provides improvements and insights into the interaction of human decisions and climate changes on regional scales.

During FY 2013, we successfully implemented a one-way coupling of a GCAM, including a water-demand model with a land surface hydrology — routing — water resources management model (SCLM-MOSART-WM). The coupled models demonstrated a reasonable ability to represent the historical flow regulation and water supply over the U.S. midwest. A spatial analysis demonstrated the relationship between the supply deficit and change in demand over urban areas not along a main river or with limited storage. Additionally, we improved the spatial representation of some of the water demand modules in the GCAM framework to track water withdrawals and consumptive use at the state level. At this stage, GCAM could choose whether to irrigate based on economics.

In FY 2014, we implemented several additional key features to the modeling framework and executed a handful of simulations to address some of the initiative’s overarching research questions. More specifically, we have:

• extended the modeling domain to cover the contiguous United States (instead of the pilot study midwest region)
• substantially improved the downscaling algorithm of electricity water demand in GCAM using locations of power plants, which led to improved consistency with USGS historical observations
• redefined the delineation of basins tracked in GCAM to be consistent in their boundaries with those adopted by CLM at 1/8 and 1/2 degrees spatial resolutions, resulting in the newly adopted 235 major basins that GCAM tracks reconciled all previous efforts for generating a
regional integrated assessment model to generate a 50-state regional version of GCAM focused on the United States, namely GCAM-USA, which is attracting attention from existing and potential clients as a powerful and unique research and policy tool.

- improved the coupling of the integrated water system by passing additional variables (e.g., water withdrawals and return flows) from GCAM-USA to CLM-MOSART-WM, which is an important enhancement to deal with water recycling and the effects of return flow on the water balance and upstream to downstream dynamics.

- improved the WM module to account for water withdrawals and consumptive use explicitly and track unconsumed water (i.e., return flow) in the system, where it is returned back, and its residence (lag) time.

Another important improvement is the ability of WM to distinguish and track the portions of water demands from surface water and groundwater sources. Several experiments were executed to understand the implications of different modeling assumptions for including return flows and groundwater in the overall framework. A manuscript is in preparation for submittal to a high profile peer-reviewed journal by the end of FY 2014. A subsequent paper focusing on the sustainability of future demand for groundwater pumping under two Representative Concentration Pathways (RCP4.5 and RCP8.5) is also likely.

By accomplishing all the outlined modeling capabilities and simulating the modeling framework both historically and into the future under the two RCP scenarios, this project has served as a cornerstone for the other simulations undertaken by the two other ongoing LDRD projects on numerical experiments and model evaluations. Several manuscripts regarding this work and its accomplishments are in preparation. In addition, the scientists for the current work have been awarded another LDRD project in 2015 to extend the framework with a focus on the western United States.
Energy Supply and Use
A Multi-Layer Data-Driven Advanced Reasoning Tool for Smart Grid Integrated Information Systems

Jodi Heintz Obradovich

Our objective is to develop a decision support device – Multi-layer, Data-driven Advanced Reasoning Tool (M-DART) – for improved power system operation.

Today’s information management in power grid operation tools mainly follows a stovepipe process. Each sensor network produces its own domain-specific data (e.g., phasor measurement unit [PMU], supervisory control and data acquisition, smart meter measurements), and each data source is processed by domain-specific tool sets. Next, outputs are presented to grid operators responsible for making decisions. Isolated data processing mechanisms focusing on individual data domains may not reveal the root cause of failures or accidents and assess their impact to plan for action in a timely manner. As the number of data sources increases, possible action options increase exponentially; therefore, it is a significant cognitive challenge to a stressed human operator to analyze these relationships and/or draw on relevant past experience. Current practice in the power grid operations community is to run massive offline analyses to derive model-based guidelines for online real-time operations. However, because power system components and configurations change in real time, it is difficult for offline model-based analyses to maintain relevance and effectiveness.

In view of these challenges, we are using M-DART to investigate existing reasoning tools and apply tools to perform higher level reasoning (cross-correlate and examine data sources to assess anomalies, infer root causes, and anneal data into actionable information) to prioritize problems for the human decision maker. By summarizing results obtained from different reasoning methodologies, M-DART focuses on more accurate early detection of emerging power system events and identifies highest priority actions for the human decision maker to address. M-DART represents a significant advancement over today’s grid monitoring technologies that apply offline analyses to derive model-based guidelines for online real-time operations and use isolated data processing mechanisms focusing on individual data domains.

In FY 2012, the efforts were focused on the development of M-DART. Two prototypes were implemented, one of which characterized the PMU data quality. Another M-DART tool is the Columnar Hierarchical Auto-associative Memory Processing in Ontological Networks (CHAMPION), a semantic-graph-based domain-independent reasoning system. CHAMPION can integrate multiple data types and sources. The hierarchy of reasoning components divides the analysis into portions of a potentially large semantic graph to facilitate scalability.

For FY 2013, we examined the possibility of multiple data sources for estimating small signal stability. The approach used was to develop test data sets based on a modified mini-WEC model that has as input varying loads and generation characteristics. The test data sets, which consisted of model outputs of simulated PMU and wind and “truth” data (stability estimates) were then used to construct candidate mappings to assess whether the combined information could yield a better estimate of stability than either of the single data sources. The effort during this year also commenced to drive the CHAMPION reasoning system.

During FY 2014, in addition to continuing to improve on the M-DART-specific CHAMPION configuration, we developed ontologies representing expert knowledge/higher level reasoning on expertise, including patterns, relationships among events, root causes, and appropriate actions. We developed specific appropriate test scenarios to exercise the reasoning system, integrated them into the GridOPTICS™ Software framework, and designed a computerized decision-support display to aid the operator in situation assessment and situation awareness.
To enable an effective time-critical power grid analysis, interactive visual analytic interfaces that combine complex models and data can provide necessary insights and understanding of the state and course of an existing or proposed power system.

Developing useful, effective visual analytics tools for the future power grid is a significant challenge. The power grid has three trials of scale: system complexity, big data, and computational requirements. Presenting users with interactive visual analytic interfaces that can manage these three scales while providing an intuitive representation and navigable interactions will be the primary focus of our work. We will build on existing efforts in data management, modeling, and architecture. Developing systems for interactive analysis requires specific design criteria optimal for interactive analysis, which is often at odds with storage or computation design. All three have to be accounted for in a way that balances the needs of each, where the goal is to provide the planners and operators with visual analytics tools that meet mission needs as efficiently as possible.

A prototype visual analytics system for planners to assess future grid configurations for supporting power transmission and distribution in the dramatically changing grid will be created over the next two decades. The work will emphasize adaptable visual interfaces that support deep analysis while leveraging existing modeling as well as simulation and architecture projects. We will demonstrate the value of a holistic view of the power grid of the future through powerful visual interfaces. Additionally, we will develop and deploy powerful visual steering capabilities that will allow power grid operators and planners to steer models and simulations dynamically in use cases and scenarios that represent the future power grid. As a result, this project will provide an integration demonstration capability for selected modeling and simulation tasks as well as for the GridOPTICS™ framework.

In FY 2014, in-depth design sessions were conducted with GridOPTICS™ Software System (GOSS) and model developers to derive power grid analysis use cases to serve as target domain problems for a visual modeling and analysis environment (VMAE). The primary use cases will focus on demand-response modeling using the GridLab-D distribution system to simulate retail markets at multiple feeders and the MatPower system to simulate wholesale markets. Both GridLab-D and MatPower simulations have been augmented to provide market models on other projects. Developed demand-response use cases will concentrate on distribution system and load service entity (LSE) operators and planners as users. Distribution system users would primarily focus on managing retail market auctions, while LSE users would engage a combination of auctions, incentives, and distributed generation.

To enable use cases, communications among simulated systems are supported and synchronized using the next-generation GridOPTICS™ Framework for Network Co-Simulation (FNCS) streamed into GOSS, where VMAE can access the communications stream, model parameters, and results. VMAE was implemented as a GOSS application that may publish and subscribe to the GOSS framework. Through GOSS, VMAE connects to FNCS to access the synchronized data stream among the simulations using Websockets. The GridLab-D and MatPower applications have been modified such that VMAE may steer those applications through FNCS parameters. Specific transfer mechanisms, protocols, and data formats passed in the communications stream have been fully elaborated and developed.

For visual analytics methods and tools, we developed a suite of power grid visualization techniques deemed to have strong potential to support the visual analysis of dynamic power grid data, relationships, and behaviors. The suite of visualizations allows users to view dynamic power grid data from different perspectives, including spatial, geospatial, temporal, hierarchical, logical, and categorical. They are designed to be easily configurable to different types of power grid data such as loads, bid prices, bid quantities, locational marginal prices, and generator output. Specific visualization tools that have been developed and configured for the use cases include a geospatial map of homes, feeder load display, historical load curves, geospatial tree map, circular view, incentive calculator, forward LMPs display, and feeder resource availability story flow visualization.

A configurable dashboard that organizes a set of visualizations for a particular use case and provides user interface access to simulation and visualization parameters and controls has also been developed as part of VMAE. Through the dashboard, a user may evaluate different scenarios by adjusting model parameters and immediately seeing and comprehending their effects across the set of intuitive visualizations. Simulation parameters exposed through FNCS for the use cases include outside temperature, congestion, and generator shutdowns. The realized VMAE system with dashboard and visualizations were presented to an internal PNNL advisory board during a year-end review as part of the integrated demand-response demonstration.

For FY 2015, a variety of new visual analytics techniques and tools will be developed under this project, including weather, dynamic bubble/bar, periodic spiral, parallel coordinates, and heat map visualizations. A formal user evaluation of the dashboard and the individual visualization tools will be conducted.
with potential users from the power grid industry. We will continue to research computational and visual steering paradigms and strategies for potential incorporation into VMAE. Finally, we will further flesh out and evolve the demand-response use cases in addition to investigating new ones that are of particular interest to the power grid community, such as distributed energy resources and the integration of communication and information technology networks with the power grid. The goal is to promote VMAE as a visual steering and analysis platform for future power grid applications and specific analytical solutions for challenging power grid domain problems or areas.
Agent-Based Testbed for Complex Building Control Systems

Weimin Wang

This project develops a testbed to expedite the application of advanced control theories and tools in buildings for the benefits of energy efficiency, occupant comfort, and reliable operation of the power grid.

Multi-agent systems for distributed controls have been successfully applied to robotic systems, air traffic management, and other uses. However, only small fragmented exploratory studies have been performed to date for agent-based building controls. Partly from the lack of realistic and flexible testbeds for distributed building controls, those studies are limited to either ad-hoc simulations or simply tackle simple problems for a specific building. To fill the gap, this project was initiated with the two primary objectives: to develop an agent-based testbed for distributed control of building systems and equipment and for interactions between buildings and the grid, and to demonstrate use of the testbed in investigating agent-based control approaches for representative building systems.

We are designing and deploying an advanced building controls testbed in real buildings on PNNL’s campus with the following characteristics: 1) it will support interactions among heterogeneous components and systems (e.g., pumps, air-handling units, lighting systems, water heaters, and occupant behavior); 2) it can be reconfigured easily to test/validate/demonstrate different control methodologies and tools under realistic but controllable conditions; and 3) it can be an integrated part of a larger testbed that includes renewable generation, energy storage, grid, and peer buildings. These characteristics will enable the building controls testbed to support testing and demonstration of new control solutions and technologies developed from other projects.

In FY 2014, we identified the testbed requirements from different aspects such as testbed core characteristics and capabilities, data collection, monitoring, communication, experimental setup and management. Based on these requirements, we proposed the building testbed infrastructure. The building tested supports both physical and virtual devices. To achieve distributed controls in real buildings, each application-specific controller is associated with a single-board computer installed with VOLTRON™, an agent execution platform developed at PNNL. Different control algorithms can be implemented as different agents in the single-board computer. When testing, the applicable control logic implemented in VOLTRON™ will override the original control logic in the corresponding application-specific controller. The multi-node communication capability of VOLTRON™ enables a controller to retrieve data from related controllers if necessary. A high-level computer is an interface for communication with external entities. The infrastructure was implemented at the Building Diagnostics Laboratory (BDL), a test facility on PNNL’s campus. A small test case on the single-duct variable-air-volume system at BDL was created to try out the key VOLTRON™ functionalities to be used in the testbed.

The testbed infrastructure can support different control topologies depending on the location of control functionalities. For example, centralized controls are achieved if all single-board computers at the bottom level provide no control capabilities except passing data while the high-level computer has all of the control functionalities. Similarly, hierarchical controls can be achieved by introducing middle-level single-board computers and allocating control functionalities accordingly.

In FY 2015, we will: 1) expand the building tested to include additional systems, devices and whole buildings; 2) enhance VOLTRON™ to address the issues found from BDL testbed implementation; 3) integrate the building testbed into the whole CCSI testbed structure including the power grid, testbed management, and simulations; and 4) implement representative use cases in collaboration with other projects. These activities will lead to further refinement of the building testbed infrastructure and demonstration of its advantages to run experimental controls through use cases. By the end of next year, we anticipate that most of the building testbed will be ready to support testing and demonstration of advanced control theories and tools from future projects.
Aggregate Load Modeling and Control for Power Grid Regulation Services

David P. Chassin

This project is modeling aggregated loads for the design and analysis of distributed control strategies to support demand-based regulation services for the grid.

Modeling controllable load is a vital step toward full integration of renewable resources, where the appropriately chosen and calibrated models will enable bulk-power system controls using demand resources. The aggregate load modeling problem has been a long-standing challenge and remains one of the principal obstacles to scalable, fast-acting demand-based control solutions that use buildings to enhance and support bulk power system planning and operations. This project bridges the gap between the temporal and physical scales of end-use load and aggregate demand control models that has prevented current load control solutions from being included comprehensively in the larger problem of optimizing energy, power, and ramping resources allocation in bulk power systems.

We are following up on prior work modeling electric loads in general and demand response in particular. Previous work was based on a variability power spectrum as a function of a set of independent components that can be used to study both generation and load variability. Aggregate load was modeled as though it is composed of underlying models, which could be directly measured or indirectly disaggregated from existing data. The key relevant observation is that when under control, the periodic components of loads have phases that are expected to change based on component behavior in well-defined ways compatible to the mathematical formalisms used in modern control theory.

In FY 2014, we examined the economic and control models of individual and aggregate load to determine which provided the best chance of linking signals to individual devices and aggregate response in frequency domain to the market-based signals coming from the bulk power system. No models were found extant that supported a distributed aggregate load control strategy suitable to treatment by classical control theory. This led our project team to conclude three possible research directions. Two are covered by other projects on extending control theory and developing distributed systems using that theory. The third is to change the distributed aggregate load system so that it is treatable using standard theory. Thus, in collaboration with the University of Victoria’s Economics Department, we examined oligopoly behavior for distributed resources when under control of nearly real-time market-based systems, such as those demonstrated in the Olympic Peninsula GridWise Demonstration and the America Electric Power Northeast Columbus gridSMART Demonstration projects. The principal result of this effort was identification of revenue adequacy criteria when demand response is competing with distributed resources in real-time distribution capacity markets. This result provides the basis for developing bidding strategies for distributed generation as well as demand response.

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The utility revenue adequacy frontier shows how utility revenue can fall below the wholesale cost of electricity.

PNNL also collaborated with the University of Victoria’s Electrical Engineering Department to develop a new residential thermostat based on the design used in both the Olympic and Columbus projects. Analysis of the new thermostat design suggests that it will give rise to a linear time-invariant aggregate load control system. In addition, a patent application has been filed for this residential thermostat.

During the next 2 years, we will analyze aggregate control systems that emerge when this new thermostat design is employed and demonstrate that it can simultaneously provide economically dispatchable energy, capacity, and ramp resources from an aggregation of controllable building loads. We will also implement exemplary market-based control strategies based on this analysis for primary, secondary, and tertiary grid services required by grid operators.
Barrier Analysis and Assessment for the Appliance & Commercial Equipment Standards Program

David M. Anderson

This project demonstrates the opportunity available through regulatory action for capturing greater national energy savings in future appliance rulemakings. This work will lead to increased value to the nation by removing barriers to higher levels of energy savings.

DOE’s Appliance and Equipment Standards (ACES) program has regulated the energy performance of numerous types of appliances and equipment for many years. Enacting standards requires that the standards be both technologically feasible and economically justified. However, technical and market barriers prevent the setting of standard that may result in higher national energy savings were it not for the barriers.

In this project, we examined recent rulemakings for selected appliances and equipment for which there are substantial unrealized savings between the selected performance level and the maximum potential performance level. We have investigated what barriers have prevented the selection of standards that would result in higher national savings. Ultimately, the goal is to provide a potential roadmap of future research for DOE to consider, which would directly address the barriers identified in the study.

During FY 2014, this project was a success in a number of ways. We completed a report for the eventual consideration of DOE that illuminates the technical, market and other barriers preventing current standards from capturing the full potential national energy savings. Several new staff at PNNL are expected to support future rulemaking work for DOE and have been able to gain introduction and background to the appliance rulemaking program through our internally funded research on prior rulemaking activities.

The study resulted in the identification of a set of specific research areas that could be addressed by DOE to identify the barriers. The products examined include water heaters, distribution transformers, dishwashers, commercial refrigeration equipment, and clothes dryers. The cumulative unrealized energy savings from the most recent rulemakings for these products is over 32 quadrillion Btu through the year 2045. The study purposely focused on products for which substantial national energy savings potential remains uncaptured by regulation. The barriers identified are expected to be responsible for significant portion of the unrealized potential savings. This information should help the DOE ACES program to identify options for targeted research on these barriers, with the goal of that research to enable future rulemakings to consider standard levels that could capture much of the current potential savings. The study also provides an initial example of a process that could be implemented into the regular operation of the ACES program to make certain that the rulemaking process always has current information about national energy savings potential.

<table>
<thead>
<tr>
<th>Product</th>
<th>Efficiency Option</th>
<th>Barrier</th>
<th>Potential Options for Resolution</th>
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<tr>
<td>Distribution transformers</td>
<td>Amorphous steel cores</td>
<td>High negative INPV; low domestic capacity material</td>
<td>Study options for market acceleration</td>
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<td></td>
<td>Symmetric cores</td>
<td>Potential viable screened out early or not considered: insufficient technical information</td>
<td>Study technology performance</td>
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<td>Diswashers</td>
<td>Energy/water-saving option packages</td>
<td>Increased cycle times/loss of consumer utility</td>
<td>Study design option packages in the 9% of the market currently at maxtech, including consumer utility surveys</td>
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<tr>
<td>Commercial refrigeration equipment</td>
<td>Vacuum-insulated panels</td>
<td>High LCC/first cost</td>
<td>Study component cost reduction options</td>
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<tr>
<td>Clothes dryers</td>
<td>Two-stage modulating heat and moisture sensing w/ multi-speed airflow</td>
<td>High LCC</td>
<td>Study component cost reduction options; update 2011 findings on electronic controls</td>
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<td></td>
<td>Inlet air preheating with variable airflow</td>
<td>High LCC</td>
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<td></td>
<td>Heat pump + supplemental technologies</td>
<td>High LCC; requires supplemental technologies</td>
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Selected barriers by product and research options
Complex Systems Control Testbed

Rick M. Pratt

This project provides an experimental and testing infrastructure in which distributed control methodologies and tools can be validated and verified.

The rapid growth of intermittent and decentralized renewable resource electrical generation, the ongoing addition of dispatchable loads (e.g., hot water heaters, electric mobility) to utility portfolios, and the growth of the smart grid has led the electrical transmission, generation, and distribution sectors to begin researching control system methodologies other than centralized or hierarchical control. Distributed control is a new control methodology that has the potential to meet these rapidly growing requirements. The complex control systems testbed will be a unique capability sought out nationally as a flexible, reconfigurable, and scalable operational capability to evaluate formally distributed control system theories, technologies, and tools. The agent-based testbed will be a cohesive, adaptable infrastructure built initially from existing connections to load and generation resources and then extended by leveraging additional grid resources, including renewable energy technologies and buildings, to offer an environment in which distributed control methodologies and tools can be validated and verified by staff, collaborators, and partners. The testbed capability and new capabilities from the theory and tools focus areas of this project will provide DOE with a sound scientific basis for growing its energy programs to develop a controls-based research agenda in the building technologies, electricity infrastructure, and smart plug-in vehicle areas.

Our project work is focused on developing a reliable, flexible, scalable, and adaptable testbed that enables experimental or virtual evaluations of advanced theoretical methodologies and new technologies by gaining control system access to campus and regional physical infrastructures such as Lab Homes, electric vehicle (EV) charging stations, EMSL photovoltaic array, and energy storage projects using the PNNL-developed agent-based VOLTTRON™ platform for distributed control system development.

The project effort FY 2014 effort was divided into two major areas. First, the test bed control system requirements document was created that integrated both buildings and grid perspectives. This document has been reviewed with comments integrated. Next, existing PNNL infrastructure and capabilities were identified and evaluated for integration into test bed. Those components selected for FY 2014 implementation included Lab Homes EV charging stations, VOLTTRON™ agent-based control platform, and local weather conditions.

During FY 2014, six VOLTTRON™ agents were developed and tested using simulated Lab Homes loads and emulated EV charging. These agents were then tested using existing Lab Homes loads actual EV charging loads. In addition, two use cases were developed to test the agents and control system. Use Case 1 tested how plug-in electric vehicle (PEV) charging can contribute to maintaining a constant home power goal while home loads cycle ON/OFF. Similarly, Use Case 2 tested how PEV charging can contribute to maintaining a dynamic home power goal while home loads cycle ON/OFF. The dynamic home power goal was based on the BPA forecasted load curve.

We found that the VOLTTRON™ agents demonstrated that controlled or Intelligent Vehicle Charging and associated load aggregation can significantly reduce residential transformer loading in high PEV concentration zones without significantly delaying PEV charge complete times. Additionally, the agents demonstrated variable EV charging rates can regulate the home demand and shift loads on appliances, including HVAC and water heater cycle ON/OFF. The dynamic home power goal provided results similar to the static load use case. Because the dynamic home power goal was more restrictive, the potential for other control system enhancements became apparent (i.e., shifting water heater ON time by a few minutes or placing EV charging stations in standby mode). Ultimately, these use cases contribute to providing potential methods to reduce the number of entities needed to participate in aggregation services. This is possible because the home or business demand can be significantly smoothed and aggregation potential is enabled.

In FY 2015, our test bed development plans will provide a much more diverse platform to test and develop advanced distributed control algorithms. These plans include integration of buildings and the Lab Homes test bed integration. We will attempt to supply additional controllable loads, including Lab Homes HVAC and water heater control and energy storage. These additional inputs to enable control system development will expand the number of variables needed for consideration, including BPA current and forecasted load as well as wind, solar, hydro-electric generations. Additionally, we will develop an integrated test bed configured by the experimental management system to interact with the simulators.
Decision Theory for Incentive Compatible Mechanism Design

Abhishek Somani

The goal of this project is to develop new and analyze existing transactive control mechanisms to enable the coordination of thousands of smart grid assets acting out of self-interest.

Distributed control of a complex system may be viewed as a problem of incentive compatible mechanism design so that the emergent outcomes from actions taken by agents acting out of self-interest are consistent with the overarching control objective. Mechanism design theory (MD), a field of microeconomic study originating from game theory, is a framework for deriving efficient system (or social) outcomes from populations of strategic interacting agents. In game theory, we normally construct a model of the strategic interaction (the interaction being a “game”), formulate the appropriate agent utility functions and then solve for equilibria, which are stable points in which agents choose not to change their strategies. MD is the inverse approach: instead of determining the outcomes from a model of the game, we design the game (i.e., the rules) to reach specific outcomes. Usually, these outcomes maximize (or minimize) some social or system objective function.

In this project, we will show that large, complex system control can be realized via mechanism design and multi-agent learning. Advancements will be made at the interface of control, mechanism design, and learning. We initially used agent-learning methods to derive smart HVAC agents’ bidding behavior double auction retail markets, like those used to manage feeder constraints in the recently concluded AEP gridSMART smart grid demonstration project. The bidding strategy in double auction markets is derived without assuming a model for the agents’ economic behaviors using a reinforcement learning algorithm. The results for comparing the model-based and model-free approaches demonstrated that the model-free bidding strategy gave similar performance to the model-based bidding strategy. Successful representation of economic behavior using model-free approaches will be useful in deploying similar methods for other devices or a group of devices such as within a building.

The reinforcement learning algorithm can be improved by performing parameter tuning based on certain global evaluation metrics. The algorithm can also be improved by making the reinforcement learning process more sophisticated, such as predicting possible impacts of future actions and sensing more information from the environment. Finally, model-free approaches can be applied to represent economic behavior of devices in other market-based mechanisms as well, such as those involving bilateral negotiations to buy and sell energy. We will work to develop these alternate approaches in FY 2015.

Also during FY 2014, we proposed a method to coordinate the distribution of electric power/energy within a campus microgrid that employs automated negotiating and bargaining among building agents that satisfies conditions put forth by both the physical system and semi-cooperative game theory. Consider a campus comprising n buildings. Let i for i = 1, 2, . . . , n denote the i-th building. The campus manager determines Q-goal(t), the power consumed must not be exceeded by the campus’ buildings during the time interval [t, t + 1]. The manager derives Q-goal(t) = f(•) from incentive signals, schedules (or forecasts) received, budgetary limits and considerations, efficiency objectives, etc. It then computes threats Q-threat i(t), one for each building i, such that Σ Q-threat i(t) ≤ Q-goal (sum of the building power does not exceed the goal) and Q-threat i(t) ≥ Q-running(t), for all i, (the threat exceeds the minimum power requirement of the building). It then announces Q-goal(t), Q-threat to all building agents. The campus manager provides a finite period of time for the buildings to negotiate allocations; otherwise, the campus manager penalizes building i with allocation Q-threat i(t). The buildings begin negotiating Q(t), Q(t), . . . , Q(t), where Q(t) ≥ Q(t) is building i’s allocation. A building forecasts its demands, with the option to defer consumption until later time intervals. Buildings bargain by announcing offers and countering. The negotiation ends when no new offers are announced or the time expires. A valid allocation is arrived at when Q(t) ≥ Q-threat , for all i, and Σ Q(t) ≤ Q-goal. If more than one valid allocation is negotiated, the campus manager chooses the one that minimizes a secondary set of objectives (e.g., it chooses the allocation that minimizes overall cost). The campus manager then reports Q(t) = Σ Q(t) to the distribution system.

For FY 2015, we will develop protocols to implement the negotiation process between buildings and work toward a demonstration of a virtual test-bed consisting of buildings as well as generation and storage devices.
Development of a Framework to Quantify and Monetize Comparative Risk at Deep Fluid Injection/Extraction Sites

Casie L. Davidson

The unique framework created from this project will strengthen and broaden the applicability of PNNL’s world-class capabilities for identifying and addressing risks associated with human activities in the subsurface.

Current tools within the Geological Sequestration Software Suite (GS3) can quantify physical outcomes associated with perturbation of the subsurface at fluid injection sites, including displacement of reservoir fluids, mobilization of heavy metals, and modifications to the stress regime that could fracture a reservoir or drive existing inactive faults to failure. While of value to project siting and management decision makers, these consequences have greater potential if they could evaluate the entire set of project risks and mitigation options on a common basis. Quantifying monetary costs and benefits under specific operational scenarios provides a powerful decision support tool for project operators, insurers, and regulators and is applicable to a range of subsurface energy projects such as hydraulic fracturing, enhanced oil recovery, natural gas or compressed air energy storage, and CO₂ sequestration.

This project’s subsurface risk framework (SUBSURFR) integrates a number of PNNL’s high impact capabilities, including GS3, Subsurface Transport over Multiple Phases (STOMP) reservoir simulator, and PNNL Online Environmental Information Exchange (PHOENIX) decision support and data visualization environment. It applies PNNL’s subsurface modeling tools with expertise gained through risk assessment and uncertainty quantification programs to quantify consequences of leakage and/or system failure at fluid injection or extraction sites. We built this exclusive framework for articulating project risks in the context of monetary consequences, enabling an integrated, quantitative approach to incorporating risk in decision making and management of subsurface development projects. By integrating existing modeling tools with newly developed methods, this framework offers a comprehensive decision support tool to evaluate risks and mitigation options on a common cost basis.

The project developed first-order costing algorithms to allow for monetization of outputs from the reservoir simulation, uncertainty quantification, and consequence impact assessment process. Designed as a tool that could reside within the GS3 knowledge management system and allow for access to and integration of data developed as part of a project siting and management process, SUBSURFR incorporates multi-run simulation ensembles into an uncertainty quantification (UQ) process that allows for derivation of descriptive statistics for scenario- or site-specific simulation ensembles. Use of STOMP within the GS3 system enables the use of multiple modeling domain realizations derived based on the degree of uncertainty and potential variability in key reservoir parameters (e.g., porosity and permeability). The UQ analysis outputs for a given scenario are then used to inform risk and cost analysis for P05, P50, and P95 variants on that scenario, reflecting the unique outcomes associated with the variability of inputs used in the domain realization and simulation processes.

Raw outputs for the full ensemble as well as the descriptive statistical outputs for each operational scenario, health risk analysis, monetized project outcomes, and key project metrics (e.g., maps of CO₂ plume and area of increased pressure, number of wells required, overall project cost) are presented for evaluation and interactive drill-down via a purpose-built implementation of the PHOENIX visualization environment. This scenario can be expanded to allow users to create on-the-fly cross sections and timeseries plots to evaluate the plume over time and at areas of interest. The framework was developed to be applicable to a wide array of potential users, though it also allows for client-specific implementation to serve regulators, industrial operators, or others seeking a tool to enable cost-optimized project management with a robust risk quantification capability.

Data flow between core analytical modules to the user interface, which presents an environment for viewing and comparing across operational scenarios using a variety of tools and system outputs, including plume maps, key project metrics, and costs.
Distributed Control of Large-Scale Complex Systems

Jianming Lian

Modern systems such as electric power systems and building systems are becoming more interconnected and complex. In contrast to centralized control, distributed control is emerging as a promising paradigm for the control of large-scale interconnected systems.

Although there has been significant progress in distributed control theory for large-scale complex systems, the existing theoretical results cannot be applied to the domains of grid and building due to the ignorance of practical system properties that are specific to application areas in grid and buildings. The objective of this project is to lay the preliminary theoretical foundation for a future distributed control paradigm in the areas of electricity infrastructure and building technology. The resulting theory will be applied to establish the theoretical foundation for a newly proposed concept of transactive control in the domains of grid and building and to enable the distributed optimal control of smart grid assets for demand response.

In FY 2014, a market-based control framework was developed to coordinate a group of autonomous responsive loads to achieve system-level objectives with price incentives. This framework has the structure of hierarchical decentralized control and consists of the supervisory layer and the device layer. In the supervisory layer, the coordinator represents a double-auction market. In the device layer, the responsive loads can be either thermostatically controlled loads or deferrable loads. At the beginning of each market cycle, the coordinator collects the bidding information from each responsive load and then determines the clearing price that is used by each responsive load to determine local control inputs independently.

There are four essential elements inside the proposed market-based coordination framework, all of which are described in detail below.

Responsive load modeling. The dynamics of each responsive load can be described by a generic switched system model, where discrete states represent the different operating modes. The switching between different operating modes is determined by algebraic equations, and the continuous states within each mode will evolve according to the continuous dynamics described by differential equations.

Local user response. Each user of the responsive load is self-interested and has different preference over energy consumption and energy cost. This preference is fully characterized by a local selfish optimization that maximizes the individual net surplus for a given clearing price. After solving this selfish optimization, the user response will be described by an energy curve that maps the clearing price to the energy consumption.

Global optimal coordination. The coordinator achieves the optimal energy allocation by maximizing the social welfare and respecting the distribution feeder capacity constraint. The obtained optimal energy allocation is actually implemented by the clearing price, which is the coordination signal sent to each responsive load. The determination of the clearing price requires the coordinator to have enough knowledge about the individual energy curve of each responsive load.

Local bidding strategy. In order for the coordinator to determine the clearing price, a new concept of sufficient bidding is proposed. Sufficient bidding is the bidding information based on which the coordinator can effectively determine the clearing price. Obviously, all the private local information is definitely a sufficient bidding. However, this sufficient bidding may be impractical. First, individual users may not be willing to disclose their preference due to the concern of privacy. Second, it will cause large amount of information exchange and impose some great challenges on the communication bandwidth. Thus, the practical sufficient bidding will be the parameters characterizing the local energy curve.

The proposed market-based coordination framework can be successfully applied to establish the theoretical foundations of the transactive control scheme in the Olympic Peninsula and AEP Ohio gridSMART demonstration projects. Further, the concept of sufficient bidding in this framework can be used to improve the current bidding strategy deployed in the field, which is heuristic and cannot guarantee the feeder capacity limitation.

In FY 2015, the practical implementation of the proposed market-based coordination framework will be considered by dealing with unknown load model parameters through learning algorithms. The proposed framework will also be incorporated into GridLAB-D™ so that it can be tested for different realistic scenarios.
This project is developing a capability at PNNL that will allow the analysis of the challenging problem of reducing energy use in buildings against a situation in which more than 40% of the U.S.’s primary energy is spent.

PNNL’s Building Energy Codes program has conducted national level simulation studies for DOE for almost three decades, but the existing suite of tools used to manage such analyses cannot scale to the massive computing resources available today. Whereas current studies may involve a few tens of thousands of building energy simulations, future problems will require millions. This project aims to extend the existing simulation capabilities to the required new scale by reusing/modifying existing tools where possible, selecting extant tools (whether internal to PNNL or externally available where possible) and building new tools where needed. The objective of this research is to design a massive scale simulation capability flexible enough to accommodate the challenging building energy efficiency problems of the coming decades, using whatever existing and yet to be developed domain-specific simulation tools are required.

Future improvements related to the work of this project will involve nuanced and multi-faceted solutions that require the heavy analysis capability. Such a capability design successfully implemented will put PNNL in a strong position of leadership in the field of national and international scale buildings research. Ultimately, the results of our project will enable PNNL to possess an unrivaled ability among DOE laboratories to deploy simulation analyses rapidly using a variety of existing or future tools addressing the energy efficiency challenges of the next several decades.

In FY 2014, the research team conducted a thorough literature search and performed an evaluation of known tools relevant to the needs of this project. The search and evaluations considered both internal to PNNL and external sources of software tools and techniques. Based on those reviews and using the team’s experience with the existing (old) parametric simulation capability at PNNL and the stated requirements of the new system, the team developed a specification for an Extremely Large Scale Building Energy Simulation Infrastructure (ELSBESI). The ELSBESI design expresses the requirements in terms of an example system (though alternative systems are possible) with five components: a Workflow Description Language (WDL) for defining workflows; a WDL interpreter and converter (for old project workflows); a database schema to hold workflow definitions and simulation/analysis progress information; a workflow executive to manage execution on a massively parallel compute engine (e.g., the PNNL Institutional Computing [PIC] cluster); and a suite of user tools that allows both interactive and programmed/scripted control of all processes.

The major finding of our work thus far is that there is no existing tool that solves the general problem of massive scale building energy simulation. PNNL’s existing tools come the closest in terms of the semantics of expressing and developing large parametric simulation efforts, but do not scale to the level of millions of runs per research question as will be required. Other existing tools were found to be either too focused on solving a particular problem: not flexible to accommodate arbitrary simulation tools and processes or not yet envisioned workflows or too focused on human-machine interfaces, graphical input mechanisms, and the like to be useful generically. These findings validated the need for a custom infrastructure design.

During FY 2015, we will implement and thoroughly test the ELSBESI design produced in FY 2014. The team plans to work closely with ongoing PNNL projects involved in cluster-based studies of building energy or problems in other domains to make sure that the best extant tools and capabilities are brought to bear on the ELSBESI implementation.

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Energy Supply and Use
**Future Power Grid Control Paradigm**

Karan Kalsi

This project introduced a novel control paradigm that enhances reliability and efficiency of the future power grid by exploiting the value of new monitoring and information technologies coupled with new business needs and policy changes.

Under the premise that transmission system loading will continue to increase and the trend will be toward maximum utilization of transmission system will be close to thermal capacity, security and reliability are crucial issues for the future power grid. The problem of power system security and reliability is evident considering past events such as the 2003 Northeast Blackout, which swept out a large geographical area in 9 sec, affected 50 million people, and caused $10 billion dollars in losses. With the advent of the smart grid, the current power grid requires a new look at monitoring and operation capabilities and a unique design of the control architecture.

This project constructs a new control paradigm based on robust, coordinated, and distributed control architectures. The proposed control paradigm for the future power grid can enable system wide control, allow more integration of renewable energy sources, exploit the potential of demand response, and significantly reduce the risk of cascading failures ultimately leading to blackout events. The performance of control scheme is benchmarked against current practice using several test systems. The suitability for high performance computing (HPC) will be evaluated to ensure broad applicability of the proposed architecture on large-scale systems. Our work will contribute to helping create a more flexible, reliable U.S. energy infrastructure.

In FY 2012, we offered a novel modeling framework that represented multi-machine power systems as large-scale interconnected systems. Automatic generation control (AGC) was modified and coordinated with decentralized robust controllers to restore tie line power to their scheduled values. We also studied the interactions of typical remedial action schemes (RAS) with the distributed hierarchical controller to identify a path for optimal coordination of two control actions. It was demonstrated that the proposed robust control strategy reduced the burden on the RAS, which in turn reduced system stress from tripping of generators.

Distributed generation, demand response, distributed storage, smart appliances, electric vehicles, and other emerging distributed smart grid assets are expected to play a key part in the transformation of the American power system. Due to the variability and uncertainty associated with these resources, there is much trepidation from system planners and operators about the controllability of these resources and how they affect grid infrastructure stability. With the addition of renewable generation, more resources are needed to compensate for the uncertainty and variability caused by large-scale integration of renewable resources. Our work in FY 2013 tested the robustness of the distributed robust control architecture with different levels of high penetration of wind in the system.

The above scenarios involve a three-phase short-circuit fault followed by tripping a generator, while the wind speed experiences a sudden increase. The higher the level of generation variability caused by wind power, the larger the frequency deviation from its nominal value under conventional control. On the contrary, the proposed robust controller manages to recover the frequency faster and keep it within tighter bounds.

Conventional generators are an important reactive power source and contribute significantly in maintaining voltage stability. The increasing penetration of wind farms will displace some of the conventional generators, and their capability to supply reactive power may need to be replaced. By increasing the amount of wind generation in the power system, the system reactive demand is being changed with increasing demand/supply volatility. A three-level hierarchical voltage control architecture was successfully applied in...
Europe and China that consisted of primary, secondary, and tertiary voltage regulation. Implementation of this scheme may vary for different requirements and definitions of voltage regulation in different countries.

Several weaknesses have been determined, however: the architecture does not consider discrete actions (such as on/off status of capacitor banks and switchable reactors), does not consider the future system status, and does not address uncertainties arising from the system topology in load/wind forecast.

The decentralized robust control strategy proposed in FY 2012 and FY 2013 may increase wear and tear of the speed governor if activated constantly. Also, the transmission line congestion could be significantly increased possibly creating stability issues. In FY 2014, a new capability was incorporated into the proposed decentralized robust controller, accomplished by applying a look-ahead dynamic simulation to examine the system performance subject to possible contingencies and to determine when and where to activate decentralized robust controllers. It can be seen that placing the robust controllers on different generators can result in significantly different transient stability routines. Performing the look-ahead analysis can help operators to determine the appropriate candidate set of generators to activate the pre-installed controller based on frequency stability indexes.

Some future tasks could involve generalizing the proposed control design to other types of energy resources such as wind generator and energy storage; determining new market rules for rewarding generators with decentralized robust controller activated; studying coordination with frequency responsive demand side management approaches; and validating and testing on large-scale system such as the Western Electricity Coordinating Council model.

Activating the robust controller on Generators 13 and 16 yields the best frequency performance.
The GridOPTICS™ software system (GOSS) facilitates the creation of new, modular, and flexible operational and planning platforms that can meet the challenges of the next generation power grid.

The U.S. power system is evolving at a rapid pace. New intermittent distributed power generation and storage technologies, new control paradigms, and new higher fidelity sources of monitoring system state such as phasor measurement units (PMUs) are being deployed today. All of these advances are causing the power system to become more dynamic and have more uncertainty. Computational analysis of the power grid for operational and planning purposes needs to evolve to match this emerging dynamic behavior. In turn, software tools available for power grid analysis were developed under a traditional, sequential, workstation-based software paradigm and are locked into existing vendor software systems for energy and distribution management. This makes it difficult to infuse novel and emerging analysis and data management techniques into power system operations to meet growing computational and big data needs.

The GOSS project is developing a flexible, scalable software architecture that engenders innovation in power grid analytics and data access. Through a set of open application programming interfaces and a robust, high performance and extensible implementation, we are creating a framework in which new and novel data management, analysis, and user-facing technologies can be easily integrated. Primary achievements for GOSS include integrating a range of data collection, analysis, simulation, and visualization technologies to support the operations and planning of the future power grid; providing a framework for integrating novel operations and planning technologies with external power grid systems, including energy and distribution management systems developed by software vendors; providing a client software interface to the GridPACK numerical library; and creating an interface to launch and collect data from high-performance computing applications.

In FY 2013, we developed a GOSS prototype that supports the requirements of high frequency data access and upload from operational, planning, and visual analytics tools running on platforms from Windows workstations to high performance computers. The current prototype was integrated and tested with multiple tools and applications, including PMU data cleaning and event detection, graphical contingencies analysis, NIS forecasting and shared perspectives, and distributed systems architecture.

To provide data to these applications and store generated results, the GridOPTICS™ framework supports data source interfaces for retrieving and uploading PMU measurements (raw/cleaned), load schedule, power grid network topology, and contingencies for the power grid. Currently, these data sources include MySQL and GridMW. Developers building software tools using GOSS reported that they benefited from data reusability and automated translation, time-stamp alignment for different sampling resolutions, multiple data source support in one query, easy-to-implement client interface, multiple language/platform support on the client side, and support for one-time and recurring (event-based) queries.

For FY 2014, we continued to integrate with more power grid applications such as the framework for network co-simulation, operation and planning fusion, and web-based visual analytics. The data source support was extended to include KairosDB, a NoSQL store for time-series data, in addition to MySQL and GridMW. We continued to support developers building software tools using GOSS. In addition, the GOSS platform was extended to be more modular and easy to deploy for a new installation. The GOSS framework was also updated to be deployed as an OSGi component using Apache Karaf, which allows develop-
ers to deploy, install, or add new features to the framework easily and simply for adding a new data source or integrating a new application.

A tutorial for GOSS was conducted during a future power grid workshop, where we received good feedback and are in contact with some interested stakeholders for further research. We participated in numerous demonstrations throughout the year to showcase both the ease of integration and benefits of having a middleware platform for power grid applications. Early in the year, we organized a presentation to display integration with other projects to show contingency analysis results from multiple utilities on the single user interface.

Performance benchmarking was one of goals that was completed. Testing was done for different parameters such as varied numbers of concurrent clients and messages. This exercise helped us to verify and present the efficiency and scalability of the platform. Another goal achieved this year was security. Role- and data-based access control were added to the framework using LDAP, JAAS, and SSL technologies, enabling GOSS to handle data flow restrictions within or across utility. Finally, an invited presentation was given at a smart grid international workshop.
The integration of renewable sources into the nation’s electrical infrastructure will provide many social and environmental benefits. Before high levels of penetration can be achieved, technical and operational problems must be solved and optimal control schemes developed to overcome current barriers to greater adoption.

Operational impacts of high penetration levels of solar photovoltaics (PV), including voltage rise, voltage flicker, phase balancing, and power factor correction, are of significant concern to distribution utilities and may pose a barrier to integration. To study these impacts and develop effective mitigation strategies, it is necessary to combine detailed models of hardware as well as a time-series simulation environment that can capture system-level effects.

To build a platform that can address the above issues successfully, PNNL and the National Renewable Energy Laboratory (NREL) are collaborating on the integration of real-world devices and detailed system-level simulations in a hardware-in-the-loop (HIL) environment. Expertise in system-level modeling within the GridLAB-D simulation environment at PNNL has combined with the knowledge of hardware and laboratory facilities at NREL. Leveraging the capabilities of both institutions, the tools and capabilities essential to accelerate the integration of renewables can be developed. Specifically, the HIL system embeds PV inverters at the NREL Energy Systems Integration Facility (ESIF) into a simulation of a test feeder running within GridLAB-D in the PNNL Energy Infrastructure Operations Center (EIOC). The inverters communicate with the GridLAB-D model in the EIOC using Java Script Object Notation (JSON) at 1 sec or faster intervals over a User Datagram Protocol (UDP) link.

In FY 2013, all scheduled pieces of the HIL system were successfully tested. The IEEE 123 node distribution feeder was selected as the simulation model and populated with detailed physics-based models of both residential loads and solar PV. A secure tunnel was established between the EIOC and ESIF in accordance with the cyber-security requirements of both laboratories. Communication tests were successfully performed between a JSON link demonstration script acting as a proxy for GridLAB-D and for the hardware set-up on the Opal-RT real-time machine in ESIF. The test script used the same protocols, ports, exchange rate, and configurations as the final HIL setup. Additional tests established the capability of a GridLAB-D simulation to operate in real-time mode, communicated via JSON link to a proxy script at ESIF, and sent continuously updated values to a local HTML user interface and display. Communication and control pathways were successfully established between the Opal-RT HIL real-time machine, the inverter, and the solar simulator. The necessary work to enable the Opal-RT machine to communicate via JSON link was completed and tested.

In FY 2014, the final step of integrating each piece of the HIL system was completed. Prior to this time, the system was used to perform initial experiments, focusing on validation of GridLAB-D inverter and PV models and then testing and developing inverter control schemes within simulation and on the actualinverters. Our efforts added capabilities to the GridLAB-D HIL platform on two fronts: expanded communication and new sub-second HIL experiments. The GridLAB-D hardware-to-simulation communication options were expanded to allow the integration of additional PV inverters and additional pieces of hardware such as building the Energy Management System and Community Energy Storage accomplished via interface to VOLTTRON™, an agent-based distributed control and sensing platform. Sub-second simulation capabilities of GridLAB-D were made compatible with the real-time analysis mode and HIL experiments. Many of the operational impacts discussed above are expressed at a faster timescale than the 1s timescale of FY 2013 work. HIL experiments conducted with ms temporal resolution allow more complete validation of GridLAB-D models of inverters, building EMS components, and more accurate modeling of control response.
**Impacts of Communication Network on Distributed Control**

Di Wu

_We are studying the effects of communication network on distributed control where system components are not physically co-located and information needs to be exchanged through imperfect communication channels._

Studies devoted to investigating communication network effects in control occur mainly in two categories: networked control system (NCS) and multi-agent coordination (MAC). Many NCS studies are dedicated to estimation within lossy networks, stability analysis, and controller synthesis but primarily consider centralized control schemes. Thus, little attention has been paid to network effects on distributed control. MAC studies focus on control of different agents for achieving a desired coordination in a centralized or distributed manner such as consensus, formation control, task assignment, and estimation. However, in many engineering applications, effective distributed control algorithms are required to allocate resources properly autonomously and optimally.

As communication network behavior impacts are crucial to distributed control, network effects such as time delay and packet dropout can degrade the performance of control systems designed without considering these effects and even fail control and coordination algorithms. As such, the objective of this project is to evaluate network effects in distributed control systems and suggest control protocols that can best accommodate various network effects. In addition, a great effort will go toward improving the control problem formulation to represent building and grid system characteristics and constraints more comprehensively.

In FY 2014, we reviewed literature of distributed control for building and grid applications. There are only a few studies focusing on distributed control in power systems, mainly during the past 3 years. The proposed applications include frequency control through load management, multi-agent based load shedding, distributed economic dispatch, and economic and automatic generation control. All of these studies essentially solve the same optimization problem, where the objective is to maximize utility minus cost, subject to constraints such as power balance and (static) operating range of each facility.

Consensus algorithm, gradient method, or consensus-like algorithms have been proposed for control and coordination. For example, gradient method is used in frequency control through load management work by assuming that system imbalance can be estimated locally from frequency measurement. Leader and follower algorithms are designed for distributed economic dispatch: the leader collects system imbalance and leads other agents to increase or decrease price; and the followers adjust their power output automatically according to prices.

It has been shown that convergence is guaranteed under ideal communication and indeed, performance has been studied theoretically and/or through simulation. However, potential impacts of communication network effects on these algorithms have not been investigated. We studied communication network effects such as time delay, packet drops, and asynchronous effects on different control algorithms. We found that these communications may affect algorithm performance (such as convergence speed and optimality) and cause non-converging algorithms. For example, some distributed control algorithms work perfectly, assuming all agents update synchronously. However, if updates of agents are out of step at any iteration, the algorithm still converges but fails to achieve global optimal. Some algorithms may even fail to converge when communication delay or package dropout is present, resulting in an oscillating power imbalance within the control system. Our proof shows that errors in received information may fail control algorithms as well.

We examined the control and optimization problem formulation based on which the control algorithms are developed. In most of the existing studies, the dynamics of controllable resources and power system constraints are not reasonably considered. As a result, the proposed control and coordination algorithms may yield some solutions that violate the dynamics and therefore cannot be followed. In addition, control of energy storage requires model of multi-period dynamics. Moreover, it is possible to obtain some solutions that violate physical system constraints, such as thermal and voltage limits. To solve these problems, we established a task for FY 2015 in which we will reformulate the problem by incorporating the resource dynamics and physical system constraints. New control algorithms will be proposed and studied with and without network effects, respectively.
Market Design Analysis Tool

Abhishek Somani

The project is designed to take an end-to-end view of the power system, placing importance on retail market mechanisms and interaction with wholesale markets.

Distribution level assets, including demand-response, distributed generation, and energy storage, can be used to provide grid services (energy and ancillary) to manage intermittency due to renewable sources. The incentives for demand-side resources to provide the needed flexibility may be derived from the provision of grid services, which requires appropriate modeling and monetization of these services as well as rules for participation of distribution level assets in the wholesale markets. The use of demand-side resources, however, will not proliferate unless they are controllable in order to avoid additional uncertainties. Starting at the bulk power system level, the value of operational flexibility is accelerating due to an increasing penetration of renewables and distributed energy resources (DERs). Proliferation of DERs also present challenges to distribution system operators and utilities, and it may not always be possible to directly control every device.

This project is investigating various mechanisms that will need to be established at the retail level to help coordinate and control their responses. For example, an American Electric Power gridSMART demonstration used a double-auction based transactive control mechanism to coordinate responses of residential HVAC systems. However, given the relatively low number of participating households, the impact of these responsive assets was minimal in both the physical system as well as the wholesale markets. It has been shown that participation by large enough number of responsive demand-side assets can have an impact on wholesale markets, creating instability in the system. Hence, modeling a bidding behavior of a load-serving entity/aggregator to represent aggregated demand-side assets in the wholesale markets is another challenging issue that this project addresses.

To model and put value on flexibility at the bulk power system level, we are using the concept of multi-interval economic dispatch (MiED), allowing the representation of inter-temporal system ramping requirements in an International Organization for Standardization’s economic dispatch problem, which helps to dispatch available generation and demand-side resources in the most efficient manner. MiED was implemented in MatPower, which showed cost savings compared to single-period economic dispatch formulation. Price-based incentive signals from MiED were used to clear retail markets, using an extension of the gridSMART double auction mechanism, which also help to coordinate the response from DERs. The feedback effect of retail market participants on wholesale market outcomes is also being investigated and will be the most substantial task for this project in FY 2015.

The retail-wholesale interaction issues were presented during an internal annual review using an integrated demonstration platform. The demonstration utilized GridLab-D’s retail market model to interact with MatPower-based wholesale market to illustrate new market design ideas being developed under another market design project. The communication between the two market simulators was achieved, and the demonstration also utilized advanced visual analytics concepts to validate the state of the markets, resource availability, projected demand curves, and related issues. In addition, the demonstration was designed to help integrate various research components to inter-operate using the data management function provided by the GridOPTICS Software System (GOSS). Ultimately, the demonstration presented a compelling argument to showcase how it can integrate its research portfolio to address a variety of concurrent challenges related to a wide variety of issues, including market-based control and coordination of distribution level assets; the use of demand-side resources to provide grid services such as ramping/flexibility reserves; and regulatory and policy design for integration of demand-side resources at a large scale.

The concepts of MiED and the look-ahead determination of responsive demand-side assets were designed initially during FY 2013. The implementation of those concepts started at the beginning of FY 2014 and will build in FY 2015, including collaborating more extensively with the visual analytics team to expand on the capabilities of the integrated retail-wholesale simulation platform and its visual steering in real time. The end product may be useful for utilities or third-party aggregators that need to determine the availability and flexibility of resources within its distribution footprint. The project will also test forward-looking market design concepts that are best suited to utilize maximally the flexibility of demand-side resources. Finally, we will look for opportunities for the project to be supported by programmatic funding that will allow further development of concepts and tools.
This project advances decision support for the next generation of power system operation by integrating analysis results from planning into real-time operation and improving planning functions with fresher, more accurate operation information.

The U.S. power system is accommodating new intermittent power generation technologies, controlling paradigms, and supporting the deployment of automation technology at all levels of the system. With this dynamic behavior brings the burdens of incorporating the predictive capability from planning to enhance today’s power grid operation. These pressures are manifesting themselves in a more smooth integration between the functional roles of planning and operations.

The goal of this project is to provide an initial set of tools that enable a bi-directional exchange of data between operations and planning environments based on existing integration and messaging framework developed under the GridOPTICS™ software system (GOSS). These tools should allow the results of traditionally operational planning studies to be reflected in relevant real-time tools available to the system operator and support initialization of the planning analysis tools with current data from the operational system. By understanding scenarios that drive the interplay between operations and planning, we will articulate a set of common tools to help bridge these two worlds. While the objective can service a large number of operational scenarios, the project is structured to identify a core set of capabilities that can demonstrate the bidirectional flow of information in a small subset of scenarios. The outcome will reduce the difficulty with integrating operations and planning while respecting the natural differences between their domains and design centers.

In FY 2013, we successfully evaluated a set of candidate tools and selected an uncertainty analysis (ramping) and transmission tool to support a set of illustrative use cases that demonstrate the benefits of operation and planning fusion. For FY 2014, we continued our effort of system design and requirements identification for extensions to the GridOPTICS™ framework needed to support the information exchange between planning and operation for the identified use cases. We also engaged three power companies to help conduct visualization and cognitive science visualization. In particular, a presentation of use case design was delivered to industrial experts from CALISO, who showed strong interests in our tools and confirmed that the concept of web-browser type, an XML based visualization tool developed in this project, aligns with industry need.

The primary technical progress in FY 2014 was that two demonstration cases based on the ramping tool were developed to show the usability of the overall project framework and to establish that the fusion of planning and operation can help provide better decision support and improve system reliability. These demonstration cases involve four tools that have been integrated on the GOSS framework and can communicate to each other: 1) a ramping engine tool to read forecast data from GOSS, create predictive ramping capacity data, and archive the data to the GOSS database; 2) a web-based visualization tool to visualize the ramping tool outputs from the GOSS database; 3) the PowerWorld tool to present the system status from the operation side; and 4) a model conversion tool to transform the node-break to bus-branch model. A paper that focuses on the demonstration cases for the IEEE PES GM 2015 is being drafted. In addition, a document of experimental design for evaluating the effectiveness and usability of the developed tool is ongoing as well as the effort of integrating the transmission tool into GOSS and communicating with other tools for new use cases.

For FY 2015, we will continue the effort on improving the UI/UX of the visualization tools by interacting with domain experts, enhancing the use cases to streamline the bi-directional interface between planning and operations, and conducting a user study experiment to evaluate the effectiveness and usability of the developed tool.
Optimal Sizing Tool for Energy Storage in Grid Applications

Di Wu

The tool developed in this project will enable the sizing of an energy storage system (ESS) to advance the ESS industry toward a market competitive deployment into the nation's electricity infrastructure.

Using ESS for grid applications is not a new concept. Prior to the 1980s and as a result of the limited flexibility of steam plants, projected nuclear builds, and the fuels act, many power system engineers in United States began to study energy storage technologies. More recent developments in energy storage and power electronics are making the application of ESS technologies a viable solution in order to increase flexibility and improve the reliability and robustness of power systems. However, many of these studies have not been devoted to ESS technologies for grid applications. Most existing solutions consider only one or two grid services together, such as balancing service and energy arbitrage. Considering battery cost under today's technology, it is vital to capture multiple value streams simultaneously and determine the most economic corresponding battery size.

The objective of this project is to develop an optimal sizing tool for battery storage system considering multiple grid applications. This energy storage sizing tool can be used to evaluate economic performance and determine the optimal size of battery storage in different use cases while considering multiple power system applications. This tool is a first that provides a co-optimization and sizing capability for systematic and local grid services.

To determine the optimal size and operations of ESS, the key challenge is the modeling of bundled grid services, ESS physical constraints (state of charge constraints, maximize charging, charging and discharging efficiency, and maximum power rate), and inter-temporal constraints (operation of battery in different hours interdependent from limited energy capacity). The value streams of energy storage identified by existing ESS studies were incorporated into this tool, including energy arbitrage, balancing services, and outage mitigation. Economic analysis is thus required to represent values from applications with variable sizes of ESS under different operations. An engineering optimization and simulation engine are then developed to assess system requirements, formulate the optimization problem, and model battery operation. The sizing tool combines engineering and economic components and can select sizes of ESS to optimize the battery operation for single or bundled grid services so that total benefits are maximized.

Optimal sizing formulation and method vary with use cases, with two considered: ESS behind the customer meter (for energy time shifting and demand charge reduction) and the utility owned ESS (for energy arbitrage, balancing service, capacity value, distribution deferral, and outage mitigation). In the first of two sizing methods, a large optimization problem is formulated to model the annual battery operation and corresponding value from different applications with a time step size equal to 1 hr. In the second method, a bi-level optimization problem is formulated. On the lower level, a co-optimization problem will determine the optimal operation and corresponding revenue for any given battery size. On the upper level, the particle swarm optimization is used to determine the ideal size. In both cases, capital cost as a function of battery rated power and energy capacity at the AC side is converted to levelized annual cost. In addition to these two methods, the sizing tool enables users not only to obtain the optimal battery size but also to observe how the benefit (revenue/application value minus battery cost) varies with different battery sizes.

The sizing tool and its graphical user interface (GUI) are developed in MATLAB®. In the GUI, users can select use cases, functions, grid services and specify battery parameters, and input file locations. Once optimization is complete, the user can view a results summary or detailed list in the selected output location or plot a battery power output and state of charge.
Engineering and Manufacturing Processes
To address the challenges of studying alloys, we are building and demonstrating a deposition system capable of producing films with systematic composition variations for combinatorial studies for rapid evaluation of high entropy and other complex metal alloys.

Complex multi-element alloys such as high entropy are a new area ripe for exploitation for lightweight, high wear, and other applications. Unlike traditional alloys that typically have a majority constituent, high entropy alloys are near equimolar of four or more elements. They have recently attracted interest for a range of applications, including next generation high-strength lightweight metals. To study these alloys, a wide range of compositions must be evaluated, and significant work remains to identify the ideal alloys and to understand their structure plus mechanical and electrochemical properties before they can be used. The identification process is further complicated by the large number of potential alloy variations and the difficulty in lightweight materials, as vapor pressures of the constituent elements vary over orders of magnitude, making direct melting difficult.

To combat the above issues, we built a five-element combinatorial deposition system under this project as well as the alloy modeling tools needed to focus efficiently on potential new alloy systems. First, the thin film deposition system we developed is capable of co-deposition of up to five separate elements using magnetron sputtering from 50 mm targets. The sources were all configured with high strength magnets to enable sputtering of magnetic materials such as Ni and Fe. The system was initially configured to produce an equimolar alloy of Al, Ti, Ni, Cu, and Zr in the center of a 150 mm substrate, with variations of each element between 10% and 30%. The sources can be easily repositioned in the system to increase or decrease overall variation for a broader alloy search or refinement of composition around a target value. In addition to metal alloy systems, the deposition chamber is equipped with a range of gas sources to enable deposition of oxides, nitrides, and carbides for high temperature and high wear applications.

To control the alloy composition predictively, a set of tools was developed to model the resulting entropy and enthalpy of the alloy system and enable efficient deposition of the target alloy space. In ternary alloy systems, the entire phase space can be represented in barycentric space in the familiar triangular phase diagram. However, these higher order alloys require more complex modeling. For the current system, there are five degrees of freedom (five sources) resulting in a 4D phase space surface. To represent this scenario, we used Waschpress coordinates to produce 2D pentagonal slices through the 4D phase space. By making multiple slices, it is easier to visualize the alloy variations. We then used the full model to visualize the higher dimensional spaces to ensure that the targeted alloy was achieved.

Demonstrating the capabilities of the system, a series of films of different thicknesses were produced using the AlTiNiCuZr system. The sources were rotated based on modeling to achieve the broadest alloy composition samples and variations in alloys. To understand limitations of thin films versus bulk materials, samples of different thicknesses were made, ranging from 200 nm to 2 μm. It was found that the thicker films tended to peel off of the substrate, so an additional Ti adhesion layer was added.

After growth, the films were analyzed using X-ray fluorescence and energy dispersive spectrometer to measure alloy composition and transmission electron microscopy (TEM) and X-ray diffraction (XRD) to evaluate the crystal structure. The compositions were approximately in line with the target values, though some variation was observed likely due to the interaction between the different magnetron sources. Both the TEM and XRD showed short range order but no crystallinity, indicating that we successfully formed a solid solution.

Future work will include demonstrating bulk materials of equivalent composition and structure as well as extensive mechanical properties testing.
Graphene Oxide Based Structured Laminar Membranes

David W. Gotthold

Consisting of hierarchically stacked, overlapping molecular layers, laminar membranes are a fascinating and promising new class of materials. One example is GO, a membrane recently demonstrated to be leak-tight to almost all gases, including the normally hard-to-contain hydrogen and helium, but providing no barrier to water vapor. To enable practical applications for this new class of structured materials, we must recognize two key fundamental questions. First, we need to understand the mechanism responsible for water transport in laminar membranes (such as GO) and the influences of structure and surface chemistry on the transport properties. By using the surface chemistry and structure as well as measuring the resulting properties, we will be able to separate the relative effects. Second, we need to develop a scalable synthesis route to make commercially viable separation membranes.

Tackling the above challenges, we are developing a sufficient fundamental understanding of the structural and chemical mechanisms that enable the extreme water transport observed in GO membranes to enable scaling this membrane technology for use in a range of water separation applications. This scenario will include understanding the role of surface chemistry and structure to enable improved interlamellar bonding for enhanced strength and reliability as well as identifying opportunities for tuning the transport for specific applications. To enable scaling, we will demonstrate a high-solid loading ink that can be processed using standard production techniques such as inkjet printing or slot-die coating. Ultimately, the design of stable, functional separation membranes from GO will require a multi-level understanding of the structure/function relationship to membrane transport mechanisms as a function of temperature and time.

To understand the relationship between structure, chemistry, and performance, we created membranes from a range of different GO sources with the goal of obtaining various flake sizes from 100 nm to 100 μm in nominal diameter. The GO prepared at PNNL was done following a published improvement from ACS Nano in which graphite flakes are oxidized with potassium permanganate, sulfuric acid, and ortho-phosphoric acid. The GO is recovered through multiple rinsing steps with distilled water (by centrifugation) and then re-suspended in fresh water.

Membranes of GO were prepared by filtration and consisted of several micrometer thick multilayer stacks of GO molecules. The GO flakes were suspended in water using bath sonication followed by stirring. Aqueous suspensions of GO were drawn through 47 mm diameter alumina filtration membranes using a filtration apparatus with mild vacuum. Free-standing GO membranes could be easily peeled from the alumina, provided that they were at least 4 μm thick. In addition to the variable flake sizes, membranes were made with various thicknesses from 5 μm to 100 μm. These membranes were evaluated using mixed gas permeability testing (with O₂, N₂, CO₂, and H₂O) and exhibited very high selectivity for H₂O with N₂, O₂, and CO₂ at or below the system measurement limit, correlating to a selectivity greater than 10⁴. The water vapor permeation rates varied across two orders of magnitude, with a peak around 10⁻⁵ mol/m²s/Pa. In addition, significant variation between the different graphene sources and preparation methods was observed, and we have begun modeling the vapor transport properties and correlating with the observed variations.

To measure the GO flakes properly and precisely, we developed multiple measurement methods though work remains to optimize the process. Specifically, we implemented a fluorescent quenching microscope capable of optical measurement and a scanning electron microscopy-based technique for measuring deposited flakes. We have begun to correlate this data with optical scattering methods suitable for in situ characterization. High resolution transmission electron microscopy measurement of both the flakes and membranes has shown that there is significant variation in the material structure depending on the original source material.

In FY 2015 work will focus on two areas. First, we will continue to develop synthesis processes for both the GO flakes and the material that enables large-scale membrane manufacturing. The goals will be to refine the requirements for the flake size and surface chemistry and then develop more rapid synthesis methods. We will also continue the initial work done on gel-based coating to form the membranes, as this has the potential for large-area scaling. Second, based on the characterization of membrane performance and flake structure performed this year, we will develop models for the water transport through the membrane. To support both of these efforts, we will continue to refine the characterization tools available for use with 2D materials as well as for high selectivity membranes.
We are demonstrating a novel manufacturing method for an efficient joining of metals to polymer composites through a mechanical interlock between materials during the assembly process.

Enabling an efficient use of metal and polymer composite vehicle components through new solid-state joining techniques is a critical path to meeting the 30% weight reduction DOE targeted. The lack of fast, reliable, and robust manufacturing processes for joining dissimilar materials has been identified as a key weight reduction technology gap for light- and heavy-duty vehicle systems in recent DOE Vehicle Technology Office workshop reports. Maximizing structure efficiency through advanced joining is also necessary to realize the full potential of advanced composites in lightweight aircraft and aerospace structures.

Our project objective is to enable multi-material design and efficient material use in manufacturing by demonstrating the joining of metals to plastics using friction stir scribe technology (FSST). Through this process, an in situ rivet-like fastening mechanism between metal and plastic parts can be effectively and efficiently produced by simultaneously inducing local flow of the polymer matrix and mechanically disrupting the surface of the adjoining metal part into the polymer interface. Conceived and developed at PNNL, FSST has been used successfully to join materials with different melting points, such as magnesium and steel, through creation of in situ mechanical interlocks at the material interfaces. The novel process overcomes the limitations of traditional friction-based approaches by eliminating the need to mix immiscible systems and can be used to produce spot or continuous weld lines. By extending these concepts from previous work that joined dissimilar metals to the rapid joining of metals to lightweight polymer composites, PNNL can effect more streamlined manufacturing, reduce weight in transportation components, and facilitate an efficient use of high performance materials.

Friction stir tools and fixtures were designed and fabricated to join 1/8 inch thick thermoplastic polymer plaques to 1/16 inch thick aluminum sheet, including the unique scribe tool tip used to disrupt the metal into the plastic interface to create the mechanical interlock. In a laboratory demonstration of the joining assembly process, plaque of polymer or composite (4 to 6 inches wide and 6 to 11 inches long) were clamped atop a piece of aluminum sheet of similar dimension. The rotating tool was plunged through the plastic and into the metal, then progressed along as straight line to form a continuous weld. Process parameters including tool depth, rotational speed, angle and progression speed were systematically varied to determine their effects on the joint. Multiple tool geometries were also explored.

The quality of the FSST weld was assessed visually and mechanically. Surface finish as a function of weld parameters was qualitatively evaluated. Specimens of 0.5 inch width were cut from the joined panels using water jet milling. Cross-sections of the interlock region were polished and optical micrographs recorded to observe the geometry of the formed interlock. The specimens were pulled in a universal test stand in tensile mode to determine lap shear strength of the joint. Next, the mechanism of joining was investigated through imaging of the interlock region of the specimens. Scanning electron microscopy and energy-dispersive X-ray spectroscopy were used to confirm that no phase changes occurred in the aluminum of the interlock. X-ray microtomography enabled a visualization of the aluminum in the composite and the fiber reinforcement of the composite in the region of the interlock.

Demonstrating the feasibility of the in situ fastener production concept, we successfully joined aluminum to polypropylene, polyamide (6,6) and high-density polyethylene. In a subsequent demonstration, we successfully joined aluminum to discontinuous glass fiber- and carbon fiber-filled polyamide (6,6) plaques. These successful demonstrations suggest that FSST is a viable and promising method not only for joining dissimilar metals in a multi-material product but also for joining of metals to plastics and polymer composites. Advantages of this technique to create fasteners within the material during assembly relative to use of conventional fasteners include lighter weight, few parts, and faster assembly time.
Low-Cost Conformable Metallic Foam

Vineet V. Joshi

Our project is developing a novel, low-cost method for synthesizing a conformable metallic foam that will overcome many of the processing and cost issues that prevent the use of this energy saving material system.

Metallic foams have been evaluated for many years in automotive applications and have been shown to reduce the mass of vehicle structures while retaining or improving many required structural characteristics such as specific stiffness, strength, durability and energy absorption. Foams can take either the form an open structure of interconnected pores similar to that of a sponge or a closed structure of pores not connected to each other. Thus, metallic foams that can conform to any given shape are of wide interest in lightweight structural members, impact/crush tubes, fluid filters, catalytic supports, and biomedical implants. However, no known technique is commercially available that can form conformable metallic foams for these applications. In addition, none has met the needs of the automotive industry due to cost (both material and processing), and there has been no implementation to a scale that would impact domestic oil consumption.

Our project is using a mixture of pressurized liquid molten metal and a second phase that either decomposes or undergoes a phase transformation into gas upon depressurization. The primary advantage of this method is that the foam precursor can be handled as a dense liquid or slurry prior to “foaming” similarly to the method that polyurethane foams are handled. By handling the foam as a liquid, the precursor can be injected into a structure such as an “A” pillar of an automobile and allowed to foam in-place. This process will conform to the geometry of structure that it is injected into, mechanically bonding by the expansion pressure and possibly metallurgically by chemical reaction (diffusion bonding). There currently are no metallic injectable metallic foams; therefore, foams are available only as “boards” that must be machined to shape and therefore prevent in injection into complex shapes like A and B pillars or roof beams.

Our work in FY 2014 was to demonstrate foaming using a mixture of pressurized liquid metal and a second phase that either decomposes or undergoes a phase transformation into gas upon depressurization. A high pressure system that can withstand temperatures up to 700°C has been developed. In the current technique, the CO₂ is used as foaming agent. The system uses a known quantity mixture of CO₂, and molten metal and is pressurized anywhere between 1500 and 5000 psi at high temperatures and ejected in a low pressure die, wherein the CO₂ transforms to gaseous phase and the metal solidifies while conforming to the shape. The image shows a successfully conformed foamed part.

Ultimately, we successfully demonstrated a technique to foam metals using the “soda pop” concept to understand the system conditions well to control the operation and foam the material into desired shape. We designed and developed a new high temperature pneumatic valve for the system; in addition, a new melting system has been purchased to cast billets of required compositions and dimensions.
This project addresses knowledge gaps in atomistic level research to enable basic mesoscopic materials research that will impact energy, materials discovery and genome, and transportation applications.

The goal of this effort is to develop a basic level understanding of the thermodynamics and kinetic mechanisms of non-equilibrium systems involved in materials processing and synthesis. The dynamic response to temperature and stress gradients such as those developed under processing conditions are explored at a fundamental level to bring a fine scale interpretation to these mesoscopic processes. Newly developed simulation capabilities provide a mechanism for validating the link between atomistic structure features and mesoscopic response and allow us to focus experimental efforts on those concepts most likely to succeed and to explore the cost effective materials processing and synthetic routes.

During FY 2014, our specific project goals were divided into two primary objectives. The first was to develop and extend materials simulation capabilities to non-equilibrium conditions under applied field gradients, and larger materials system configurations with realistic representations of heterogeneities. The second objective was to develop a tiered, multiscale capability to explore chemical composition spaces of materials for phase stability using a combination of knowledge-transformed materials information and first principles methodologies. While computational approaches to simulating materials behavior have become an essential part of the materials discovery and development process, assessing the viability of synthesis and fabrication is less straightforward and often glossed over. Temperature, pressure, and stability of target phases and compositions remain computational challenges, often determining whether a material can or cannot be made under the conditions and with the materials at hand, as well as an assessment of the level of difficulty to be encountered in the materials development process.

Theoretical and computational studies were used to address several issues associated with materials development and processing. First, in order to have a systematic approach to the local heterogeneities often encountered in larger scale materials systems, we explored new methodologies that can address mesoscale-sized systems in dynamics simulations. Specifically, temperature-dependent surface energies for Mg alloys were developed as first principles capabilities to evaluate temperature and stress-dependent surface energies for lightweight alloys. In addition, we generated software capabilities for simulating large scale metallic and semiconductor cells.

Thermodynamic properties form the critical juncture between modeling simulation and materials synthesis. A priori materials informatics approach to heats of formation without cell coordinate information has been demonstrated using the following methods. First, we developed coarse-grained materials knowledge models to estimate thermodynamic properties. Next, we established an informatic “hess-like” thermodynamic cycle for the prediction of heats of formation trained against a broad range of semiconductor, insulating and insulating materials. Lattice energy model - $R^2=0.958$, $CV_R^2=0.957$ was compared against the experiment. Finally, we created software and compiled an informatic database of thermodynamic properties, physical descriptors, and reference energies. The new capability allows us to estimate formation enthalpies in anticipation of potential synthetic pathways and assess stability of new materials, their lattice energies, and structural information.

Finally, the interaction of adlayers that are often used to facilitate materials processing was examined. The test case was exploring the temperature dependence of MnBi-type magnetic materials. Our systematic investigation uncovered an approach that could be used to predict which cell structures and type of adlayers could be used to control the magnetic power and extend their utility in high powered applications.

Unit cell structures of MnBi-Co(Fe)-Co(Fe) alloys
Atomic Level Investigation of the Phase Stability of Transition Metal Surfaces Under Reactive Environment

Libor Kovarik

We are investigating the stability of platinum (Pt) group catalytic nanoparticles during exposure to elevated temperature and reactive environment and establishing guiding principles for the accelerated discovery of next generation catalytic materials.

Transition metal catalytic nanoparticles supported on oxide or non-oxide substrates are import catalytic materials. When exposed to a reactive gas environment, the nanoparticles can undergo number of morphological, structural, and surface transformations that have significant impacts on catalytic properties. To establish the structure-property relationship that provides a scientific basis for the design of the future generation of catalysts, there is a significant research effort dedicated to the atomic level understanding of nanoparticles under a reactive environment.

The goals of this project were to investigate phase stability of Pt group catalytic nanoparticles during exposure to the oxidizing environment and to establish guiding principles for an accelerated discovery of the next generation catalytic materials. To achieve these goals, we applied and further developed the state-of-the-art aberration corrected environmental transmission electron microscopy (ETEM) imaging capabilities for atomic-resolution imaging under dynamic operating conditions. ETEM provides a unique capability for the imaging of complex geometries of supported nanoparticles, revealing the atomic nature of surfaces and subsurface regions. However, there are still several challenges associated with imaging under a reactive environment, and the development of new approaches and imaging methods is required. In this project, we focused on developing a capability for mixing and switching mixtures of gasses inside ETEM, which is critical for achieving atomic resolution imaging. Our initial gas unit for delivering gases to ETEM was built previously, and for FY 2014, we made significant upgrades to enhance the rate of switching, made improvements to computer controls, and designed new protocols to achieve a drift-free environment during the switching of reactive gases.

The main portion of our research focused on the phase stability of palladium (Pd) catalytic nanoparticles in an oxidizing environment. For Pd-based catalysts, the phase stability under an oxidizing environment is crucial, as many Pd-based catalysts are used in various oxidation reactions. Under complex temperature and reactive environment conditions, the interaction of Pd with a substrate can result in intriguing properties such as hysteresis of PdO dissociation/formation during heating/cooling cycles. The origin of this phenomenon has remained poorly understood; therefore, as a part of this project, we studied the role of chemical and crystallographic interaction with the substrate on the nucleation and growth of oxide species.

In particular, we investigated Pd nanoparticles supported on CeO$_2$ and SiN$_x$ and identified distinct and previously unknown surface structures in the initial stages of oxidation. In the case of Pd supported on SiN$_x$, we found that exposure to oxidizing environment leads to the formation of a complex 2–3 atomic layers of PdSiO$_x$, while for Pd supported on CeO$_2$, we found a distinct monolayer of PdO. The type of initial oxide layer was found to have a significant influence on the stability of Pd nanoparticles (nucleation and growth of PdO). For Pd supported on SiN$_x$, the initial oxide layer impedes the phase transformation. Importantly, the high quality of atomic level images enabled us to address the structural nature of surface oxides. For example, for Pd supported on CeO$_2$, we identified that the surface monolayer on (100) is closely related to “($\sqrt{5} \times \sqrt{5}$)-27”-PdO, but with a modified orientation relationship compared to the formation on bulk.

Pd nanoparticle surfaces during initial stages of oxidation: a) Pd nanoparticle supported on SiN$_x$; b) graph of inter-columnar spacing from the surface oxide and metal phase; c) Pd nanoparticle supported on CeO$_2$; and d) graph of inter-columnar spacing from the surface oxide and metal phase.
In addition to studying the role of chemical interaction, we focused on the role of crystallographic interaction with the substrate by comparing epitaxially and weakly attached nanoparticles. In the temperature range of 300–400°C, the weakly bound Pd nanoparticles were shown to oxidize fully, while the epitaxially attached nanoparticles underwent only partial oxidation. Coherency strains from the substrate were identified as a strong inhibition of the phase transformation.

As a part of this effort, we also focused on a detailed analysis of the nucleation and growth of PdO. Very importantly, we found that the transformation does not follow the classical picture of nucleation and growth in which the oxide forms in core shell arrangements. Instead, we determined that the transformation begins from a single nucleation event, which then gradually transforms the microstructure without the formation of an oxide shell. Atomic-level imaging also enabled us to determine the kinetics of the nucleation and growth and to address the crystallographic nature of the transformation.

Apart from the work on Pd nanoparticles, we also addressed restructuring of surfaces of bimetallic Pt–cobalt (Co) nanoparticles. During oxidation experiments, we captured how Co migrates to the nanoparticle surface, forming epitaxial CoO film, and subsequently islands via strain relaxation. During reduction, Co migrates back to the bulk, leaving a monolayer of platinum on the surface. This work was performed in collaboration with Brookhaven and Lawrence Berkeley national laboratories. We additionally established a collaboration with a group from the Georgia Institute of Technology. In this work, we used ETEM to addresses how the preparation methods affect nickel species present on alumina-supported catalysts.

Work on this project established important new capabilities for catalytic research under high temperature and environmental conditions. The applications also provide a new level of understating for Pt group-supported catalysts. At the present time, this work has led to three peer-reviewed journal publications and seven presentations. Several other publications are currently being prepared for submission.
Bridging Length Scales in Complex Oxides: From Point Defects to Defect Superstructures

Peter V. Sushko

We are exploring collective phenomena in complex oxides and thus advancing defect engineering approaches to the synthesis of new materials and design of their functionalities.

Collective behavior of defects offers new opportunities in materials design and synthesis. Defects are routinely used to modify materials properties such as n- and p-type dopants in semiconductors, which are optically active impurities in scintillators and structure modifiers in glasses. Often, these modifications can be traced to the effect induced by individual defects: the higher their concentration, the more pronounced the effect. Exploiting collective behavior of defects can yield new approaches to the engineering of novel materials structures and functions.

The overall objectives of this project are to advance fundamental understanding of defects and defect superstructures in oxide hosts, explore their properties using theoretical and computational methods, and identify the parameters affecting these interactions at several length scales. The project is focused on ternary and quaternary oxides of perovskite and corundum lattices. Density functional theory combined with wavefunction based ab initio quantum chemical methods are used to investigate the thermodynamic stability of these materials and the relationship between their chemical composition, optical properties, and oxidation states and local structure of metal ions. The success of this project will lead to new principles for defect engineering in a wider class of materials and provide insight needed for their practical synthesis.

As an overarching theme for FY 2014, we considered the effect of oxygen deficiency or excess on the structure and electronic properties of the metal ions in three prototype systems. The results of these studies provide the basis for judicious choice of the processing conditions needed to synthesize materials with desirable properties. First, we investigated the perovskite SrCrO$_3$, in which the Cr ion is formally present in a 4+ oxidation state ($d^5$ electronic configuration) and occupies the octahedral lattice site. This system is electronically degenerate and, according to the Jahn-Teller theorem, transforms to a lower symmetry configuration. Our findings demonstrate that at high oxygen chemical potential, the electronic degeneracy in SrCrO$_3$ is lifted by octahedral distortions, emits oxygen and adopts the SrCrO$_{2.8}$ stoichiometry while at low oxygen chemical potential. This change in oxygen content affects 80% of the lattice Cr ions, half of which retain the 4+ oxidation state and become tetrahedrally coordinated, while the other half remain octahedrally coordinated but adopt the 3+ oxidation state. This scenario leads to the formation of regularly spaced quasi-2D oxygen transport channels in which O$^{2-}$ ions diffuse with the calculated barrier of less than 0.2 eV, and their diffusion mechanism is reminiscent of the Grotthuss mechanism of proton diffusion in water. Reported in Nature Communications, the results of this study show promising pathways for the design of advanced materials for applications in fuel cells and thermochemical energy storage technologies.

Doping often results in undesirable effects. For example, Cr$^{3+}$ ions occupying Ti$^{4+}$ sites in SrTiO$_3$ (STO) significantly improve its ability to absorb sunlight. However, Cr$^{4+}$ are naturally compensated by oxygen vacancies ($V_{O}^{\circ}$), which are detrimental to the electronic transport characteristics. We investigated the mechanisms of co-doping STO with equal amounts of Cr and La, which occupy Ti and Sr sites, respectively. Our calculations suggest that at conditions corresponding to bulk synthesis, co-doped Cr and La impurities are distributed randomly. However, if Cr and La are co-evaporated during the layer-by-layer STO film deposition, they preferentially occupy neighboring lattice sites and therefore compensate locally and suppress the formation of oxygen vacancies. These results allow an estimate of the energy scale corresponding to the association of formally charged impurities during the growth process (~150 meV) and identify the experimental regimes that correspond to the random distribution of ions in a quaternary oxide.

Finally, we investigated the effect of oxygen excess on the optical properties of Fe$_{2}$O$_3$–Cr$_{2}$O$_3$ and Fe$_{2}$O$_3$–V$_2$O$_5$ solid solutions and oxidation states of metal ions in these systems. We found that oxygen readily incorporates as neutral interstitial atoms in Fe-rich (Fe$_{2}$Cr$_{1-x}$)$_{2}$O$_3$ solid solutions. It binds to a lattice O$^{2-}$ ion, thereby forming an O$_{2-}$ species but affecting neither the oxidation states of the metal ions nor the optical absorption spectra. In contrast, Fe-rich (Fe$_{2}$V$_{1-x}$)$_{2}$O$_3$ solid solutions accommodate excess oxygen as negatively charged species. This effect manifests itself as the appearance of V$^{4+}$ and V$^{5+}$ species instead of the expected V$^{2+}$ and higher-than-expected optical absorption energies.

In FY 2015, we will investigate the dynamic effects leading to the formation of the low-dimensional aggregates of V$_{0}^{\circ}$ in electronically degenerate materials such as SrCrO$_3$. We will also investigate approaches to chemical modification of these aggregates.
This project investigates the lithium ion conduction mechanism in solid state electrolyte at room temperature to enable next generation energy storage technologies with improved safety attributes.

Solid-state electrolytes are crystalline solids with high ionic conductivities that were intensively investigated a few decades ago. The progress in room temperature solid-state electrolyte, however, is relatively sluggish probably due to the availability and stability of many liquid electrolytes with remarkably higher conductivity at room temperature. With increased global demand for high energy and the imperative for energy independence, solid-state electrolytes regained extensive interest because they substantially improve the safety attribute of high energy batteries such as lithium ion batteries in which flammable organic solvents are usually used and function as fuel in case of fire. For other solid-state electrolytes operating at medium temperature (200–600°C), for example, proton-conductive electrolyte has not been thoroughly explored yet may hold great promises in the electrochemical conversion of natural gas, a large reserve in the United States, into liquid fuels.

In an effort to search for new solid-state electrolytes with high ionic conductivity, it is critical to understand the mechanism for fast ionic transport in solids. This project leverages PNNL’s strong capability in advanced characterizations to promote the understanding of ion conduction pathway in solid electrolytes and guide the rational design and synthesis of various solid-state electrolytes for a wide range of applications.

During FY 2014, a novel solid state electrolyte was discovered (with a patent application in process) that may open a new avenue for this field to explore the ion transport at room temperature. A systematic investigation on the bulk electrolyte properties with the interface evolution between the electrolyte and the electrode was performed to understand further the conduction mechanism of this type of solid electrolyte. Based on the support from this 1-year LDRD project, two proposals using the preliminary results gathered from this project were submitted, one patent application is under process, and one manuscript is in preparation.

The specific tasks undertaken in FY 2014 and their outcomes are described below.

**Materials preparation and engineering.** An innovative salt has been identified to have high ionic conductivity at room temperature. As a result, a pellet-making process by using this moisture-sensitive salt was developed, which provides a good background for further modifications.

**Cell testing.** The new solid electrolyte was extensively tested in lithium symmetric cells by using different current densities and capacity limits. Stable cycling has been demonstrated that suggests the good ionic conductivity of this new electrolyte. Current work in this area involves the testing of the electrolyte in the cells after the optimization of mixing procedures to distribute the active materials homogeneously in the solid conduction matrix.

**Characterizations of the electrode/electrolyte interface.** X-ray photoelectron spectroscopy and transmission electron microscopy (TEM) will be combined to understand the microstructure evolutions on the interface between the solid electrolyte and electrode. The knowledge gained will be used to guide the cell design and materials preparation.

While the method has been used on electrode materials, the in-situ observation of solid-state electrolyte by TEM technique is rarely reported thus far. Thus, the strong in-situ TEM capability at PNNL will enhance the understanding of the microstructures of solid electrolyte and the charge transfer process under the real electrochemical environment. The knowledge gained will be extremely helpful to guide the modification of existing electrolytes and design novel new ones for various applications.
Developing Next-Generation Multimodal Chemical Imaging Capability by Combining STEM/APT/STXM/HIM

Suntharampillai Thevuthasan

This project will develop a common analysis platform for integrating multiple microscopies to characterize commercially viable catalyst materials with metal or metal-oxide nanoparticles supported on porous metal oxides and Li-related energy storage materials.

Complex materials relevant to energy and environmental applications undergo dynamic transformation during their life-cycle that is critical to assess structure-property relationships. For example, in developing next generation energy storage capabilities, one must understand the degradation mechanism of the current state-of-the-art high performance electrode materials during repeated charge-discharge cycling in a battery so that such mechanisms can be arrested or retarded by suitable microstructural modifications from an innovative design of electrode materials. For environmentally relevant materials, it is important to recognize the influence of nanoscale structure and composition of natural and anthropogenic atmospheric aerosols on global climate because of their impact on precipitation acting as ice and cloud condensation nuclei.

We employed the chemical imaging capability along with computational simulations to understand the structure, composition, and chemical state correlated with material behavior. This multimodal approach uses nanoscale 3D compositional analysis by atom probe tomography (APT) and high resolution structural characterization by aberration-corrected transmission electron microscopy (TEM) in EMSL, along with scanning transmission X-ray microscopy (STXM). Through this approach, we will examine the state of elements in Na and Li-ion battery cathode materials as a function of different synthesis conditions and at different stages of electrochemical cycling. This process will not only improve our understanding of starting and degradation of microstructures with electrochemical cycling but also improve the synthesis conditions as well as development of protective coatings and other microstructure modification methods that can prevent battery capacity fading during long-term charge-discharge cycles. A similar characterization approach will be used to understand the nanostructure and chemistry of atmospheric aerosols through the 3D compositional analysis of aerosol particles.

Continuing from FY 2013, a significant focus was establishing a baseline for quantification and imaging by the different chemical imaging methodologies utilized in this multimodal chemical imaging effort. The first effort was to evaluate possible inaccuracies in analyzing the 3D nanoscale composition of heterogeneous energy materials using APT. Gold nanoparticles embedded in MgO was our candidate model system due to its importance as a catalyst for CO oxidation. APT analysis was directly correlated with high resolution STEM and computational simulations to understand non-hemispherical specimen shape evolution during APT analysis of the Au-MgO system. Through this effort, we identified and explained the aberrations in the final APT reconstruction, leading toward a more accurate analysis of such heterogeneous energy materials by APT analysis. This work was published in the Journal of Physical Chemistry Letters and is shown in the figure.

Understanding field evaporation of metal-dielectric composite materials during APT analysis by direct coupling of aberration-corrected STEM and APT analysis with computational simulations.

Throughout FY 2014, a continuous effort was focused on understanding distribution in Li-ion battery cathodes using APT analysis. With a low atomic weight, Li cannot be accurately imaged or quantified using scanning transmission electron microscopy (STEM) or energy
dispersive spectroscopy in TEM. On the other hand, APT analysis is equally sensitive to all elements in the periodic table and can be uniquely suited to image and quantify the Li distribution. Thus, in FY 2014, we achieved the first direct imaging of Li distribution in two advanced Li-ion battery cathode materials, Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$. A non-uniform distribution of Li, Ni, Mn, and O was observed in Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, and uniform distribution of all elements was observed in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ in agreement with energy-dispersive X-ray spectroscopy results. As of FY 2014 end, the manuscript on this work is in preparation, and the preliminary results were presented at a number of conferences, leading to several ongoing collaborative projects with both Lawrence Berkeley (LBNL) and Oak Ridge national laboratories.

With Advanced Light Source beam time (lines 11.0.2 and 5.3.2), we conducted STXM and XANES on pristine and cycled Li-ion battery cathode materials and specifically layered Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ and Li$_{1.5}$Mn$_{0.5}$Ni$_{0.5}$O$_2$ spinel materials for Mn and Ni L edges and O K edge. We subsequently collected STXM images and XANES spectra from a number of pristine and cycled Na-ion battery cathode materials synthesized differently, leading to different starting capacities as well as different extent of capacity decay during battery testing. Specifically, NaMn$_{0.33}$Ni$_{0.33}$Co$_{0.33}$O$_2$ and Na$_{0.44}$MnO$_2$ materials were analyzed in STXM and XANES for Mn, Ni, Co L edges, and Na, O K edge.

Also during FY 2014, we initiated the first set of experiments using multimodal chemical imaging for understanding the nanoscale structure, chemistry, and chemical state of mineral dust atmospheric aerosols. This initial effort focused on understanding the influence of sulfuric acid coating on kaolinite and Arizona test dust on their ice nucleation properties. This effort will be continuing into FY 2015. Finally, with beam line scientists at Advanced Light Source and together with LBNL, we initiated the first set of experiments for developing in situ STXM liquid cell holder to study the lithiation of Si nanowires, which are candidate anode materials for next generation Li-ion batteries.
Development of Graphene/Ionic Liquid Hybrid Material for Ultracapacitors

Vijay Murugesan

This project focuses on developing graphene-ionic liquid based designer interfaces to achieve high energy density ultracapacitors that can power modern technologies ranging from portable electronic devices to large-scale electric grids.

Molecular interaction at electrode-electrolyte interfaces is the basic science that drives all energy storage and conversion devices. Our predictive understanding of the impact of electrode surface chemistry and nature of electrolyte ions on their molecular-level interfacial interactions, however, is seriously limited. This situation impedes our ability to predict, control, and design optimal interfaces. For example, formation of electric double layer capacitance (EDLC) that arises from interfacial interactions is the driving force of supercapacitor performance; hence, with a rationally designed interfacial region, we can achieve optimal EDLC and high energy density supercapacitors. Thus, this work focuses on designing an optimal interface between graphene (G) and ionic liquids (IL) by understanding their interfacial molecular structure.

Graphene is widely reported as suitable electrode material for high energy density lithium-ion battery and supercapacitor technology. However, fickle performances are reported for graphene based electrode materials. For example, the engineered surface modification of graphene such as nanostructural designs, doping, and/or surface functionalization yields relatively higher performance. Many ongoing research efforts are working to design optimal graphene surface for supercapacitor applications, with performances related to the purity and structural homogeneity of the graphene material that depend heavily on surface properties. Therefore, to design the G-based electrode materials rationally, we need a clear understanding about the role of G surface defect groups and its effect on final device performances.

The major challenge in developing a G-IL nano-hybrid structure in FY 2012 was to prevent restacking of graphene sheets to allow intercalating the ILs in desired thickness between individual graphene layers. Such an intercalation required controlled interlayer spacing (i.e., IL thickness) and more favorable affinity between the ILs and graphene. We developed an industrial friendly synthesis method for preparing G-IL composite material using ionic liquids that allowed us to intercalate IL molecules successfully between successive graphene layers with significantly reduced restacking phenomena. In FY 2013, we performed a combined experimental and theoretical analysis of complex G-IL interfacial region. Our analytical results were correlated with statistical and electronic structure-based computational analyses. Time-averaged spectroscopic parameters such as NMR chemical shift, vibrational frequencies, and core-level spectra were calculated at the density functional theory level for the molecular models taken from snapshots of MD simulation trajectories. This interplay between the experiment and the computational approach led to a reliable interfacial molecular structure.

Our uniquely combined theoretical and experimental approach led to fundamental molecular insight about role of surface functional defect groups on G-IL interfacial region, with the results summarized as follows. First, BMIM cations orient parallel to the graphene layer due to π-π stacking interaction and form a primary interfacial layer, which is subsequently capped by a layer of TfO anions. BMIM cations can interact with functional groups on the graphene surface just as they interact with regions of defect-free graphene; however, the disorder in the BMIM orientation near the electrode surfaces is greatly amplified by the presence of defect groups. Next, TfO anions are repelled by the pure graphene surfaces due to π - orbital interactions; however, the hydroxyl defect groups can attract the TfO anions by offering a hydrogen bonding environment. Finally, the distance between the electrode and the electrolyte’s ion is controlled by the defect groups through protrusion forces. Because the EDLC is directly
related to the ion-electrode separation distance, the fickle performance is likely from the non-quantified surface defect groups in the graphene electrodes.

A molecular-level understanding of the electrode and electrolyte interfaces gained within this project through the combined theoretical and experimental analysis explained the fickle performance of graphene-based electrodes that has been widely reported in literature. Further, it enabled the design of the porous carbon with minimal hydroxyl group as optimal electrode material. Also, through MD simulation guidance in the temporal evolution of electrolyte molecule is tailored by introducing organic co-solvent. The organic co-solvent increased the conductivity through enhanced molecular mobility and suppressed the detrimental passive layer formation during the cycling process. These designer-interfaces with porous carbon and mixed electrolytes were tested by both electrical and electrochemical methods up to 500 charge-discharge cycles. More extended cycling and stability tests are in progress. The designer-interface with porous carbon-ionic liquid gives a high ultracapacitor performance (270 F/g) with a power density of 2300 W/Kg (see table).

Major accomplishments, outcomes, and scientific impacts of this project are as follows. A novel ion implantation-based electrode fabrication for supercapacitor application was filed as an invention report. Based on project results, the lead author delivered the keynote address at a regional symposium. In addition, two research highlights focused on our designer electrodes work were published, and the team was interviewed by the Materials Resource Society (MRS) Bulletin editorial office for a news article about our work on supercapacitors. Finally, our work from this project over the past fiscal year has been published in Nano Energy, RSC Advances, ECS Transactions, and the Journal of Physical Chemistry Letters.

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*Rated capacitance of BC series supercapacitors from Maxwell
†Total cost PNNL system is assumed as 100 times raw materials cost
Development of Hard X-Ray Emission Spectroscopy Nanoprobe
Nancy J. Hess

We are developing an in situ probe of the electronic structure of battery materials during operation to gain fundamental knowledge of irreversible transformations that adversely impact battery performance.

Battery lifetime and performance can be improved by elucidating mechanisms that lead to irreversible transformations and changing electronic structure. Much of the previous work on battery materials relies on ex situ measurements and less direct measurements of electronic structure with lower spatial resolution. Understanding the detailed electronic structure of multivalent ions is fundamental to many fields of chemistry and materials engineering, particularly in energy storage and materials. X-ray emission (XES) is complementary to X-ray absorption spectroscopy (XAS), as it provides element-specific measurement of oxidation state, bond length, and neighboring ligand identity. However, unlike XAS, XES is a “more local probe” of the electron-electron interactions, so it provides more detailed electronic structure information such as orbital splitting, spin state, magnetic properties, and bond character and is less influenced by structural disorder and thermal effects. Through the use of low-cost, element-specific XES spectrometers, we are constructing a modular system that is capable of investigating the electronic structure of the transition metal, lanthanide, and light actinide elements within a variable temperature sample environment and with spatial resolution ultimately at the nanometer scale.

In collaboration with the University of Washington (UW), the Advanced Photon Source (APS), and Stanford Synchrotron Research Laboratory (SSRL) we studied the chemical and physical structure of Na/NiCl2 ZEBRA battery cathodes. The addition of sulfur in small amounts as FeS to these cathodes has been found empirically to extend their lifetime significantly, and we studied the cathodes with a range of complementary techniques to understand why. Specifically, sulfur XAS maps collected at SSRL showed that the surface of the Ni particles was covered by a uniform layer of metal sulfides, most likely a mixture of both iron and nickel sulfides. The spatial distribution of the coating was not strongly influenced by FeS content. In addition, transmission X-ray microscopy (also performed at SSRL) indicated that iron migrates to the grain boundaries between nickel particles, and the sulfur may therefore promote this segregation.

Similar to the sulfur maps, nickel XES maps were obtained at APS using the modular spectrometer that was developed at UW. In contrast to the sulfur distribution, we observed a significant difference in the spatial arrangement of NiCl2 on the surface of the Ni particles as a function of FeS content. Low sulfur samples contained isolated pockets of NiCl2, while higher loadings showed Ni grains that were much more uniformly coated with NiCl2. The sulfur therefore acted as a surface modifying agent that increased the contact area between Ni and NiCl2, resulting in the improved battery performance observed. The ability of XES to discriminate between the chemical forms of Ni within a complex cathode structure was crucial for this investigation. The Ni surface chemistry appears to drive a large scale (mm) segregation of the cathode into Ni-rich and -poor regions when sulfur is not present. X-ray computed tomography studies at PNNL revealed that the Ni-rich regions became electrically isolated from one another at low sulfur contents, further deteriorating battery performance.

The results from these studies are described in two manuscripts and will help design new batteries with improved performance. The XES techniques developed will also find application in a range of studies in other scientific fields such as environmental geochemistry and catalysis.
Directed Mesoscale Synthesis of Tunnel Structured Materials for Energy Applications

Eugene S. Ilton

The rational design of materials with properties optimized for energy applications is vital to a sustainable future. At its most fundamental level, this project is using theory to design materials with interesting properties relevant to energy storage and conversion.

Explicitly called out in the area of mesoscale science as examples of designed and self-organized systems, the synthesis of epitaxial thin-films can be guided by theoretical predictions. Specific materials of interest are tunnel structured Mn oxides that are intrinsically mesoscale in spatial and compositional dimensions and are crucial in technological applications such as Li batteries, catalysis, fuel cells, electrochemical capacitors, sensors, and groundwater remediation. However, the complexity and poor quality of natural, hydrothermal, and electrochemically synthesized Mn oxides has hindered efforts to understand their fundamental structure-property relationships, thus preventing full technological potential. To address this issue, we are using molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) to make high-quality MnO2 single-crystal films for characterization and experimentation in conjunction with computational modeling. Our interest in mixing Mn/Ti stems from our measurements showing that Mn lowers the band gap of rutile (TiO2) whereas Ti increases the thermal stability of MnO2. Most previous thin film work has taken an “Edisonian” approach. In contrast, we are melding experiment with theory to provide a predictive capability, forming the basis for the rational design of epitaxial films with interesting properties.

Results integrated over FY 2013 and early FY 2014 on the successful synthesis of homogeneous single-crystal (001) and (110) oriented MnTi1−xO2 rutile-structure films have been accepted for publication. This work highlighted the limits of Mn/Ti mixing as function of film thickness, success in expressing the unstable (001) face, which provides high surface area access to the 1×1 tunnels and the usefulness of ab initio thermodynamics to explain film stability as a function of growth conditions and Mn/Ti composition. The ab initio thermodynamic model included compositional and bulk lattice strain effects as well as temperature and O2 pressure. At the end of FY 2014, we added the effect of surface energy. Results on atomistic modeling of mesoscale Li diffusion in Mn/Ti tunnel-structured materials have also been accepted for publication. Importantly in FY 2014, we deposited thick films that can now be used to test functionality.
Further, we synthesized a diversity of films driven by theoretically predicted properties that manifest a range of compositions and structural/compositional heterogeneities whose function can be compared and contrasted. A recent result illustrates our goal of rational design, in which we use theory to predict compositions of MnₓTi₁₋ₓO₂ films that should significantly facilitate Li diffusion in the tunnels. Given this incentive, we made the film. Specifically, atomistic modeling showed that alternating cation rows that only contained Ti or Mn greatly lowered the activation energy for Li diffusion relative to films where Mn and Ti were homogeneously mixed. In other words, a compositionally layered structure should perform better than one with a perfect solid solution. Further, these layer-structured films can be designed in a variety of flavors and pose an exciting area for continued work linking predicted and measured properties. Functionality tests will evaluate whether the layered films yield improved performance.

Three methods spanning macroscopic to atomistic scales for probing functionality are highlighted. First, the three electrode test provides macroscopic information on Li intercalation reversibility and voltage, and capacitance. In particular, we want to test whether using films that expose relatively large areas of the (001) surface will improve performance (i.e., extent and rate of Li intercalation). An advantage to the thin film approach is that one can preferentially express desired surfaces while independently varying the film volume. Initial results indicate that the 13% Mn films have low conductivity, and we are turning our attention to higher Mn films. Conductivity for the layered structures is also low and requires a new approach that we will work on in FY 2015. Next, we are collaborating with Argonne National Laboratory to perform in operando synchrotron based X-ray reflectivity measurements that will provide microscopic information such as preferential Li intercalation in different layers of the layered-structure described below. Finally, in situ transmission electron microscopy will be used to derive atomistic level information on Li diffusion, including potential formation of defects, upon cycling that could lead to poor performance.

We will follow a three-pronged approach in FY 2015. First, we will expand our ab initio thermodynamic model to include coherent strain to the substrate and oxygen defects. We will then have a powerful theoretical tool for predicting epitaxial thin film stability. Second, we will model Li diffusion for layered MnO₂/TiO₂ films that are coherently strained to the substrate, which is the real-case scenario. Lastly, we will focus on functionality testing as described above. In particular, the layered structures of interest present the (110) surface will require changing our approach; thus, we will mask the substrate in order to make nano-scale single-crystal islands that allow access to the tunnels expressed on the (001) surfaces. This combination of theory and experiment provides a powerful methodology for exploring intrinsic structure-property relationships for predicting and then synthesizing thin films with promising properties for energy applications.
Fundamental Mechanisms of Nucleation and Growth of Particles in Solution

Marcel D. Baer

This work will provide the necessary theoretical framework and simulation tools that enable an understanding of the microscopic principles of nucleation, growth, and self-assembly.

Inorganic polymeric materials form a large class of materials ranging from sol-gel networks to metastable zeolites and hybrid metal-organic framework materials. The synthesis and use of these highly engineered systems has evolved over the past 100 years from “black magic” into at least a technical art. The next step—the one that approaches modern science—requires the continued development and application of a gamut of synthetic methods, illustrative model systems, characterization techniques, and interpretation via computation and simulation that can bridge from quantum mechanics through fluid and structural mechanics.

We want to understand the growth kinetics of size selective molecular clusters that form the secondary building blocks of polymeric inorganic networks in a joint experimental and theoretical effort. Our focus will be on the use of molecular models to mimic and understand the underlying principles of assembly of surfaces of inorganic oxide supports and their related surface-grafted organometallic fragments. This project is developing new research capabilities for the simulation of reactivity and structure in complex heterogeneous and homogeneous environments and establishing a theoretical framework and using simulation tools to understand the microscopic principles of nucleation.

In the experimental focus of the project during FY 2014, we aimed to provide an understanding of how silica particles nucleate and grow from monomeric silane species. We used a solution-based acid catalyzed hydrolysis reaction to grow octameric polyhedral oligomeric silsequioxane (POSS) starting from a monomeric R’Si(OR)3. We monitored the reaction progress as a function of temperature and pH during the assembly process utilizing mass spectroscopy and solution phase 29Si NMR to identify intermediate oligomers that were formed during the process. Our current results show that we formed significant amounts of tetrameric species with small amounts of octameric, decameric, and dodecameric species; however, almost no dimeric species were seen during the growth process.

The theoretical effort in FY 2014 was focused on ion-pairing as the first step of nucleation and growth for calcium carbonate in the high dilution limit. We used state-of-the-art ab initio density functional theory (DFT) and classical force fields (FF) representations of interaction. Currently, FFs are the only atomistic descriptions to study nucleation of CaCO3, and have predicted a wide range of molecular mechanisms, including classical nucleation, the formation of pre-nucleation clusters, and spinodal decomposition. We computed the potentials of mean force for a single pair of CaCO3, which showed that the DFT ion pair is much less stable (by 4 kcal/mol) than the FF predicted one, and that the stability of mono versus bi-dentate coordination in the contact ion pair is reversed. There exists a barrier to pair formation in DFT that will have significant influence on the kinetics of pair formation and dissociation.

During FY 2015, we are interested in extending the POSS studies to look at microscopic tools, particularly cryo-transmission electron microscopy, to study particle growth. We will also develop a kinetic model of the growth process and study the effect of pH on growth kinetics. The CaCO3 affords a more direct connection to Classical Nucleation Theory, which has been a successful and widely used theory to predict nucleation rates. We will use the ab initio PMFs of ion-pairing to coarse-grain the ion-ion interaction in the condensed phase and study the nucleation of small clusters and their free-energetics using dynamical nucleation theory.
Generation of Versatile Chemicals from Natural Gas in a Fuel Cell

Olga A. Marina

The objective of this work was to explore new electrochemical routes to convert methane to liquid fuel and chemicals.

Currently, methane conversion to chemicals is achieved mainly through the intermediate synthesis gas production via steam reforming, partial oxidation, or autothermal oxidation, followed by the catalytic upgrading to ammonia, methanol, and synthetic hydrocarbons. Direct methane conversion into value-added products, such as methanol, formaldehyde, alkanes/alkenes (C2-C4), olefins, and aromatics is of high interest and could revolutionize the chemical value chain. In the electrochemical device, oxygen ions are supplied through the oxygen-ion conducting solid electrolyte, providing control over oxidizing conditions needed to limit deep oxidation. In contrast with heterogeneous catalysis, oxygen is co-fed with methane in to initiate oxidative coupling and is likely to lead to the CO2 formation at high reaction temperatures. Electrochemical promotion also enables reaction to proceed at temperatures much lower than in heterogeneous catalysis (i.e., with no electrical bias).

In this project, we evaluated methane conversion inside a reactor similar to a solid oxide fuel cell. Specifically, electrochemical routes of converting methane directly to light hydrocarbons were explored. Our primary focus was on the electrocatalyst development, with the goal of identifying a formulation that provided high catalytic reactivity for methane activation to C2-C3 products, long-term stability, and compatibility with the yttria-stabilized zirconia (YSZ) electrolyte.

Oxidative coupling of methane was studied using SrRNiO3-δ and BiYSmO3 electrocatalysts, chosen in consideration of literature data. Sr0.75Na0.25NiO3 and SrNi0.75Li0.25O3 powders were synthesized using glycine nitrate method with stoichiometric and non-stoichiometric glycine amounts. Phase purity was analyzed by X-ray diffraction and compounds were further enhanced by 50% excess Na or Li to aid stability during calcination. Bi1.5Y0.3Sm0.2O3 powder was synthesized by co-precipitation method. The obtained powders were used to produce electrode inks, which were deposited on the YSZ-electrolyte discs to serve as oxide-based anodes. Lanthanum strontium-doped manganite was used as cathode on the opposite side of the electrolyte disc. Current collection from both electrodes was achieved using Au paste and Au wires.

Electrochemical cells were tested in the temperature range 600–800°C using CH4/Ar, CH4/O2, or CH4/O2 as reactant gases. Electrochemical measurements were conducted using DC and AC techniques. Reaction product analysis was performed using quadrupole mass spectrometry, and post-test anode characterization was performed using scanning electron microscopy.

The feasibility of C2-C3 hydrocarbon formation at 700–800°C via electrochemical route was demonstrated using Sr0.75Na0.25NiO3 and SrNi0.75Li0.25O3-based electrodes. Under open-circuit conditions with no electrical bias, no C2-C3 hydrocarbons or oxygenated (methanol or formaldehyde) products formation were observed. When cells with Sr0.75Na0.25NiO3 and SrNi0.75Li0.25O3 electrodes were polarized, C2H6 and C3H8 formation was obtained in the electrochemical pump mode.

The conditions of C2-C3 formation were broadly mapped, with no reaction products observed in the fuel cell mode. The open circuit potential was low, and the electrode resistance remained high, indicating low to no activity toward methane activation. In electrochemical pump mode when oxygen evolution on the anode was expected, leading to likely more oxidizing conditions, C2H6 and C3H8 formation was observed. Thus, the C2-C3 hydrocarbon yield was directly related to the cell polarization: higher currents resulted in larger C2-C3 yields. In general, the electrode resistance in the pump mode was significantly lower compared with that in fuel cell mode. While C2-C3 yield remained low in the small button cell test setup on the order of few percent, the selectivity was high, as no significant CO2 formation was observed.

Transient behavior of C2-C3 product formation was observed, which is product yield decreased in time at a fixed cell potential, likely indicating on the limited oxygen capacity of the electrode. The results were reproducible. A silver addition to Sr0.75Na0.25NiO3 and SrNi0.75Li0.25O3 electrodes resulted in substantially improved electrochemical cell behavior, especially in electrochemical oxygen pumping mode. Yet silver also promoted synthesis gas formation, coinciding with accelerated methane decomposition, though observations are not consistent with coking, as no associated H2 production was found.

On the Bi1.5Y0.3Sm0.2O3 – Ag electrode at 600 and 700°C, low CH4 conversion was observed, with the main product being CO2 and only minor amounts of C2 products. The Bi1.5Y0.3Sm0.2O3 – Ag electrode appeared to possess excellent electrode properties to be used in oxygen pumps.
High Aspect Ratio Functional Composites for Thermal Optical Applications

David M. Reed

We are developing novel composite structures that will change reversibly from transparent (or any underlying color) to opaque in a targeted temperature range. Innovative design strategies are employed to fabricate inexpensive functional materials for applications in the energy management of buildings, vehicles, and consumer markets.

Composite materials have been used extensively in electronics, optics, and structural material application sectors because resident collective properties are often unique and not found in single-phase materials. The diameter, morphology, volume fraction, and connectivity of phases within the composite material can also be used to tailor the desired properties. Transparent structural composites (i.e., glass fiber-loaded polymers), however, have been limited applications because of their tendency to have a narrow temperature window in which they are transparent. With changes in temperature, these composites become opaque due to refractive index mismatch accompanied by interfacial light scattering. The refractive index variation of polymeric materials with temperature \( \frac{dn}{dT} \) is often one or two orders of magnitude higher than for inorganic glasses. This difference between the \( \frac{dn}{dT} \) of the polymeric matrix and filler phase determines the rate of change of the mismatch in refractive indices and controls the temperature dependent transmission of the composite. Over a small temperature range where the refractive indices are matched, the composite will remain transparent. Methods have been employed to achieve this effect (thermochromic pigments, electrochromics, and meta-materials), but their use is limited by their high cost.

For this project, optical grade polymers were selected based on refractive index match to standard compositions, namely E and C glasses. The refractive indices were measured on the glass fillers and polymer matrices as a function of temperature using the Becke line technique and the prism coupler method developed at PNNL. During FY 2014, we focused on thermosetting epoxy systems because of their availability and ease to fabricate into films (optical grade thermoplastic polymers will be investigated in more detail in FY 2015). The E and C glasses chosen have a wide range of morphologies and aspect ratios available (i.e., particulate, fiber, and flake). An index-matched composite with controlled microstructural features of the filler phase provides a path to realize a composite that can reversibly change from transparent to opaque with temperature. The filler aspect ratio and temperature dependence of the refractive index of the polymer are two important parameters that determine the breadth of the transparent window and the width of the temperature window in which the composite transitions from transparent to opaque, respectively. Manipulating the morphology and chemistry of the composite will allow the thermo-optical response of the composite to be tailored over a broad temperature range.

The thermosetting epoxy resin system from Dow Chemical is widely available with various catalysts and diluents that can be added to change the crosslinking density and resulting molecular structure. These additives give the ability to tailor the refractive index and therefore match the glass filler (E glass \( \sim 1.56 \), and C glass \( \sim 1.52 \)) at different temperatures. The refractive index of the epoxy resin varied from 1.59 and 1.50 between 20 and 90°C with a temperature dependency of \( -10^{-4} \). Significant progress was made on improving the refractive index characterization technique as a function of temperature and has been instrumental in providing the ability to measure a broad range of polymers in a timely manner.

Currently, composites are being fabricated with E and C glass fillers with different aspect ratios and the epoxy resin systems with different refractive indices. Composite samples are prepared via casting or extrusion with fillers oriented perpendicular to incident light. Significant progress has been made to ensure wetting of the filler by the matrix and that samples are void-free after fabrication. Initial transmission results as a function of temperature are encouraging for the high aspect ratio composites, as a broad transparent temperature range was observed as predicted.

Work in FY 2015 will focus on smaller aspect ratio fillers and percentage loadings to further refine the breadth of the transparent temperature window. Additional studies will examine polymeric system with matched refractive indices but with different temperature dependencies to tailor the reversible window for switching from transparent to opaque.
High Information Content Polymers and Their Assembly into Structural Motifs

Chun-Long Chen

We are developing high-information content polymers to understand their self-assembly into higher order structural motifs, an ability that will ultimately enable biomimetic functional materials.

High-information content polymers will mimic the ability of proteins and peptides to exhibit secondary and tertiary structure, as well as self-assemble into oligomeric complexes and extended ordered matrices. The self-assembled materials developed in this project can perform functions beyond protein- and peptide-based materials. This work will lead to an understanding of the pathways of assembly and the thermodynamic and kinetic controls on those pathways, the rates at which assembly occurs, and the degree of order in the final structures. In short, we seek to create a scalable, robust approach to synthetic high information content polymers with sophisticated functions, use powerful methods of investigating self-assembly to develop a fundamental understanding of assembly in these synthetic systems, and integrate polymer synthesis, characterization, and theoretical modeling to create a true predictive science of synthesis for high information content polymeric materials.

During FY 2014, two types of sequence-defined polymer sequences were designed and synthesized for self-assembly of highly-ordered materials, including 2D pore-forming networks whose sequences will be used as model systems to understand their assembly pathway and dynamics for future prediction. In situ atomic force microscopy (AFM) was used to characterize the dynamics of network assembly in solution to determine the pathways of assembly and the thermodynamic and kinetic parameters as a function of polymer length, sequence and chemistry. Over ten sequences were discovered and synthesized for self-assembly using AFM and transmission electron microscopy (TEM) to imagine the end products that peptoids self-assembled both in solution and on substrate surfaces. Different conditions such as varying pH were used to investigate peptoid self-assembly. Assembled materials include 2D porous networks, free-floating 2D crystalline nanosheets, 1D nanoribbons, and 0D micelles.

Similar to peptide and protein self-assembly, peptoid self-assembly is highly sequence-specific and pH sensitive. Because these polymers are sequence-specific and can be easily modified, we were able to tune their chemical characteristics, such as the patterning of monomers for self-assembly, rationally. We observed that a slight change of sequence design caused dramatic differences in polymer self-assembly. For example, we made large quantities of free-floating 2D sheets when one peptoid was changed from alternating polar and nonpolar sequence to a diblock-like patterning with polar residues at the N-terminus while all non-polar residues were located at the C-terminus. By simply conjugating one fiber-forming peptoid with 6-aminohexanoic acid, we made peptoid-based porous membranes.

The assembly pathway of peptoids has been characterized in real time using in situ AFM. For the assembly of porous networks, 3 nm-high particles were found to be basic building blocks which ultimately assembled into a 3-fold symmetric fibril network. The structure of the network in the plane parallel to the surface was determined by 5 Å-high particles that were bound to mica surface possibly mediated by calcium ions. Based on these results, we proposed a model to describe the mechanism of the self-assembly. Initially in this model, the peptoid molecules lay down on the mica surface, which gives the 5 Å-high particles. Later, the molecules “stand up” and match with another molecule, possibly from solution, to form the 3 nm-high bi-layer particles. The bilayer particles then start to grow by adding more bilayer molecules to the end (x-y directions) and on the top (z-direction). The kinetics of peptoid assembly was also investigated using in situ AFM. We found that the nucleation rate dramatically increased after about 25 min, possibly from the saturation of 5 Å-high particles on mica surface. We also found that the time period before the increase of the nucleation rate decreased when the concentration of calcium ions was increased, while the nucleation rate increased as the peptoid concentration increased. These results provide us useful information to understand kinetic controls on the assembly pathway and to extract thermodynamic parameters (e.g., interfacial energy).

In addition, we designed another class of synthetic sequence-defined polymers whose architecture does not involve peptide bonds. The chemistry behind the architecture provides facile approaches for the incorporation of side-chains as “R-groups” into the monomer structures such that diverse monomers can be produced. Different monomers can be introduced to create sequence-defined polymers. The synthesis can be performed using either protected monomers appended to a growing polymer chain and deprotecting the terminus of the chain before each monomer addition or assembled by a submonomer synthesis approach that does not require monomer protection or deprotection steps. Using these R-group substituted monomers, we performed batch synthesis of homopolymers, solution-phase synthesis by addition of one monomer at a time using deprotection steps, and a solid-phase method using a submonomer approach to create polymers by extending the chain a fraction of a monomer at time.
We have been developing a multi-scale simulation framework to facilitate experimental design and high-information content polymer system creation with the goal of forming ordered structures and pore networks. These simulations will provide insights about the key forces governing folding and assembly in such systems, which are currently poorly understood. For example, we are validating a coarse-grained model based on the MARTINI model to model peptoid self-assembly into highly ordered structures both in solution and on substrate surfaces. We used one coarse-grained particle per peptoid residue and created pseudo-bond and angle potentials for the backbone based on reference distributions of the \(N_i-N_j\) distance and \(\alpha\) angle from atomistic simulations with different backbone amide states. The residue \(i-j-k\) pseudo-angle potential was switched depending on whether the \(i-j\) amide bond is cis or trans. Potentials were constructed by Boltzmann-inverting the reference distributions and fitting the resulting energies to standard MARTINI potential forms. Residue interaction energies were calibrated to reproduce the experimental density and octanol/water transfer free energy of the model compound \(N,N\)-dimethylacetamide (DMA). We selected the MARTINI particle type, P2, with the closest octanol/water transfer free energy and modified selected interaction energies to reflect that DMA molecules cannot hydrogen-bond to each other or donate hydrogen bonds to other polar molecules like water. By comparison to an atomistic simulation of an all-trans sarcosine 12-mer, the coarse-grained simulation recovers the pseudo-bond and angle distributions.

We also modeled another class of synthetic sequence-defined polymers to inform experimental designs structurally. In this synthetic polymer system, variable-length non-amide linkers connect core elements bearing sidechains. The cores and linkers were parameterized using the generalized amber force field, and 500-ns replica-exchange MD simulations were used to explore the conformational space of short polymers. K-means clustering was used to identify favored structures. Simulations of hexamers suggested several favored motifs with different backbone/backbone hydrogen bonding and \(\pi\) stacking configurations, while 12-mers showed more globular structures. These simulations suggest that imine sidechains increase helical propensity and chiral linkers increase conformational order.

Peptoids with different side chain chemistry self-assemble into different architectures such as nanosheets, porous network, and nanofibers. The dynamics of network assembly of one peptoid (with carboxyl group and chlorobenzene) was investigated on surfaces using \textit{in situ} AFM. The pathway of assembly and the thermodynamic and kinetic parameters were determined. These results significantly contribute to our understanding of the mechanisms of assembly as well as the thermodynamic and kinetic controls on the pathways of assembly.

During FY 2015, we will investigate designs that incorporate a three-fold “hub” to drive formation of hexagonal peptoid networks and side chain functionalization to provide ion-selectivity for molecular separations. We will continue using \textit{in situ} AFM to characterize the dynamics of assembly of other peptoids with different side chains, as we anticipate that these studies will show the difference in the pathways of assembly and the thermodynamic and kinetic parameters among different peptoids. Ultimately, we will understand how polymer length, sequence, and chemistry affect the assembly pathways and the thermodynamic and kinetic parameters which therefore will enable rational design of biomimetic functional materials. For molecular simulation, we will focus on expanding the coarse-grained simulation framework to model the micron-scale self-assembly of the polymers on the mica surface, with help from atomistic simulations of key side-chain interactions.
Hybrid Electrodes for Next Generation High Energy Ultracapacitors

Satish K. Nune

We are developing solution-based strategies for carbon architecture synthesis with large surface areas and controlled pore distribution for improved mass/charge transfer properties from an enhanced electrode/electrolyte interface.

Undoped porous carbons have been commonly used as high surface area electrodes in supercapacitors because of their low cost, good processability, and high stability. However, their electrochemical performance is limited because their charge storage mechanism solely depends on the adsorption of electrolyte ions onto the electrode surface. In comparison, nitrogen-doped porous carbons have drawn attention because of their superior electrochemical properties from an additional mechanism of charge storage known as pseudo-capacitance, in which charge is stored through a rapid surface reaction. Yet nitrogen-doped carbons are generally synthesized using complex methods such as chemical vapor deposition (CVD), arc discharge, plasma treatment and thermal annealing with ammonia which often suffer from composition control.

For this project, we used the isoreticular metal-organic framework (IRMOF-3) with ligands that contain nitrogen as self-sacrificial template to produce porous nitrogen-doped carbons. MOFs serve as both the carbon and nitrogen source and act as soft templates to generate porous carbons. Therefore, nitrogen-doped porous carbon obtained through the direct carbonization of MOFs is especially promising because it offers a simple approach free of additives and extraneous steps. As IRMOF-3 has a high surface area, carbons derived from these MOFs are also expected to have high surface areas. Specifically, MOF-5, MOF containing Zn and terephthalic acid, was studied as nitrogen-free control.

Carbonization of MOFs results on carbons with varied nitrogen content and ideal graphitic content, overall influencing the electrochemical performances. To investigate carbonization temperature on nitrogen content, ideal graphitic content that influence overall electrochemical performance, we carbonized IRMOFs at 600, 700, 800, or 950°C, resulting in carbonized-IRMOF-3 or CIRMOF-3s. XPS analysis was used to quantify the nitrogen content. As the temperature increases from 600-950°C, the nitrogen content decreased from 7 to 3.3 atomic %. Raman spectroscopy was used to investigate the structural properties. Carbon derived from IRMOFs at 950 had the highest $I_d/I_g$ ratio, while CIRMOF-3-600 had the lowest $I_d/I_g$, suggesting that a higher carbonization temperature results in more ideally graphitized sp² carbons. Galvanostatic charge/discharge measurements were performed on various CIRMOFs. Nitrogen-doped porous carbons exhibited exceptionally high capacitance, specific energy density 30 Wh kg⁻¹ and with specific power of 1.01 KW kg⁻¹. This energy density is higher than that of typical untreated carbon nanotube (5–7 Wh kg⁻¹) and other hierarchical porous carbons. The energy density obtained is 7 times higher than commercial activated carbons frequently used for supercapacitors.

To increase the capacitance and energy density, we synthesized carbon composites using other pseudocapacitive materials such as polyaniline (PANI) and manganese oxide. We synthesized the supercapacitor electrode materials, which have capacitive contribution from pseudocapacitance and electric double layer capacitance (EDLC). Our initial cyclic voltammetry (CV) data of C/PANI looked promising at 550 F g⁻¹ at 10 mV s⁻¹ in 1M sulfuric acid. However, galvanostatic charge/discharge measurements showed only 214 F g⁻¹, which is similar to that of just nitrogen-doped porous carbons. Our several other attempts resulted low capacitances, probably from pore blockage of nitrogen-doped carbon by PANI.

We demonstrated for the first time a simple and efficient one-step method to obtain high surface area porous carbons from renewable low-cost lignin precursors. We also showed the synthesis of lignin-derived porous carbons through direct carbonization without addition of activation or templating agent. The molecular weight of the lignin precursor is important, as is the extent of oxygen consumption during carbonization, where lower molecular weight lignin precursors produce less defective and higher surface area porous carbons. The renewable low molecular weight Kraft lignin-derived porous carbon possessed the highest surface area. These carbonized residues exhibited relatively high electrochemical performance in terms of specific capacitance, energy density, and power with good capacity retention.
Imaging the Nucleation and Growth of Nanoparticles in Solution

Ayman M. Karim

We are developing in situ characterization tools for imaging the synthesis of nanoparticles in solution. Direct real time visualization would allow a fundamental understanding of synthesis mechanisms and accelerate synthesis development to make materials with specifically engineered nanostructures for a wide range of energy storage and conversion applications.

The synthesis of nanoparticles in solution is the most promising tunable method but is not well understood due to the difficulty of experimentally observing the nucleation and growth processes. Consequently, most synthesis efforts rely on trial and error from the lack of a fundamental understanding and paucity of in situ characterization tools. Our goal is developing new in situ tools for imaging the nucleation and growth of nanoparticles in solution by combining microfluidics, X-ray absorption spectroscopy, and atomic-resolution aberration-corrected transmission electron microscopy (TEM). The project will result in an in situ microfluidic cell and development of data collection and analysis techniques for the study of nanoparticle nucleation and growth with ms time resolution using synchrotron techniques and ex situ atomic-resolution aberration-corrected TEM.

We designed a novel microfluidic silicon/pyrex reactor for Pd nanoparticles synthesis that allows for ms time resolution during the entire synthesis duration to observe nucleation and nanoparticle growth. The reactor allowed us to study Pd nanoparticles synthesis with X-ray absorption fine structure (XAFS) and small angle X-ray scattering (SAXS) in the same reactor. Combining in situ XAFS and SAXS, we determined the synthesis mechanism, which was found to be nucleation limited: a slow, continuous process while the growth was surface catalyzed by nanoparticles. According to the literature, this type of nucleation typically leads to large nanoparticles with broad size distribution. In contrast to classic nucleation and growth theory, we discovered that particle growth was arrested at a certain size. XAFS results showed that the scenario was from increased bonding with the capping agent, causing existing particles to stop growing after a certain size. New nuclei continued to form new particles through the same mechanism (although at slower rate) until the remaining precursor in solution was depleted. Therefore, we showed that it is possible to synthesize Pd nanoparticles with narrow size distribution despite slow nucleation. This is the first report of Pd nanoparticles in 1 nm with narrow size distribution based on understanding synthesis mechanisms and not trial and error.

The reactor used for these studies was designed for Pd (K absorption edge = 24.35 keV) and other metals with similar absorption energies (> 20 keV). We showed that the reactor design can be modified easily to accommodate thinner windows for the characterization of elements with lower X-ray absorption energies (as low as 9 keV) and high quality XAFS was collected for Pt (11.56 keV) precursor solution in the modified reactor.

Our work in FY 2014 focused on the design and fabrication of a droplet flow microreactor for high temperature nanoparticles synthesis and developing data acquisition methodologies for XAFS and SAXS. The droplet flow reactor has advantages over the single phase flow reactor that we used during the first 2 years of the project. In addition, the droplets act as well stirred nano-batch reactors (on the order of nanoliter each), where the concentration gradients are minimized, leading to much narrower particle size distribution. We were able to screen compatible two-phase systems that allowed us to eliminate metal deposition on the walls and reactor fouling, a major issue for high temperature synthesis. The droplet flow microfluidic reactor and XAFS/SAXS data acquisition methodology will be developed using Pt nanoparticles synthesis; however, it can be generalized to other nanoparticles synthesis systems.
Improving Magnetoelectric Coupling in Novel Single-Phase Multiferroic Thin Films of the MTiO₃ (M = Fe, Mn, Ni, …) Family

Tamas Varga

This project is enabling the design of multiferroics via the control of chemistry and physical properties, providing key knowledge to the rational synthesis of novel materials with potential technological impacts on information storage, energy, and semiconductor industries.

Multiferroics (materials that are both ferromagnetic [FM] and ferroelectric [FE]) can be employed as new four-state memories for future data storage applications and in photovoltaic devices for energy applications. However, the coupling of FM and FE in single-phase multiferroics is inherently weak. Our objective is to understand the physical origin of the coupling of polarization and magnetization through theory and use that knowledge to design novel multiferroic materials that perform better. Building on our success in stabilizing NiTiO₃ in the theory-predicted structure in epitaxial thin film form and showing the coexistence of polarization and ferromagnetism, our hypothesis is that alloying/doping MTiO₃ will affect FM (and possibly FE) properties and, in turn, their coupling. Ultimately, we wish to demonstrate that the resulting multiferroic properties are superior to earlier results in related single-phase systems.

In the design of new multiferroic materials by predicting the specific compositions that meet our design criteria, we began by performing a series of theory calculations to study the origins of FM/FE formation and stability in the dopant metals Cr, Co, Mn, V, with an eye on making doped MTiO₃ phases such as CrₓM₁₋ₓTiO₃ next. We examined how the electronic structure of the transition metal in the magnetic site (M = Fe, Co, Mn, Ni) affects the energetics and magnetism in MTiO₃ phases. To make better multiferroic materials in the MTiO₃ family, we will need to increase the magnetic moment on the transition metal M and/or enhance ferroelectric polarization in the compound.

We first looked at the magnetism by calculating the density of states (DOS) for metallic Fe, Co, and Ni, and the magnetic moment in MTiO₃ phases for M = Fe, Co, Mn, and Ni. There appears to be a rigid shift in the calculated DOS with the number of electrons on the magnetic ion, which results in a linearly decreasing magnetic moment going from Mn to Ni. These findings suggest that the smaller atomic number metals (such as Mn and Fe) may be better candidates as the M cation in MTiO₃ multiferroic materials.

Density functional theory calculations of the ground state energies for the antiferromagnetic (AFM) and FM states of Co, Cr, Fe, Mn, Ni, and V suggest that Cr may be a good candidate to create doped MTiO₃ (M = Fe, Ni, Mn, Co) such as CrₓM₁₋ₓTiO₃ with enhanced FM moment relative to the MTiO₃ end member as the FM state of Cr has a favorably low ground state energy in the desired structure. Based on this theory work, efforts are now underway to synthesize both pure CrTiO₃ or Cr-doped NiTiO₃ phases.

On the synthesis side, building on previous results from related materials, efforts to date have focused in two directions: to stabilize new end members FeTiO₃ and MnTiO₃ with the desired structure as epitaxial thin films and to explore a new deposition and substrate options to improve film quality. For the new end members, FeTiO₃ and MnTiO₃ have been successfully synthesized in epitaxial form using pulsed laser deposition (PLD). Physical property characterization of the samples is underway, but structural results suggest that epitaxial films with the desired multiferroic structure were...
made. Molecular beam epitaxy was attempted to prepare FeTiO₃ and NiTiO₃ thin films on Al₂O₃ substrates following the successful PLD growth of these samples.

Preliminary results indicate that under the first synthesis conditions, samples contained a mixture of binary oxides Fe₂O₃ and Fe₂O₃ and metallic Ni and TiO₂ instead of FeTiO₃ and NiTiO₃, respectively. Previous results from earlier work on NiTiO₃ indicated that employing Fe₂O₃ instead of Al₂O₃ as substrate may result in smoother film growth, better crystalline quality, and perhaps improved physical properties (the lattice mismatch between NiTiO₃ and Fe₂O₃ is small, thus strain is reduced). To explore this graded approach to introducing lattice strain, films on both single crystalline Fe₂O₃ substrates, and on thin Fe₂O₃ films deposited on Al₂O₃ substrates were grown by PLD. Our structural characterization results suggest that the latter, MTiO₃/Fe₂O₃/Al₂O₃, films show promise, while the Fe₂O₃ substrate itself promotes the formation of the corresponding binary oxides (Fe₂O₃ + TiO₂ or NiO + TiO₂) rather than the desired titanates.

Next, we explored the effect of substrate-exerted strain on the films grown by pulsed laser deposition (PLD). Strain was employed to control materials’ properties. We saw a dependence on the induced FM on the substrate-exerted strain as we grew films on sapphire Al₂O₃ (large compressive strain), hematite Fe₂O₃ (close match, no strain), and LiNbO₃ (tensile strain) substrates. As strain increases, the residual magnetization (FM) in the films increases. We think that this approach is consistent with the theory that it is the FE polarization that induces the FM. Strain calculations from first principles were also performed for NiTiO₃ on the sapphire Al₂O₃ substrate.

Temperature-dependent magnetization measurements carried out on different NiTiO₃ films grown on sapphire-Al₂O₃ substrates with varying Ni:Ti ratio revealed that the antiferromagnetic (AFM) transition temperature (Néel temperature; T_N) increases with an increasing amount of Ni in the structure. We argue that more Ni is in the structure, the stronger the AFM ordering becomes. Therefore, the AFM ordering temperature becomes higher as the thermal energy needed to destroy the ordering becomes larger. There appears to be a hysteretic behavior in this sample that provides insight into the domain behavior; by field cooling, we may have locked in some of the ferromagnetic and antiferromagnetic domains. This process may result in a different energy barrier to overcome in the zero-field cooled experiment than in the field-cooled one. These results suggest that we can control the ferroic properties by strain engineering and possibly push the T_N closer to room temperature.

We studied the effect of film thickness (and therefore strain) on the polarization in the NiTiO₃ films by optical SHG. We found that as film thickness increased from 10 to 100 nm, the optical SHG signal became weaker, indicating that the films were less strained and became bulk ilmenite-like at greater (~100 nm) thicknesses. Overall, our results suggest that from the systems tested, an ~30-nm thick film with slight Ni excess, deposited on LiNbO₃ would be the best multiferroic.

For FY 2015, we will continue theory calculations to determine alloying scenarios that will enhance the magnetic moment and/or the ferroelectric polarization (and thus their coupling). Certain alloys naturally create displacement effects, which may enhance the FE polarization. We will use the Berry Phase Approach to study this effect and look at the resulting effect on the FM properties. In addition, we will perform experimental characterization of the physical properties of the end members to match theoretical values and establish a relative scale for judging property enhancement upon doping. The synthesis of the phases predicted by theory calculations will be determined and will iterate between experiment and theory as experimental results become available. We are also considering mesoscale-based phase field modeling to learn about how nanoscale effects change properties of the polar and magnetic domains (mesoscale features). Finally, we will perform synchrotron beamline experiments to probe magnetoelectric coupling at the Advanced Photon Source at Argonne National Laboratory.
Improving the Performance of Li-Air and Li-S Batteries Using Polymeric and Metallic Nanomaterials

Priyanka Bhattacharya

This project is developing novel nanomaterials to enhance the performance of lithium (Li) batteries and understand their fading mechanisms.

An increased demand for high energy density batteries based on environmentally friendly materials has led to the research and development of rechargeable Li batteries, which include Li-air (Li-O₂) and Li-sulfur (Li-S). A challenge with the Li-O₂ battery is recharging the insoluble, poorly conducting Li₂O₂ discharge products to Li⁺ and O₂ during charging. Hence, Li-O₂ batteries require electrocatalysts for reducing the over-potentials of both reactions. For Li-S batteries, charge/discharge involves the creation of highly soluble polysulfide intermediates in electrolytes, causing an irreversible loss of active sulfur. Our efforts are directed toward polymers and nanostructures to trap polysulfides, thus improving the electrochemical cell cycling. The remarkable physico-chemical properties of dendrimers motivated research into the application of dendrimer-encapsulated Ru electrocatalysts in Li-O₂ batteries and their application in trapping polysulfides in Li-S batteries. Thus, our objective is to identify novel, efficient materials for high energy density applications and place PNNL at the frontier of dendrimer research in energy storage.

Dendrimer-encapsulated ruthenium nanoparticles (DENs) as catalysts in Li-O₂ batteries. In FY 2013, we synthesized monodispersed and stable DEN of average size (~2 nm). Once complexation between the dendrimers and Ru³⁺ was complete, the Ru³⁺ were chemically reduced in situ to Ru metal using 10 molar excess of NaBH₄. Complexation and reduction were monitored using UV-vis absorption spectroscopy. After reduction, the DEN solutions were dialyzed using 10,000 MWCO dialysis membranes to remove impurities. The average size of the DENs with both the hydroxyl and amine terminated dendrimers was ~2 nm. However, while the hydroxyl-terminated DEN solutions remained stable for over 2 months, amine-terminated DENs aggregated within a few days. This is because some of the Ru³⁺ complexed with the primary amines of the dendrimers that when reduced remained at the periphery of the dendrimers and unprotected, leading to aggregation over time. Subsequently, all experiments were conducted using hydroxyl-terminated DENs (G4-OH).

PAMAM dendrimers encapsulating nanoparticles demonstrated the potential for being catalysts in Li-O₂ cells. The DENs were stable for months and electrochemically stable toward Li metal and electrolyte solvents. The materials improved the cycling efficiency of KB carbon by nearly 3.3 times and lowered the charging overpotential by almost 0.4 V, creating a new state-of-the-art catalyst for Li-O₂ batteries. Most importantly, the amount of Ru used as a catalyst is 10 times less than that in the state-of-the-art work published to date. Thus, dendrimer-stabilized Ru nanoparticles enable the use of a much lower amount of the noble metal catalyst.

To analyze the nature of the discharge products, scanning electron microscopy (SEM) and X-ray diffraction (XRD) spectroscopy were conducted on discharged cathodes that were washed in dimethoxyethane (DME) for 3 days to remove electrolyte salts. Both SEM and XRD showed the presence of Li₂O₂ as the major discharge product, with some electrolyte decomposition products also observed. Charged cells showed little or no Li₂O₂, suggesting good rechargeability. XRD results showed the presence of ruthenium oxide (RuO₂) rather than Ru metal, which suggests oxygen adsorption on Ru metal surface in ambient conditions. This scenario indicates that O₂ diffuses into the dendrimer periphery and enables the use of RuO₂, as catalysts, which have been recently shown to be better OER catalysts than Ru metal. Results from this work were presented at three international conferences, and a paper was published in Advanced Functional Materials.

Dendrimers for capturing polysulfides in Li-S cells. G4-OH and G4-NH₂ dendrimers were mixed with KB-S composites in aqueous solutions for 1 day. The dendrimer wt% was 10 wt%
and S was 80 wt% in the composite. Water was dried under low vacuum at 40°C overnight, and the dendrimer-KB-S composites were cast into a slurry using a 20 wt% poly(vinylidene) fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) solvent. Cathodes were prepared by coating aluminum foils as current collectors with the slurry. The film thickness was ~150 µm. 1.4 cm diameter cathodes were punched out and dried in low vacuum at 40°C overnight. A total of 2032 coin-cells were assembled in an argon-filled glove box with O₂ and H₂O content < 0.1 ppm. The cells were rested for maximum 6 h to prevent their self-discharge and tested. Initial results showed a poorer performance of these composite electrodes. Thus, PAMAM dendrimers did not improve the performance of Li-S batteries, which could be from the insulating nature of PAMAM dendrimers. Further testing using DENs of different generations will enable us to evaluate the performance of dendrimers in Li-S batteries.

During FY 2014, we developed novel electronically conducting dendrimers based on our learning in FY 2013. PAMAM dendrimers are inherently non-conducting. To employ them as cathode materials in Li-S batteries, we synthesized electronically conducting PAMAM dendrimers by modifying their surface groups with poly(3,4-ethylenedioxythiophene; PEDOT). Hyperbranched polymers were also modified for a commercially viable approach. Dendrimer-based PEDOTs were more conducting than hyperbranched based systems. We were able to improve the conductivities using lower generation dendrimers and achieved conductivities as high as 1 S/cm. These modified dendritic polymers were used to make sulfur composite cathodes and their performance tested in Li-S cells. Initial results indicated good cycling stability and electrochemical stability of these modified polymers in the Li-S cells. Preliminary results were presented at three international conferences, and as the end of FY 2014, a manuscript is in preparation in collaboration with our industrial partners Dendritech, Inc. and Nanosynthons, LLC.

Toward the end of FY 2014, we started investigating the applications of dendrimers as functional binders for high loading S cathodes. This project has shown promising initial results in its first months. Preliminary research focused on hydroxyl and pyrrolidinone terminated PAMAM dendrimers. The electrode materials slurry was prepared by rigorously mixing 10wt% dendrimers with 80wt% Super-P-S composite and 10wt% Super-P conductive carbon additive in aqueous solutions. Cathodes were prepared by coating carbon-coated aluminum foils as current collectors with the slurry. The water was dried out at 60°C under vacuum overnight and electrodes were punched out. Li-S coin cell testing was done at 0.1C and 0.5C rates. We have successfully fabricated pinhole and crack free high loading S electrode coatings with Super-P conducting carbon matrix. This approach opens possibilities for future research into commercial S cathodes.

In FY 2015, we will investigate the electrochemical performance of high S loading Li-S cells with functional dendrimer binders. The hypothesis is that the amine groups of the dendrimers would trap Li polysulfides through Lewis acid-base interactions, preventing the loss of active S. We will also improve the conductivities and surface area/porosity of dendritic PEDOTs in order to enhance their performance as cathode materials in Li-S cells. Further, we will investigate novel applications of dendrimers as membranes to prevent the crossover of essential ions in vanadium redox flow batteries, and design dendrimer-based superatoms as efficient electrocatalysts in Li-O₂ battery systems.

Capacity-voltage profile and XRD data of Li-O₂ cells with KB carbon and DEN catalysts. A 0.4 V reduction in charging voltage is obtained with DEN as catalysts.
Internal Temperature Measurement Tool to Maximize Li-ion Battery Safety, Reliability and Life

Vilayanur V. Viswanathan

This project identifies a way to determine the internal temperature of a Li-ion cell, which will greatly simplify battery management, improve safety, and facilitate deployment for transportation and stationary use.

Battery temperature estimation by infrared or using thermocouples measures external temperature. The internal temperature can differ from the measured external temperature by as much as 10°C during dynamic operation. The determination of battery cell internal temperature is crucial to the development of optimized operational parameters for Li-ion battery systems. At present, Li-ion battery chargers rely on battery external temperature to guide the charge protocol. Specifically, Li-ion batteries can undergo catastrophic failure due to lithium plating at the anode when charged at > C/5 rate when the internal temperature is < 4°C. Charging at < 0°C leads to lithium plating even at low rates. Hence, the development of a tool to measure battery internal temperature reliably is crucial to safe battery charging, which would enable fast charge without compromising battery safety.

The objective of this research is to develop a reliable method to measure the internal cell temperature. Our work involves using a unique technique that provides a signal in response to internal cell temperature. The signal is also sensitive to the battery state of charge. The technical outcome would be a reliable way to estimate the internal cell temperature when the battery state of charge is known, resulting in reduced fossil fuel use, grid stability and reliability, greater penetration of renewables, and deferral of transmission and distribution expenses. The determination of battery internal temperature will be a significant leap forward in terms of battery management, enabling battery deployment for both stationary and transportation applications in a safe, reliable manner. In addition, by understanding the impact of high power charge and discharge on the internal cell temperature, extreme temperature excursions can be avoided.

In large part from this project, a reliable way to determine the Li-ion cell internal temperature has been developed. The steps of the process involved were determining response for the electrolyte stabilized at various temperatures, subjecting the cells at various ambient temperatures, and repeating the measurements at different states of charge and states of health. The most important findings were that the response signal magnitude to temperature is linear. It also has an ideal trend at a fixed temperature with the cell state of charge (SOC). Hence, this situation would allow estimation of cell internal temperature at any SOC based on signal magnitude. These findings validate our hypothesis that this technique can be used to estimate cell internal temperature. We also identified a trend for the response signal with the state of health (SOH). Independent from this project, we plan to conclude the SOH portion of our work because the work is time intensive, as cell degradation occurs over multi-month time frame.

Overall, the outcome of this effort is the ability of the battery management system to estimate internal cell temperature as a function of both cell SOC and SOH. In short, this work has major implications in safety, reliability, and long life of the Li-ion cells/batteries.
Ionic Liquid-Based Electrolytes for the Dissolution of Polycyclic Aromatics for Redox Flow Batteries

Wesley A. Henderson

We are developing ionic liquid (IL)-based electrolytes capable of dissolving high concentrations of organic compounds applicable as active materials for redox flow batteries (RFBs).

To facilitate the Smart Grid and integration of significant renewable (intermittent) energy sources (i.e., wind and solar energy), large-scale electrical energy storage is necessary. RFBs are one of the promising grid storage technologies, and nonaqueous RFBs, with electrolytes (catholyte and anolyte) composed of nonaqueous (aprotic) solvents, salts, and organic molecular active materials—have been proposed with their potential to have higher energy densities than for aqueous RFBs. However, the limited solubility of the active materials (electrolyte concentration) remains a critical hurdle to overcome.

Many organic compounds have a low solubility in aprotic solvents that precludes their practical utilization in RFBs for grid-based energy storage. One or more salts are a necessary component of the electrolytes to enable the battery reaction by facilitating (serving as counter ions for) the radical ion formation from the active materials. Low melting salts with organic cations, ILs may improve both the organic active material solubility and stability of the radical ions relative to aprotic solvents and inorganic salts alone. The objective of this project is therefore to develop IL-based electrolytes capable of dissolving high concentrations of organic (cyclic and polycyclic aromatic) compounds applicable as active materials for RFBs. Little is currently known about the solubility of the active materials in aprotic solvents, even less for solvent-salt (whether inorganic salts or ILs) mixtures. A greater understanding of how varying factors (solvent, ions, concentration) govern the solute solubility will delineate the potential limitations for nonaqueous RFBs and provide direct guidance for electrolyte formations and future research vectors.

The solubility of a range of active materials has been determined with an emphasis on materials that are the current focus of RFB work at PNNL (i.e., 2,5-di-tert-butyl-1,4-bis(2-methoxyethoxy)benzene [DBBB], 2,3,6-trimethylquinoxaline [TMQ], N-methylphthalimide [MPH], and 9-fluorenone [FLO]). The "solvents" for these solutes consisted of pure solvents currently utilized for nonaqueous RFB research (i.e., propylene carbonate [PC], acetonitrile [AN], and 1,2-dimethoxyethane [DME]) as well as solvent-lithium salt (i.e., lithium bis(trifluoromethanesulfonyl)imide; LiTFSI) mixtures, solvent-IL mixtures, pure ILs, and IL-LiTFSI mixtures.

In general, many of the organic active materials (DBBB, TMQ, MPH) do not have a high solubility in the ILs tested, although exceptions such as FLO were identified. Increasing the alkyl chain length on the IL cation did improve the solubility, but not to an appreciable extent. Most of the solubility testing focused on a single IL (i.e., PI15TFSI with the N-methyl-N-pentylpiperidinium cation) as this tetraalkylammonium cation is expected to have improved stability with the generated radical species relative to the more commonly used imidazolium-based IL cations.

For the organic solvents tested, the active material solubility increased in the following order:

\[
\text{PC} < \text{AN} \leq \text{DME}
\]

Solubility of active material solutes in ionic liquid-solvent (DME) mixtures.
Addition of a lithium salt (LiTFSI) to the solvents, however, increased solution viscosity, sometimes greatly, which is a key challenge because RFBs rely on pumping of electrolytes and, in some cases, reduced the solubility of the active materials.

Solvent addition to the IL did improve the solute solubility, but the solubility generally remained relatively low. In contrast to the addition of LiTFSI to the solvent, the same addition to the IL in some cases improved the active material solubility but also greatly increased the viscosity. The varying, seemingly incongruous solubility trends noted are attributed to differences in how the active materials interact with the organic and inorganic (i.e., Li⁺) cations because the active materials can serve as solvating species or complexing ligands, depending on their functionality and structure.

It is important to note that the coordination and interactions of active materials with the cations also influences the stability of radical anions formed during battery reaction (although how is not yet well understood—and the same is true for differing anions interacting with the radical cations). In addition, once the charged radical active material species are formed, the electrolyte interactions will change, which may also influence the solubility characteristics of the electrolytes. The project’s results point to key challenges related to increasing the active material content within the catholyte and anolyte while maintaining the necessary amount of supporting salt to enable the battery reactions. Such factors should be considered when formulations for RFB electrolytes, identifying future research directions and determining the feasibility of nonaqueous RFBs for grid-level energy storage applications.
We are developing membrane reactor concepts as one scalable, new material processing technology for the synthesis of transition metal nano-particles (Fe, Ni, Co) at low cost.

The nano-sized transition metals have the potential for widespread uses as specialty bulk materials, functional materials such as soft magnets, and advanced catalysis. Compared to a great number of publications on nano-particles of noble or precious metals (Pt, Pd, Au, Ag), studies about the transitional metal particle are limited. One hindrance is lack of low-cost, scalable manufacturing methods to produce sufficient quantities of nano-transition metals for new product and/or process prototype development. For our project, a membrane reactor process is proposed as the first-of-its kind synthesis of nano-transitional metal particles through liquid-phase reactions. The membrane reactor comprises two sets of micro-channels separated by a porous membrane for the feed and sweep flow. The feed fluid, containing metal precursors such as a metal chloride solution, is injected into the sweep fluid that contains a reducing agent as nano-droplets via the membrane pore. The metal ion in the droplet is reduced into nano-metallic particles inside the membrane channel.

The membrane reactor is a scalable, efficient way to divide a bulk fluid into uniform nano-sized droplets. Each membrane pore functions as a nano “inkjet” nozzle, with the droplet size controlled by the pore opening. For a membrane sheet comprising 50 nm pores at 10% surface porosity, it is equivalent to ~ 5 billion nano-ink jets per 1 cm². The membrane reactor also has a nearly linear scale-up rule. After the fundamental concepts are demonstrated and material properties understood, production can be enlarged by increasing the membrane area. Dispersion and reaction in the membrane reactor is a continuous process, with mixing and reaction intensified in the micro-flow channels. Thus, high productivity of the membrane reactor will lower the manufacturing cost.

In FY 2014, we first screened reaction chemistry of different metal chloride solutions with NaBH₄ and hydrazine as a reducing agent in a small reactor vial. NaBH₄ was identified as an effective reducing agent to reduce Fe, Ni, and Co ions in the solution into metallic particles. A membrane test cell consisting of a 2 cm × 10 cm active area was designed and built. An ad hoc testing system was assembled by using existing parts and equipment in the laboratory. Several membranes of different pore sizes and surface hydrophobicity were tested for their effectiveness. The major learning and results are summarized as follows:

- The reaction of metal ions with the reducing agent was rapid enough to occur at room temperature in very short residence times relative to batch reactors.
- The membrane had dramatic impact on the resulting particle size, morphology, and operation conditions.
- A promising membrane was identified to form nanoparticles for all the transitional metal salt solutions and their mixtures. Application of sonication to the metal solution feed further facilitates formation of uniform nano-particles.
- The continuously producing membrane reactor yields a steady stream of the nano-particle solution, fairly uniform like black liquor. The coalesce and agglomeration occurred during storage of the produced solution.

The feasibility of producing nano-metal particles on a continuous flow membrane reactor is shown for the first time, which opens a new material processing research field. As such, our FY 2015 research plans will include characterizing the produced nano-particles under a protective environment (as nano-metallic particles can be readily oxidized from exposure to ambient air) and working toward the systematic optimization of membranes to understand the correlation between particle size and productivity with membrane properties. In addition, we will perform a systematic investigation into the impacts of reaction and operation conditions on the resulting particle properties. Finally, we will develop online particle/liquid separation to produce concentrated solid suspension.

Left: The membrane test cell built and used for proof-of-concept tests; top right: the nano-metallic (Fe, Ni, or Co) particle solution produced from the reactor; bottom right: the uniform, discrete Co particle of ~10nm.
Meso-Scale Science and Technology: Manufacturing of Nanostructured Soft Magnetic Materials

Jun Cui

We are developing novel consolidation methods to enable robust, economical manufacturing of nano-structured bulk soft magnetic materials to benefit the United States in both energy security and technology leadership.

Soft magnetic materials are critical components of motor and power electronics that process over 80% of the world’s electricity. Although the most dominant soft magnetic materials are FeSi and ferrites, advanced soft magnetic materials (ASMMs) offer a better combination of magnetization, coercivity, permeability, and electric resistivity and may lead to higher efficiency, smaller size, and lower cost for power conversion devices. From limited manufacturing methods, however, ASMMs are available only in thin ribbon form (~20 μm) and cannot be used widely for motor and power electronics devices that require soft magnetic materials in bulk form. Such restriction is set by fundamental thermodynamic and kinetic requirements for forming nano-crystalline grains (~10 nm), an enabling feature of all ASMMs.

The objective of this project is to understand the thermodynamic and kinetic laws governing the formation of nanostructures in bulk materials, pushing their boundaries both theoretically and experimentally with the ultimate goal of developing a method to produce nanostructured bulk materials cost effectively. With friction consolidation, cold spray, and shock compaction as non-equilibrium processing systems that can exploit a unique combination of thermodynamic and kinetic parameters, they are also identified as the promising methods to attain nanostructured bulk materials. We will focus on developing a friction consolidation method and collaborate with external partners on cold spray and shock compaction.

During FY 2013, the friction consolidation method was used to consolidate FeNiMo flakes (~1 × 50 × 50 μm³, ball milled melt-spun ribbons). The results were mixed: while a fully dense puck (3 mm thick, 25 mm diameter) with sub-micron microstructure (~500 nm) was achieved, the consolidated FeNiMo showed signs of decomposition. FeNi₂ precipitates were observed in the grain, indicating the processing temperature exceeded the maximum allowable temperature.

In FY 2014, a series of friction consolidation runs were performed to process NiFeMo powders. Parameters such as load, rotation speed, and holding time along with the effect of external cooling fixture were investigated. About 30 g of NiFeMo powder was successfully consolidated to a 3 mm thick, 25 mm diameter puck annealed at 450°C × 2 hr and slowly cooled to remove residual stress. The electric resistivity and magnetic properties of the processed sample appears in the table.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Ms (emu/g)</th>
<th>Hci (Oe)</th>
<th>Resistivity (10⁻⁷ Ω-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock isotropic</td>
<td>79</td>
<td>0.1</td>
<td>5.9</td>
</tr>
<tr>
<td>Consolidated tangential (x)</td>
<td>76</td>
<td>0.43</td>
<td>4.89</td>
</tr>
<tr>
<td>Consolidated normal (y)</td>
<td>77</td>
<td>0.18</td>
<td>9.11</td>
</tr>
<tr>
<td>Consolidated radial (R)</td>
<td>77</td>
<td>1.20</td>
<td>5.75</td>
</tr>
</tbody>
</table>

Electrical resistance was improved by ~50% while magnetic properties were left unchanged. A TEM analysis of the sample before and after the process showed that the improvement in resistivity was attributed to the formation of 200 nm grain sizes refined from 5 μm grains of the feedstock. The ability to refine micron to nano grain size is an achievement for solid-state processing technologies; its impact to the engineering society is immediate and profound.

A meso-scale phase field model was developed to investigate the mechanisms of nanocrystalline structure formation and evolution of FeNiMo (Fe₇₃.₅Si₃₅.₅Nb₃B₆Cu₁) during thermal annealing process. The model assumed that from initial amorphous under thermal annealing, nanocrystallization was a process of diffusion controlled nucleation, growth, and coalescence. Simulations showed that the final structure depended strongly on the initial nucleus distribution of Cu-rich particles and the FeSi crystal phase. The pinning of Cu particles on FeSi crystal growth was observed; however, the number of particles was insufficient to identify the growth of FeSi grains based on the comparison of NiFeMo powder before and after the optimized friction consolidation process.
Cu concentration and particle sizes observed. This finding challenges an established understanding of the role of Cu on grain boundary pinning and highly recommends that homogeneous nucleation with a high density of nuclei should be the main factor to control grain size.

In FY 2015, we will continue NiFeMo modeling and consolidation works. For modeling, we will extend the current phase field to dynamic processing to include shear stress effect; for consolidation, we will push electric resistance to an order of magnitude higher by adding oxides/glass to the NiFeMo powder. We will also collaborate with the United Technologies Research Center to investigate the cold spray method.
To enable intermittent solar power technologies, we are developing a low-cost, highly efficient thermal energy storage for large-scale utilities to use heat when the sun is not shining or when excess energy is needed for peak times.

With a future of renewable energies for a sustainable environmental future, a key enabling technology is creating a form of heat storage to generate electricity. In this project, we are developing a thermal energy storage (TES) based on dual metal hydride (MH) beds for solar applications that have 8 times higher energy density than the molten salts, the current state-of-the-art. The metal hydride materials must be selected and developed carefully in order to meet efficient storage requirements. This TES technology stores high-temperature heat (solar energy or waste heat) that envisions a concentrating solar power (CSP) and other applications. The concept is based on a reversible thermal cycle driven by gas-solid thermochemical reactions.

Specifically, we are using a high temperature (HT) metal hydride that can generate heat at 700°C when a chemical bond is formed between a specific metal and hydrogen. When the sun is heating the HT-bed, the hydrogen is released from the metal near atmosphere pressure and moves into a low temperature (LT) hydride bed where the hydrogen is stored. When heat is needed, the hydrogen moves back to the HT-bed, and heat is generated to produce power. Our goal is to identify a low-cost alloy composition for the LT-bed that absorbs/desorbs hydrogen reversibly near room temperature at atmosphere pressure to match with the HT-bed’s hydrogen diffusion rate.

The beds are based on metals reversibly absorbing hydrogen to form metal hydrides. The compositions of the metal hydrides are crucial to obtain desired performance, and a materials development program is therefore necessary. We previously identified the HT-hydride, but we also need to identify the composition of the LT-hydride to complete the dual bed TES system. Therefore, we embarked on synthesizing several new alloy compositions during FY 2013 to identify a material that can operate near room temperature, as noted above. To keep cost low, we investigated materials based on the metals Ti, Fe, Ni, and Mn.

To identify a LT-hydride that can store hydrogen near room temperature and at atmosphere pressures, we prepared a dozen metal alloys of various compositions. Alloys that absorb hydrogen are typically prepared by arc-melting followed by heat treatment and rapid quenching. The synthesis route was optimized to lower cost of materials production. Phase composition was determined by X-ray diffraction analysis. To select LT-hydride candidates that potentially matches with the HT-hydride, we performed a literature study. Fine tuning of the composition of the LT-hydride involves synthesizing alloys to find the optimal relation between Ti, Fe, Ni, and Mn to match the performance with the HT-hydride. The most important characteristic is that the kinetics of hydrogen absorption and desorption must match up between the two beds to guarantee adequate hydrogen diffusion between beds.

A low-cost metal hydride of interest is TiFe; however, performance issues were reported with this compound. Recently, groups have found that nanosized TiFe or TiFe alloyed with a third metal performs favorably. Although more expensive, an interesting option is quasicrystals in the Ti-Zr-Ni system. We chose to focus on three materials systems with ternary compositions of Ti-Fe-Mn, Ti-Ni-Fe, and Ti-Zr-Ni. For our applications, three compositions in particular appear to be promising: TiFe_{0.8}Mn_{0.2}, Ti_{2}Ni_{0.9}Fe_{0.1}, and Ti_{0.8}Zr_{0.2}Ni_{0.1}. These materials are known to operate at atmosphere pressures as well as at near room temperature with rapid hydrogen diffusion.

Our goal in FY 2014 was to down-select the best performing LT-hydride materials for future testing with the HT-hydride in order to investigate if they matched up with respect to kinetics and hydrogen capacity to enable rapid hydrogen diffusion between the two beds for heat generation upon demand. We finalized the characterization using a quantitative volumetric technique to learn the performance of the material with respect to operation pressure, temperature, reaction kinetics, and hydrogen storage capacity. Knowing kinetics and hydrogen capacity allowed us to select the most promising candidates. We down-selected the most promising LT-hydride candidates in the Ti-Fe-Ni and Ti-Mn-Ni systems. These materials will be tested in the future with the HT-hydride. The discovery of a suitable LT-metal hydride composition enables a path forward to realize the metal hydride high-temperature thermal energy storage for solar applications.
Nanocomposite Particle Synthesis Using Switchable Ionic Liquids

David J. Heldebrant

We are developing a new methodology and process for the synthesis of magnetic FeCo nanocomposites using switchable ionic liquids. The benefits of the proposed strategy include controlled morphology and reduced waste, rate of synthesis time, and scalability.

This project will provide a new understanding about the fundamental processes underpinning controlled homogeneous nucleation and the growth of nanocomposite materials in supersaturated solutions. It will strive to identify key scientific principles to enable the predictable, scalable synthesis of nanomaterials in kg quantities by studying the nucleation of FeCo nanocomposite nanoparticles in switchable ionic liquids (SWILs). The polar ions of the SWIL can be used to solvate individual metal atoms at high concentrations, creating a “soft template” sphere of ions in heterogeneous liquid solution. These features may offer unprecedented finite control of solvation, leading to controlled nucleation and the separation of mono-disperse particles. If successful, the results will provide the scientific principles critical for understanding controlled nucleation without growth, putting PNNL at the forefront of the scalable solution synthesis of nanocomposite particles with precise control over particle size, shape, and morphology.

Four hypotheses were tested during FY 2014, as described in detail below.

Establishing super-saturation of metal precursors. Molar scale concentrations of metal precursors (Fe(OAc)₂, FeCl₃, and Co(OAc)₂) have been demonstrated. The saturation between different metal salts with numbers can be compared. With the initially studied DBU-hexanol SWIL system using CO₂, counter-ion separation has not been achieved. Future work with different SWIL systems and trigger gases may allow for the facile separation of the spectator anions from the solutions.

Characterizing solvation sphere with ToF-SIMS, NMR, and IR. Offline NMR and IR characterization of the primary solvation sphere was inconclusive due to the paramagnetism of the iron precursors and strong carbonate absorption bands respectively. Using novel liquid ToF-SIMS measurements, clear spatial chemical inhomogeneity of 100% and 50% ionic plus 100% non-ionic forms of SWILs were observed for the first time, confirming our hypothesis that SWILs contain localized clusters of ions in solution. M/z spectra from the positive and negative modes also show distinct ionic composition. It is anticipated that characterization of the ions as a function of distance from the particle surface may be feasible, as such these experiments will be proceeding in FY 2015.

Promotion of nanoparticle formation. Controlling the solvation sphere around Fe²⁺ (from Fe(OAc)₂ precursor) in DBU-hexanol SWIL systems appear to promote the formation of green rusts as an intermediate, typically described as Fe²⁺-Fe³⁺ hydroxy compounds. We previously hypothesized that the nucleation of nanocrystals could be controlled by removal of solvation spheres via slow removal of CO₂ from the SWIL solvent. Gratifyingly, we observed the formation of green rust nanoparticles only when fully or partially degassed solutions were diluted with methanol. Fully ionic SWIL solutions with Fe²⁺ do not afford nanoparticles upon addition of methanol, clearly illustrating the SWIL effect on nanoparticle formation.

Additionally, SEM imaging of green rust particles suggests the slow removal of CO₂ from SWIL solutions promotes a higher concentration of iron oxide rods than fast removal of CO₂. Studies to compare the effects of ionic solvent concentration and particle morphology are underway. Further, full characterization of the green rust is currently underway. Mossbauer and XAFS/XANES spectroscopies are currently being employed to identify the different forms of green rust that have been synthesized. Mechanism of the formation of the green rust will soon be studied using isotopically labeled CO₂.

The reduction of Fe²⁺ was not observed; however, Co(OAc)₂ was shown to form nanoplatelets of Co⁰ in DBU-hexanol SWIL solutions at elevated temperatures in the presence of a reducing agent. Full characterization of these nanoplatelets using XAFS and ToF-SIMS is pending.

Capping of particles with SWILs. Fe(OAc)₂ reduced with ethylene glycol produced 2–5 nm diameter magnetic particles made of Fe₃O₄. Particles were coated with an organic component either by diketone byproduct from glycol or SWIL surface coating, which is believed to have prevented aggregation. FeCl₃ reduced with ethylene glycol produced highly magnetic ~100–200 nm diameter rods and bundles (microns in length) that were comprised of smaller Fe₂O₃ nanoparticles in 50–100 nm domains of close-packed particles.

Nanoparticles formed from Fe(OAc)₂ and nanorod formed from FeCl₃ using SWILs.
We are developing a robust CO$_2$-selective double salt/molten phase composite membrane for CO$_2$ separation from warm syngas and incorporating the membrane with water gas shift (WGS) reaction to enhance CO conversion and H$_2$ recovery.

Carbon capture is critical in many fossil energy conversion processes. Current existing technologies for carbon capture from warm syngas are mostly based on solvent or adsorption-based processes that are energy intensive and require inefficient heating and cooling of the syngas stream. The membrane separation process holds promise due to its lower cost, easier scale-up, and smaller energy footprint. However, there has been no membrane developed for practical CO$_2$ separation from warm syngas due to the limitation of existing materials.

The aim of this project is two-fold. First, we are developing a robust CO$_2$-selective composite membrane that can continuously separate CO$_2$ from warm syngas at the temperature range of 300–400°C. In addition, we are integrating the membrane with WGS to achieve enhanced CO conversion and H$_2$ recovery. This is the first known attempt to develop a CO$_2$-selective double salt/molten phase composite membrane for CO$_2$ removal from warm syngas. Success of this work will provide the first step in PNNL advancing the state-of-the-art in composite membrane technology for pre-combustion fuel decarbonization.

High performance membrane material development.

The molten phase properties were found to play a critical role affecting the membrane performance. The molten phase present in a membrane matrix helps not only to increase the CO$_2$ adsorption/desorption kinetics and CO$_2$ sorption capacity of double salts, but also to facilitate the CO$_2$ transport through the membrane. During FY 2013, NaNO$_3$ was used as a molten phase; however, it had limitations such as strong corrosiveness, poor wetting ability on double salts, easy degradation, and poor conductivity of carbonate ions, among other issues.

Beginning with FY 2014, we focused on identifying a new molten phase that can promote CO$_2$ absorption/desorption kinetics and the transport of carbonate ions. We identified a new composition of molten phase that demonstrated significantly enhanced performance in promoting CO$_2$ sorption capacity of double salt and multi-cycle sorption/desorption stability. Compared to molten NaNO$_3$, the new phase is expected to show less oxidativeness and better conductivity of carbonate ions and holds promise as an important part of membrane material.

Scalable membrane fabrication process development and membrane characterization.

Using the new molten phase, we proved the concept of membrane separation by conducting permeation studies of membrane discs prepared using a dry pressing method, but we had difficulty improving membrane separation performance to meet project targets. Also, the membrane structure and thickness were difficult to manage in the old method. To solve the issues, we tried several new methods such as tape casting, dip, spin and wheel coating to make continuous, uniform, and thin flat membranes. However, there has been no successful thin membrane prepared thus far, mainly from the difficulty in membrane defect control. New ideas are needed to identify a facile and scalable membrane fabrication process for making robust and thin membranes with improved separation performance.

All the findings achieved so far are important to our project missions and have contributed to meeting our project goals. Based on the new findings, we have filed a provisional patent and presented the results at national conferences. As of the end of FY 2014, two manuscripts are in preparation.

Our plans for FY 2015 will cover the following areas. First, we plan to optimize membrane composition (types of double salt and molten phase) to achieve enhanced gas transport through membrane. We will also continue to explore a scalable membrane fabrication process for making thin and robust membrane with good separation performance. Finally, we will work to incorporate a promising flat-sheet membrane into a WGS reactor to evaluate CO conversion and H$_2$ recovery.
Optical Properties Modification in Complex Oxide Epitaxial Films via Alloy Formation

Ryan B. Comes

We are engineering the optical and electronic properties of complex oxide thin films by doping the materials and examining their potential applications in both solar photovoltaic cells and hydrogen cells.

There is great interest in finding new materials that can harvest sunlight effectively for converting photovoltaics and powering photochemical reactions. Because the solar spectrum is more abundant in visible than in UV light, finding photoactive materials that absorb in the visible is of particular importance. Many recent popular photovoltaic materials use elements that are either toxic or rare; moreover, their surfaces form oxides in the atmosphere, which can alter their otherwise useful properties. An ideal class of materials for future photovoltaic applications is complex metal oxides, which are already stable in air and afford flexibility in designing and synthesizing tailored materials. Complex oxides also exhibit a wide range of optical and electronic properties. SrTiO$_3$ (STO), for example, exhibits the highest reported electron mobility of any perovskite oxide. When epitaxial strain is applied, it can be made ferroelectric, producing a built-in electric polarization to separate electron-hole pairs in photovoltaic material. However, STO has a wide optical band gap of 3.2 eV, making it a poor absorber of visible light.

At the end of FY 2013, this project showed promising initial results. Initial research focused on LaCr$_x$Fe$_{1-x}$O$_3$ (LCFO) epitaxial films and multilayers. We observed new optical properties in the LCFO films that did not occur in either (LCO) or LaFeO$_3$ (LFO) films. First results on multilayer films were also promising, as we successfully fabricated films comprised of alternating LCO and LFO atomic layers. This demonstration opens avenues for future research into superlattice films and interfaces.

In FY 2014, we focused on the growth of epitaxial doped perovskite films using molecular beam epitaxy, specifically exploring the codoped Sr$_x$La$_{1-x}$Ti$_{1-x}$Cr$_x$O$_3$ (SLTCO) system. In this material, La$^{3+}$ dopants stabilize defect-free Cr$^{3+}$, reducing the optical bandgap by $\sim$ 0.9 eV while preserving the material’s semiconducting properties. This work enables the ability to use these films for photocatalytic and photovoltaic applications because the materials exhibit visible light absorption. Ongoing work is focused on engineering the SLTCO films and related an La, Cr codoped BaTiO$_3$ system to produce ferroelectric materials for a ferroelectric photovoltaic with high carrier mobility. Photoconductivity, piezoresponse force microscopy, electronic transport, and photocatalysis measurements are being performed to understand the material properties. Collaboration with theorists is supporting this work by modeling the growth process and electronic and optical properties of the doped films.

Characterizing SLTCO films via X-ray absorption spectroscopy produced novel and unexpected insights into the properties of these films. Analysis via extended X-ray absorption fine structure (EXAFS) showed that there was a greater concentration of La near the Cr dopants than would be expected based on the stoichiometry of the material. This scenario suggested that there may be a driving force for the dopants to occupy nearest neighbor sites, contrary to what was previously predicted theoretically. Modeling via density functional theory confirmed that the atomic layer-by-layer film growth process would be expected to promote this type of dopant coupling even though it is not expected to occur during bulk synthesis. This result will enhance understanding of the epitaxial oxide growth process as well as future modeling efforts for oxide films.

Optical absorption spectra for the three films, with the inset showing the actual color of samples.
**Optically Resonant Subwavelength Films for Tags and Seals**

**Kyle J. Alvine**

*Our goal is to develop a new counterfeit-resistant, tamper indicating film essential to identifying potential security breaches for use in arms control and special nuclear material tracking applications.*

There are multiple applications in the transport and handling of nuclear materials in which counterfeit-resistant tags and seals that incorporate tamper indication features are critical to identifying potential security breaches. Some examples include arms control applications such as “room within a room” or transparent tags for tamper indicating enclosures (TIE) in video monitoring equipment. Additional potential applications are unique optically transparent overcoat tags and seals with counterfeit- and tamper-indicating properties for UF₆ cylinder tracking. While different applications may require unique signatures, the tags and seals require tamper indication plus a unique signature in order to prevent counterfeiting.

We are studying and demonstrating proof-of-concept tamper indication performance of newly developed subwavelength films, which are particularly well suited to applications in tags and seals. They have a unique optical reflection that is wavelength, angle, and polarization dependent and can be tailored to operate from the visible to the infrared region to generate visibly transparent films for “room within a room,” video enclosures, or overcoat tags or seals (e.g., for UF₆ cylinders). Through this project, we expect to demonstrate tamper indication and to create a unique signature for counterfeit prevention for common tampering mechanisms (such as cutting, peeling, and tearing) in a subwavelength film.

Despite a very late FY 2014 project start, we have begun preparations for the fabrication of test samples to investigate tamper indication routes in early FY 2015. We also initiated work on a scalable coater in order to prepare larger samples, which includes both design and starting modifications to the coater head. In addition, we have started consultations into the most appropriate coupon sizes, materials, and methods of testing for tamper indication and authentication.

In FY 2015, we will prepare coupon films with a unique resonance reflection, including angle and polarization dependent response based on the size, shape, and geometry of the nanostructures within the film that can be tailored to be in the visible or infrared. These coatings also contain a unique structural defect pattern “fingerprint” due to the nature of wet deposition of the template during film fabrication that could be used as an additional check for counterfeiting and tamper indication. In addition to the angularly dependent resonant reflection, we can also incorporate oxidation and strain indication into the films for additional tamper indication mechanisms. We propose to design and fabricate such films on the laboratory scale (2–3 inches) that demonstrate tamper indication and counterfeit prevention.

In parallel, we propose to develop a basic handheld optical readout methodology for the inspection of such films. To achieve this, we will prepare a standard set of samples that incorporate the inherent angular and polarization dependent reflection of the subwavelength coating as well as oxidation and strain indicating components. For each of the films, we will introduce a common tamper damage mechanism (cutting, peeling, tearing, etc.) and a simple repair. The samples will then be inspected for tamper indication and modifications made to the design, as needed. The optical readout will be based on polarization and angularly dependent LED illumination of a particular wavelength band. This effort will be optimized in tandem with the tamper-indicating experiments.

Oxidation is one potential tamper indicator for transparent subwavelength films.
Optically Stimulated Luminescence Data Storage

David W. Gotthold

We are developing a new approach for data storage using optically stimulated luminescence (OSL) that can be scaled to high data densities with excellent data lifetime and integrity.

To meet the ever-increasing data storage need for cloud computing, scientists and engineers are constantly pushing the limit of data storage density. Hard disk drive (HDD) has been the dominant computing data storage device for the past 50 years, with over 800 million units sold in 2012. Until recently, HDD density increased by 100% every year, but advancing technology has decreased this rate to 25%. Solid-state hard drive (flash) is the storage method based ferroelectricity, where direct wiring enables immediate access to the bit. However, flash suffers memory wear and thus can be used only as short-term storage. Although CD, DVD, and Blu-ray are popular optical data storage methods, they have a significantly lower density (under 10% of HDD). Still another recent advanced storage method is holography, a promising technology because of its large density and fast data access rate, reading a page each time instead of a bit, like flash. However, precision system setup and high recording medium cost make commercialization of this technology painfully slow and ineffectual.

In this project, we are developing a new data approach that is capable of making a paradigm change in storage technology. OSL has been in use for many years as a radiation dosimetry technology. OSL media has an extraordinary linear optical response (over eight orders of magnitude for lithium fluoride [LiF]) that will enable ternary (higher-level) encoding of data in a single bit, thus storing more data in each defined location. Our objective is to prove the concept of OSL data storage by demonstrating multi-values data encoding. This information is a primary concern for potential development partners and will be key in identifying the potential market opportunities for this new technology.

Based on previous work done in FY 2013, we focused this year on understanding the market application space and key performance parameters necessary to address those markets. Our initial path was to look at long-term archival storage as an alternative to magnetic tape. However, we identified data storage where intermittent random access, such as record storage, is a better match for the performance of OSL-based storage. With that premise, we identified potential technology paths that can leverage existing data storage technologies and determined the process requirements, including storage density, read and write speeds, and unit storage capacity to meet the market requirements most optimally.

The critical technology barrier of this work is the ability to write the appropriate data quickly, so the technological work during FY 2014 was focused on the physics behind creating luminescent centers using electrons as the ionizing radiation source. To date and as previously noted, most of the OSL research and development has been in the field of ionizing radiation dosimetry, including personnel and environmental dosimetry as well as extremely high dose dosimetry for the sterilization of medical products, consumables, and the radiation processing of materials. These various dosimetry applications require the basic understanding of the OSL physics for gamma rays, beta particles, and neutrons. The lowest beta (electron) energy studied for dosimetry is driven by the human dead layer of skin. The lowest average beta particle energy studied was the 62keV $^{147}$Prometheum beta particle, as a 62 keV electron will just penetrate the human dead layer of skin and begin to reach living tissue. In contrast and for this application specifically, the desired acceleration voltages are much lower (< 5keV) both to simplify the design and to reduce the interaction volume and the resulting data pixel size.

In future work, we will build a prototype writing system that is capable of demonstrating both the density and write speed required for the selected applications.
We are developing methods for measuring photophysical properties as new research capabilities for developing and testing existing photocathode materials and designs.

Whether based on free electron laser (FEL) or storage ring designs, output characteristics and cost of new ultraviolet or X-ray sources are dependent on photocathode brightness and emittance characteristics. Novel photocathode designs could potentially reduce light source construction costs enormously—by a factor of two or more—by significantly simplifying downstream accelerator or FEL design. The international light source community recognizes the need for a more scientific approach to new photocathode development and is in the initial stages of addressing this issue.

This project will develop new capabilities for making and testing photocathode materials and enhancing photocathode designs to improve current and future light sources in a collaborative effort. Our initial goals were to increase photocathode longevity by understanding and modeling photocathode failure mechanisms. We conducted a post-mortem analysis of used (expired) photocathodes from the Thomas Jefferson National Accelerator Facility Laboratory and determined that the photocathode emission yield degrades under operating photo-injector conditions consistent with a model in which the surface Cs layer is removed from the surface by ion back bombardment sputtering. We also constructed a coupled photocathode preparation chamber and ultraviolet and X-ray photoelectron spectrometer to create and test photocathode designs.

In FY 2013, we tested the utility of thin films of KBr, in comparison with CsBr, to enhance quantum yield from Cu. We were able to identify two initial states for enhanced electron emission for both materials. The first resulted from work function lowering due to growth of the CsBr or KBr layer on Cu, and the second was due to formation of Cs or K thin films that further reduce the work function. CsBr shows a greater capacity for enhanced QE both before and after activation. The results of this study were published in *Applied Physics Letters*.

In FY 2014, we extended this work with a study of CsI on Cu(100). The quantum efficiency of Cu is found to increase dramatically when coated by a CsI film and then irradiated by a UV laser. Over three orders of magnitude quantum efficiency enhancement at 266 nm is observed in CsI/Cu(100), indicating a potential application for future photocathode devices. Upon laser irradiation, a large work function reduction to a value less than 2 eV is also observed, which is significantly greater than that for similarly treated CsBr/Cu(100). The large QE enhancement is attributed to optimal Cs metal accumulation, which is thought to be roughly 0.5 to 0.6 monolayer at the CsI/Cu interface. The results of this study were once again published in *Applied Physics Letters*.

In addition, we used ARPES under ultraviolet laser excitation to demonstrate that the electron emission properties of Ag(001) can be markedly enhanced and redirected along the normal surface by the deposition of a few monolayers of epitaxial MgO. The image shows ARPES of both clean Ag(001) and MgO/Ag(001), showing new, low-binding energy states with small spreads in their surface parallel momenta as a result of the MgO/Ag(001) interface formation. Under 4.66 eV laser excitation, the quantum efficiency of MgO/Ag(001) is a factor of seven, which is greater than that of clean Ag(001), revealing the utility of such heterojunctions as advanced photocathodes. These results were published in *Physical Review Letters*.
We are probing the structure-property relationship of next-generation energy materials to enable accelerated discovery of new materials for energy security and sustainability.

Electrochemical energy storage devices such as lithium (Li)-ion, Li-S, Li-O, Na-ion, and multi-valence ion batteries are complex, multi-component systems that incorporate widely dissimilar materials and phases in physical and electrical contact. Despite the success of Li-ion batteries, there are at least four areas where new research and development progress is needed: discovering new materials that can be used as electrodes (for both cathodes and anodes) with higher storage capacity; tailoring the microstructure of electrodes and overall architecture of the battery cell to enable high rate operation (fast charging); resolving battery capacity fading (i.e., increasing cycle life), and discovering a new energy storage concept for multi-valence ions as energy storage media.

The main objective of our research is to develop and use a combination of imaging, spectroscopy, and tomography methods to probe into the structural and chemical evolution of energy storage materials with atomic spatial and fast temporal resolution to determine the structure-property relationship and its correlation with charge and ion transport in energy materials. In particular, these chemical imaging methods will explore the new chemistry and nanostructured materials (such as Li-S, Na, and Mg ion) for energy storage with high capacity, high power, longer cyclability, and safe operation. This goal will be accomplished by developing concerted multiscale chemical imaging methodologies based on ex situ and in situ transmission electron microscopy (TEM), STEM, DTEM, electron energy loss spectroscopy, energy-dispersed X-ray spectroscopy, scanning transmission X-ray microscopy, X-ray tomography, and nuclear magnetic resonance (NMR).

In 2014, we achieved several project milestones. We use our open cell in situ TEM capability in combination with electro-mechanical calculation to study the external stress effect on the lithium ion transport behavior in Ge nanowire. We discovered that the external stress can either enhance or suppress Li ion transport. Typically, tensile stress will enhance the Li ion transport, while compressive stress leads the retardation of Li ion transport. This study sets some general guiding principle for the designing of new electrode materials. To minimum stress effect, the active component should have minimal impingement with other inactive material during the charge/discharge battery cycle.

We demonstrate for the first time an in situ capability based on liquid cell to which we can study the battery materials under the relevant operating condition using true battery grade electrolyte. The in-situ liquid TEM cell allows us to obtain information that is normally unavailable using the open cell configuration such as the SEI formation, structural and chemical evolution, and their effect on battery properties. This capability is now the key component that enables the effort of the DOE-sponsored Joint Center for Energy Storage Research (JCESR).

For cathode materials, we are collaborating with Argonne National Laboratory to probe the capacity and voltage fading mechanism of lithium rich nickel manganese oxide materials. Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ is a high voltage and high capacity cathode material for Li-ion battery. However, a major challenge of this material is the capacity and voltage fading upon cycling of the battery. We used high resolution imaging and chemical elemental mapping to identify the cause of the capacity fading, which yielded three publications. We discovered for the first time the mitigation of voltage and energy fade of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathodes by...
improving the atomic level spatial uniformity of the chemical species. The results reveal that cathodes Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ prepared by coprecipitation and sol-gel methods, which are dominated by a LiMO$_2$ type R3/m structure, show significant non-uniform Ni distribution at particle surfaces. In contrast, the Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathode prepared by a hydrothermal assisted method is dominated by a Li$_2$MO$_3$ type C2/m structure with minimal Ni-rich surfaces. The samples with uniform atomic level spatial distribution demonstrate much better capacity retention and much smaller voltage fade as compared to those with significant non-uniform Ni distribution. The fundamental findings on the direct correlation between the atomic level spatial distribution of the chemical species and the functional stability of the materials may also guide the design of other energy storage materials with enhanced stabilities.

In collaboration with Lawrence Berkeley National Laboratory, we show significant performance enhancement of electrode for lithium ion batteries based on Si nanoparticles wrapped with conductive polymer. This new material is in marked contrast with conventional material, which exhibit fast capacity fade. In-situ TEM unveils that the enhanced cycling stability of the conductive polymer-Si composite is associated with mesoscale concordant function of Si nanoparticles and the conductive polymer. Reversible accommodation of the volume changes of Si by the conductive polymer allows good electrical contact between all the particles during the cycling process. In contrast, the failure of the conventional Si-electrode is probed to be the inadequate electrical contact.

In the new chemistry for batteries, we studied the Li-S system in detail. The Li-S and Li-PS flow-type batteries are promising candidates for portable and large-scale energy storage, respectively. However, the poor stability of polysulfide species during battery cycling is a major challenge that severely hampers this technology. This instability leads to “shuttle phenomenon,” where the polysulfide molecules dissolve and diffuse to the Li electrode and causes dendrite growth through parasitic reaction. The difficulty in addressing this issue mainly originates from the significant gap between battery material synthesis efforts and current knowledge about the molecular structure and stability of dissolved polysulfide species. To unravel the structure and possible stability related reactions of polysulfide species, a combination of density functional theory (DFT), magnetic resonance, and X-ray spectroscopy studies were performed for the Li-S system. Multinuclear NMR, variable temperature ESR, and sulfur K-edge XAS analyses reveal that the Li exchange between polysulfide species and solvent molecules constitutes the first step in the dissolution process, leading to de-lithiated polysulfide ions (Sn$^{2-}$) and subsequently forming highly reactive free radicals through dissociation reaction (Sn$^{2-}$---2Sn/2-). The energy required for the dissociation and possible dimer formation reactions of the polysulfide species is analyzed using DFT based calculations. Based on these findings, we discuss approaches to optimize the electrolyte to control the polysulfide solubility.

In 2014, work covered by this project produced six peer-reviewed journal publications, four invited talks, and five conference presentations. At the same time, the lead author has been heavily involved in the focused research group activity of high capacity anode material based on Si. Looking toward FY 2015, we will focus on using in situ and ex situ imaging methods to study the energy storage materials such as Li-ion battery, Li-S battery, and multi-valence ion batteries, which are crucial for energy storage. We will closely integrate different capabilities and theoretical calculations and collaborate with the research effort of JCESR, DOE, and other projects as well as industrial organizations to push the research effort on energy storage to a high level for scientific and industrial applications.
Rare Earth-Free Phosphors for Lighting Applications

Carlos A. Fernandez

The replacement of down conversion rare earth (RE)-based phosphors will reduce market demand and U.S. dependence on foreign sources, decrease environmental impact, and enable the widespread adoption of solid-state lighting products.

Nitrides and oxynitrides have remarkable (thermal and chemical) stability and good fracture toughness while exhibiting unusual photoluminescence (PL) when activated with RE ions. For the application of RE-free based nitrides such as Mn\(^{2+}\)-doped phosphors, most of these investigations have focused on Eu\(^{2+}\) and Mn\(^{2+}\) co-activated materials. The outcome of this project is to establish a set of basic tools to correlate composition-structure/function relationship followed by demonstrating the materials prospective to replace RE-based phosphors. Ultimately, the full replacement of RE in phosphor materials will positively impact the U.S. energy capacity by accelerating the production and application of inexpensive energy efficient lighting products.

At the end of FY 2013, we demonstrated by computational modeling the feasibility of producing aluminum nitride and/or silicon nitride-based phosphors with no RE elements (i.e., using manganese as the only dopant). Our studies showed that the proposed phosphors could in theory achieve ~65–70% greater photoluminescence quantum yields (PLQY) than similar RE-based phosphor materials such as M\(_2\)Si\(_5\)N\(_8\):Eu\(^{2+}\). For FY 2014, our goal was to prove that we can reproducibly synthesize a low-cost, stable RE-free phosphor material with a minimum of 60% PLQY. This synthesis should be accomplished by employing similar conditions and infrastructure to current industrial standards for producing RE-based materials.

Based on the calculated optical activity of aluminum nitride (AIN)-based phosphor materials (\(\alpha\)-Ca\(_3\)Al\(_2\)N\(_4\)) that showed more favorable (from an optical activity point of view) theoretical band gaps (~3.3 eV, 376 nm) compared with the SiN-based systems, we synthesized Mn-doped AIN-based phosphors and worked on optimizing their optical properties. In this regard, we started with solid-state reactions of an AlN precursor with calcium nitride using manganese metal as the dopant. The novel compound obtained by the reaction of Ca\(_3\)N\(_2\) and AlN with large excess of Mn (25 mol %) obtained by heating at 1800°C for 5 h under a N\(_2\)/H\(_2\) (reductive) atmosphere exhibits PL signals much stronger than AlON:Mg:Mn system, which was one of our best phosphors synthesized in FY 2013. The Mn-doped Ca\(_3\)N\(_2\) and AlN system possess a strong orange emission with a maximum at 595 nm and full width at half maximum (FWHM) of 38 nm. The features observed in the excitation spectrum prove that the obtained compound has its emission properties closely linked to Mn doping. It is thus evident that the matrix absorbs energy in the near UV region of the spectrum and transfers energy to the Mn dopant present in the structure, which then emits visible light.

X-ray diffraction spectroscopy studies on AIN and AIN:Mn samples showed that the main component of the AIN:Mn phosphors is AIN hexagonal Wurzite phase. This phosphor was a good starting point to study the influence of a number of synthetic conditions in the absorption and PL wavelength as well as PLQY of the these class of phosphor materials. Specifically, we wanted to learn about 1) the reaction temperature on both optical absorption and PL; 2) the effect of an alternative dopant, Zn on absorption, and PL wavelength as well as PL intensity; 3) Mn dopant concentration on PL intensity; 4) PLQY values for AIN:Mn red emitter; 5) the influence of alkaline earth element in the host matrix absorption, PL, and PLQY; and 6) the influence of the presence of silicon in the aluminum nitride matrix absorption, PL, and PLQY. In the past 6 months, we performed the first four aforementioned studies. The results demonstrate that RE-free phosphors based on AIN matrices and Mn dopant have great potential to replace RE-based materials. We believe that introducing some modeling work to understand how the crystalline structure relates to the PL mechanism may be important to correlate the outcome with experimental results and to adjust absorption and PL wavelengths as well as optimize PL efficiencies.

Influence of reaction temperature on both optical absorption and PL. By varying the reaction temperature, we confirmed that the minimum temperature required to produce the red-emitting species is quite high at 1500°C. The temperature range at which we reproducibly obtained the orange-red emitting phosphor was 1500–1800°C. Lower temperatures were not enough to cause the precursors crystal lattice to diffuse to one another and react in the solid state. Therefore, only PL spectra from the host matrix were observed when performing synthesis at temperatures below 1500°C.

Effect of an alternative dopant, Zn on absorption, and PL wavelength as well as PLQY. Replacing Mn by Zn as dopant in the AIN host matrix and employing identical
Dependence of the PL spectra of the AlN:Mn phosphors on the Mn dopant concentration. Note that actual concentrations after reaction are in the 0.1 wt% to 2 wt% range.

Influence of Mn dopant concentration on PLQY. We performed synthesis on AlN:Mn phosphors with Mn initial precursor concentration between 9 mol% to 45 mol%. However, when heating the starting materials at 1500°C for 5 h, we observed via ICP-MS and EDS analysis that the actual content of Mn in the host matrix was in the 0.1 wt% to 2 wt% range. It seems that most of the Mn precursor introduced was lost by sublimation, even though the crucibles were tightly sealed. We are looking into better ways to perform reactions with minimum Mn loss by replacing a gas flow system by a static system. Nevertheless, the average PL intensities of these materials were statistically indistinguishable, which means that self-quenching of Mn at these low concentration levels (0.1–2 wt% Mn) does not occur.

Determination of PLQY in AlN:Mn phosphor. PL quantum efficiency is a key parameter to evaluate to learn about the potential of these phosphors for replacing RE-based phosphors currently used commercially. By employing a Horiba Scientific Fluoromax-4C spectrophotometer equipped with Horiba Quanta-Phi PLQY Sphere, we measured the PLQY for AlN:Mn with ~1 wt% Mn dopant. The value obtained for PLQY was 82%, significantly higher than any other PLQY value obtained for any RE-free phosphor reported thus far. The PLQY value of a standard sample Tris(8-hydroxyquinoline) aluminum(III) (AlQ3) showed the expected 20%, validating results from the RE-free phosphor material.

This work has demonstrated the great potential that this class of materials has toward replacing RE-based phosphors. The reported PLQY of 82% on the AlN:Mn red emitter has no precedent and represents an extraordinary finding toward the application of this class of materials as down-converting phosphors. Studies around the possible mechanism for photoluminescence of these materials and how the matrix elemental composition influences the optical properties of these phosphors are underway.
Rheoreversible CO\textsubscript{2} -Reactive Hydraulic Fracturing Fluids for Unconventional (Tight) Oil Production

Carlos A. Fernandez

**The goal of this project is to develop a rheoreversible environmentally friendly fracturing fluid for enhanced unconventional oil recovery.**

Three different concepts exist for hydraulic stimulation of a reservoir, depending on rock, formation, and fluid properties, namely hydraulic proppant fracturing (HPF), water fracturing (WF), and hybrid fracturing (HF). Independently of the approach, a cocktail of rheological modifiers account for ~1 wt% of the fracturing fluid, including gellants, acids, corrosion inhibitors, friction reducers, clay control, crosslinkers, scale inhibitors, breakers, iron control modifiers, and biocides. Though in small concentrations, all these additives are the primary source of environmental contamination as they accumulate in deep aquifers and recently appeared in water wells above ground. They are also difficult to remove from the formation after fracture creation limiting hydraulic fracturing production enhancement. Another key issue is the volume of wastewater that must be treated and disposed.

Our basic project concept is generating CO\textsubscript{2}-promoted crosslinking reactions on polymer solutions activated only at the reservoir to promote rapid volumetric expansions and increase mechanical stress in constrained environments. The idea is to build on the fracturing fluid technology currently being developed for enhanced geothermal systems (EGS) and modify the chemistry to introduce volume expansion and mechanical stress at lower temperatures relevant to tight oil reservoirs (40–130°C). This work will reduce the dependence on imported oil and contribute to the national economy by 1) introducing a potential average saving on reservoir stimulation of $1.5M per well (as of 2011); 2) enhancing fracture permeability followed by aiding to oil recovery; 3) decreasing water usage by half (an average saving of 2M gallons) for fracturing; and 4) using small amounts of inexpensive, environmentally benign polymers.

HP/HT rheology experiments were performed on a number of polymer candidates to evaluate volume expansions in the presence of CO\textsubscript{2} at two different temperatures (50°C and 130°C) relevant to reservoir conditions. This scenario was accomplished by employing a pressurized system consisting in three-window view cell equipped with sapphire windows, pressure generators, temperature and pressure controllers, transducers, and a CCD camera connected to HD video recording. A number of amine-based polymers with different MW were evaluated, including polyallylamine, polyethylenimine, and polyacrylamide among others.

As described, the volume expansion occurs as a result of a crosslinking reaction between the pendant amines in the polymer and CO\textsubscript{2}. This reaction is a Lewis acid-base reaction where carbamate salt forms followed by dehydration reaction to a urea linkage; hence, the fluid pH may play an important role in the degree of crosslinking. The results for a set of amine-based polymers are evaluated at two different reservoir temperatures in either deionized water (DIW), a pH=7, or pH=10 buffer solution. Volume expansion of up to 100% the original volume was observed for polyallylamine (PAA), polyacrylamide and polyethylenimine aqueous solutions in pH=7 buffer or DIW at temperatures as low as 50°C. Also, the molecular weight of the polymer did not appear to play a major role. These results are very encouraging and demonstrate that the application of CO\textsubscript{2}-activated expanding polymers can be potentially extended to unconventional oil recovery.

Laboratory-scale hydraulic fracturing experiments were performed using the rock cores prepared from rock samples collected from field sites in order to learn about the potential of these polymer solutions to create/propagate fracture networks in highly impermeable crystalline rock. The rock core was placed in a state-of-the-art cradle designed to expose the entire sample to the desired confining pressure while isolating the central hole drilled to introduce the fracturing fluid via high pressure stainless steel tubing. The confining pressure was applied using water at relevant reservoir P/T conditions using ISCO hydraulic pumps while the polymer and CO\textsubscript{2} were injected in a similar fashion via a hand pump and an ISCO pump, respectively.
Fracturing experiments were performed at 50°C employing as fracturing fluids: a control experiment water/CO₂ (with a pH=7 buffer) and PAA/CO₂ (MW=17K Dalton, PAA 1 wt% in pH=7 buffer). The applied differential pressure (effective stress) required to fracture the rock cores with conventional fluids (control experiments) was 40–50 % higher than the differential pressure required for fracture creation/propagation when employing PAA/CO₂ fluid system. More importantly, the permeability of the rock samples fractured with PAA/CO₂ fracturing fluids were orders of magnitude higher than the permeability of rock cores fractured using conventional hydraulic fracturing fluids (2–3 mDarcys for PAA/CO₂ as compared to < 1 µD for pH=7 buffer/CO₂). Representative XMT images of the rock cores before and after fracturing for both aqueous PAA/CO₂ (with pH=7 buffer) fracturing fluid and DIW/CO₂ (i.e., pH=7 buffer w/o PAA) fracturing fluid are shown. It is clearly observed the presence of fractures created/propagated during fracturing experiments employing PAA/CO₂ fracturing fluids that connected the central hole of the rock core to its external surface. Two fractures also extend 8.5 mm along the longitudinal axis of the rock core (fractures opening range 110–140 µm). Control experiments showed no fractures at the resolution of the instrument (25 µm).

Our work shows that the application of CO₂-expanded fracturing fluids can be extended to low temperature reservoirs, dramatically enhancing the permeability of crystalline rock materials compared to current technology. The results demonstrate that creation/propagation of fracture networks using these environmentally friendly fracturing fluids is, in principle, possible.

This novel fracturing fluid technology shows volume expansions of 100% its original volume upon reaction with CO₂ at temperatures of 50°C and creates fracture networks on highly impermeable crystalline rock cores with permeability values orders of magnitude higher than the ones obtained when fracturing with conventional fracturing fluids. As a result, PNNL fracturing fluid technology potentially represents a great alternative to industrially available fracturing fluids for cost-effective and competitive tight oil recovery.

During FY 2015, our research will focus on understanding the chemical mechanisms involved in the volume expansion upon CO₂ injection as well as learn about the viscosity, stability, and recyclability of these novel fracturing fluids. A patent application was recently submitted, and a publication in a peer-reviewed high impact journal will follow. The team is also having conversations with BP and YPF (Argentina) in search for commercialization opportunities for this technology.
Robust Hierarchical Zeolite Frameworks

Miroslaw A. Derewinski

This project will provide a molecular description of the formation and arrangement processes during synthesis of microporous crystalline silicates using PNNL’s advanced measurement capabilities as basis for the synthesis of nano-sized and mesoscopically structured zeolites with tailored chemical and textural properties.

Molecular sieves based on Si and Al as well as Si, Al and P are key materials for sorption, ion-exchange and catalysis in modern industrial processes. The success of these materials is related to unique combination of their structural versatility, robustness and chemical properties. Extending existing knowledge about the formation mechanisms of molecular sieves will enable our main goal: synthesis of new materials with tailored properties. This project provides a way to design and prepare robust, porous frameworks structured on a mesoscale level that combine increased accessibility of catalytically active sites, enhanced stability, and catalytic performance for demanding catalytic processes, including biomass conversion and exhaust treatment as well as processes carried out at low temperatures (<100°C) in a liquid phase. Specifically, we plan to explore with in situ NMR the kinetics of formation of selected zeolite structures (BEA, MFI) to assay the role of structure-directing agents and synthesis parameters (temperature, chemical composition) on nucleation and crystal growth, to determine the impact of framework defect sites on stability of zeolites in aqueous environments and propose synthesis and post-synthesis approaches to limit the number of such defects, and to enhance transport in micropores by decreasing the size of zeolite-like particles to several nanometers and assembling them into ordered (lamellar) mesoporous materials.

This project is yielding information about the synthesis and post-synthesis approaches that enable preparations of new, more stable and active zeolite based materials. In FY 2014, we prepared stable colloidal suspensions of zeolite-like nano-structures (~5 nm in diameter, XRD amorphous) subsequently assembled them into layered structure in the presence of surfactants. HRTEM analysis has shown that the layers are packets of several ultrafine (3–5 nm thickness) sublayers separated by slit-like mesopores (~2 nm). New lamellar structures containing dispersed nanoparticles provide enhanced access to active (acid) sites, resulting in reduced residence times of the molecules in the confined space of micropores. In our test reaction, the enhanced mass transport led to improved selectivity to desired products by decreasing the extent of undesired secondary reaction. Our preliminary studies have shown that new materials are highly active for low temperature isomerization of α-pinene as compared to conventional acid catalysts.

One of the factors limiting application of zeolites as catalysts in biomass conversion is their low stability in aqueous environments. Stability of zeolites in contact with water appears to depend on the presence and concentration of framework defect sites (hydroxyl nests) consisting of four hydrogen-bonded Si-OH groups. In the last year, we started determining the role of defect sites in destabilizing zeolites in water environments. A series of high silica zeolites (MFI, BEA), isomorphously substituted with two heteroatoms of different stability in the zeolite framework: aluminum and boron were synthesized. Selective, post-synthesis elimination of less stable B atoms (monitored with NMR spectroscopy) leads to formation of defects. Different amounts of boron introduced (and subsequently removed) generate materials having proportionate levels of defects. We found that high temperature healing of defect sites increases the stability of zeolites (BEA). Currently, we are studying the post-synthesis incorporation of Si into defects via treatment with alkylchlorosilanes.

To delineate mechanisms of zeolite formation we had proposed to monitor and analyze elementary steps of nucleation and crystal growth of zeolites by combining kinetic experiments with in situ MAS NMR, using unique high temperature and high pressure NMR rotors developed at PNNL. This task was not finished because the cells were not available but will be undertaken in 2015.
Ultra-Low Background Polymers for Structural Applications in Radiation Detectors

Jay W. Grate

This project focuses on the materials required for ultra-low background insulation (i.e., plastics) for next generation detectors in high energy physics programs.

Ultra-low background radiation measurements are essential to several large-scale physics investigations such as those involving neutrinoless double beta decay, dark matter detection, and solar neutrino detection. Ultra-low background counting is also of value in applied radiation detection applications associated with nuclear security and treaty verification. To detect low probability events, it is essential that the background noise of the measurement systems be driven to the lowest achievable levels. Hence, the radioactive contaminant species in the materials used to make and house radiation detectors must be minimized. Radioactive impurities in materials can arise from naturally occurring isotopes, radionuclides generated by cosmic ray interactions, and anthropogenic sources. The radioisotope purity required for these detectors goes well beyond even the best industry practices for chemical purity.

Considerable work has been done to purify germanium as the primary semiconducting detector material. Ultra-pure copper production for low background systems is well underway for structural parts requiring electrical or thermal conductivity. However, there remain needs for electrically and thermally insulating dielectric materials with extremely low background radioactivity. The materials must be especially low in uranium (U), thorium (Th), and potassium (K) and not be contaminated by radon daughter products. This project is focused on plastic polymers for use as structural materials. Specifically, thermoplastic polymers represent the class of dielectric materials capable of meeting the requirements for low background, mechanical rigidity, and suitability for forming or machining into detector parts. These materials cannot be evaluated or qualified for detector applications unless a method exists to assay the polymers for trace contamination. The development of assay methods is coupled with sourcing, evaluating, and improving plastic polymer materials.

We made great strides in sourcing and obtaining thermoplastic materials early in the supply chain to prevent grinding, pelletizing, thermoforming, handling, and transporting activities from contaminating and confounding our ability to understand the inherent purity of the plastic materials. Both nonfluorinated and fluorinated materials with excellent structural properties have been obtained in flake, powder, pellet, or 3D printed forms. We also made progress in assaying samples of these plastics for U and Th. In one approach, a solution containing the metals and radionuclides from the plastic is analyzed by inductively coupled plasma mass spectrometry (ICPMS). The challenges to this approach include breaking down the plastic and creating the solution, the absence of reference materials as laboratory control standards, and avoiding contaminating sample solutions with traces of metals from the container materials used in sample preparation. In another approach, we used laser ablation (LA) to sample polymer materials for ICPMS analysis, which reduces sample preparation challenges and is a new method development from the lack of certified materials as matrix-matched standards, a fundamental problem in using LA-ICPMS as a quantitative method.

We are developing relationships with plastics manufacturers who synthesize polymer materials and contacting fabricators who form polymers into solid shapes. By analyzing materials from these partners and material samples to which we applied additional purification procedures, we will achieve very high standards of purity. These analyses require fundamental new assay method development. In the coming year, we will finalize the dissolution analysis of our initial materials, complete a new protocol for polymer analysis by LA-ICPMS, and begin purification methods on polymer samples to achieve ultra-high purity in a polymer suitable for structural detector applications.
Understanding and Controlling of the SEI Layer (Solid-Electrolyte Interface and Interphases) in Multivalent Energy Storage Systems

Guosheng Li

Demonstrating elegant electrochemical performances of new electrolytes, this project will achieve a breakthrough of magnesium (Mg) battery for energy storage applications.

Electric energy storage has recently gained increased attention for use in improving the future efficiency of electric power grids, stimulating the growth of renewable electricity generation, and providing alternatives to fossil fuels for transportation. Mg batteries have been considered the most attractive (beyond lithium ion battery technology) because of their substantial prospective benefits. The theoretical volumetric capacity of Mg metal (3823 Ah/L) is much higher than that of Li metal (2062 Ah/L). The eighth most abundant element in the earth’s crust, Mg costs less than lithium. Thus, successful research and development of a Mg-based battery can bring substantial benefits for stationary energy storage and transportation applications.

Rechargeable Mg batteries have long been considered a highly promising technology. Despite an increasing investment in Mg battery research, much more needs to be done to develop practical Mg batteries. The most challenging technical hurdles include the need for electrochemically stable Mg electrolytes, stable current collectors for cathodes, and highly active Mg$^{2+}$ intercalating cathodes. By integrating truly novel and innovative discoveries related to Mg electrolytes, stable current collectors, and reliable cathodes, this project has made tremendous progress toward the development of an Mg-based battery for energy storage applications.

Two novel electrolytes were developed in FY 2013: electrolytes consisting of Mg[BH$_4$]$_2$ in an ethereal solution and an MgCl$_2$/THF-based electrolyte. The superior electrochemical stability of the MgCl$_2$/THF electrolyte was demonstrated in a Mg battery for future application in high energy density Mg batteries. The electrochemically stable cathode current collectors, novel nanoparticle cathode materials, and hybrid Mg/Li battery technology developed under this project are breakthroughs for developing a high-performance Mg-based battery.

Three important breakthroughs crucial for developing practical Mg batteries were made in FY 2014. First, the current collector is a critical component in all battery systems including Mg-based batteries. The strong corrosive nature of electrolytes developed thus far for Mg batteries posts rigid requirements for the associated current collectors and other cell components such as the cell case. Current research has identified several potential anode current collectors, but no practical cathode current collector has been identified. The superior electrochemical stability of W and Mo as demonstrated in this work could have a significant impact on the research and development of high-voltage, low-cost rechargeable Mg batteries.

Next, we developed a facile method for synthesis of Chevrel phase nanocubes and examined their application for multivalent energy storage. Our results demonstrate that the as-synthesized nanocubes were mostly single-crystalline and had well-defined phase, size, morphology, and composition. When used as electrode materials for Mg$^{2+}$ intercalation, they exhibited higher reversible capacity and better kinetics at ambient temperature.

Finally, a novel design of hybrid batteries that combines Mg and Li electrochemistry has been developed and tested. This device has a Mg anode, a Li$^+$ ion intercalation cathode, and a dual-salt electrolyte that contains both Li$^+$ and Mg$^{2+}$ ions. Experimental results showed that these batteries combined the advantages of different materials and delivered an outstanding rate performance (105 mAh/g at 15°C) and superior cyclic stability (~5% capacity drop for 3000 cycles at 10°C), along with reasonable output voltages. The inherent safety and reliability features of such devices make them promising for many applications, especially large-scale static energy storage. The design of batteries discussed and studied in this work could also provide a new approach to high-performance energy storage systems.

Developing a MgCl$_2$-based electrolyte and acquiring a fundamental understanding of its electrochemistry in a non-aqueous solution lays the foundation for our efforts during FY 2015.
Mathematics and Computing Sciences
A New Modeling Approach for Biology: Combining Natural Selection and Thermodynamics for Biodesign and Natural Systems

William Cannon

This research is using thermodynamics to understand natural selection and biological adaptation so that changes in the environment can be predicted and national policies can be developed to mitigate the economic consequences of these changes.

Ideally, the modeling of metabolism would use kinetic simulations, but these models require knowledge of thousands of rate parameters, the measurement of which is very labor intensive. The best option currently is to model reaction fluxes only, without regard to the law of mass action. However, this convenience also limits the predictive power of the methods. Not only does the range of solutions span many orders of magnitude, but also metabolite levels and energetics are next to impossible to predict from flux values.

We are developing an alternative approach based on rigorous statistical physics. Our objective is to apply the statistical physics of reversible processes to microbes and to evolve the system by selecting of the most-fit microbes based on free energy production. Our ultimate goal is to integrate statistical physics and physical chemistry with the study of biological processes, thereby enabling much more predictive simulations that can inform research decisions and strategies in the laboratory.

This year, we published a mathematical description of the approach and developed a comparative study of including the niche-specific thermodynamics of the tricarboxylic acid (TCA) cycles of the heterotroph *E. coli*, the cyanobacterium *Synechococcus* sp. PCC 7002, and the green sulfur bacterium *Chlorobium tepidum*. The TCA cycles are autocatalytic reaction cycles that turn high-energy carbon compounds into low energy by-products used for cell biosynthesis and store the processed energy in ATP and NADPH.

The TCA cycle of *E. coli* operates in an environment in which the breakdown of saccharides is used to provide energy for cellular growth and maintenance. In contrast, the cyanobacterial TCA cycle operates in an environment in which photosynthesis provides a significant amount of NADPH and ATP necessary for growth, yet despite high ATP and NADPH concentrations, the TCA cycle in cyanobacteria must be able to produce three carbon precursors necessary for synthesis of biopolymers. The reductive TCA cycle of *Chlorobium* operates in a low oxygen environment and uses sulfide and thiosulfate as electron donors and CO₂ as a carbon source. Green sulfur bacteria such as *Chlorobium* only contain photosystem I, which produces large amounts of ATP and reduced ferredoxins. These cycles operate efficiently to produce biosynthetic compounds despite the different environments.

The ability to characterize each microbe in its environment thermodynamically is extremely important for natural selection. This concept boils down to whether an organism can competitively harvest enough energy from the environment in an efficient manner. Robustness of a microbial community is also related to energy extraction — that is, whether through complementary interactions a set of organisms can couple their respective processes in such a manner that the whole is greater and more resilient than the sum of its parts. For this, we are following the concepts of ecologist Howard Odum, statistician Lotka (of the Lotka-Volterra predator-prey model), and physicists Boltzmann, Schrodinger and Prigogine.

To implement this vision, we are simultaneously developing the high-performance computing framework to simulate billions of microbes co-existing in a microbial community. Biocellion, the software infrastructure we developed to implement our vision, takes a single cell model (such as ours based on statistical thermodynamics), and runs many of them in parallel to simulate a large number of cells. Biocellion allows these individual cells to interact either physico-mechanically or indirectly via exchanging environ-
mental chemicals which are delivered by diffusion and/or advection. The currently released version of Biocellion considers only local interactions between cells or cells and their micro-environment. We recently added a capability to incorporate flow into the simulation that will allow us to also incorporate long distance communication between distant cells via flow.

To date, we have simulated as many as 1.7 billion individual (albeit simple) cells in a community. Biocellion is designed to exploit a range of parallel computers from multicore desktops to Cloud computers and leadership class supercomputers. Biocellion combines the existing HPC software (such as CHOMBO PDE solver developed by Lawrence Berkeley National Laboratory) with newly developed software to simulate various coupled processes in different spatial and time scales. To address this multiscale computing challenge using parallel computers, we customized the existing software, developed new algorithms, and adopted a heterogeneous set of programming models and system software such as Partitioned Global Address Space (PGAS) Global Arrays, MPI, and Thread Building Block (TBB).

Biocellion is being used by collaborators at the Institute for Systems Biology, Utah State University, and the Fred Hutchinson Cancer Research Center. We also started an collaborative effort to model glioma (brain cancer) with the Institute for Systems Biology and Northwestern University. The Institute for Systems Biology is additionally pursuing the establishment of a skin modeling consortium to include commercial partners, and Biocellion enabled them to envision developing a large-scale high-fidelity skin model with commercial value. Biocellion is distributed via Biocellion SPC, and additional 17 users from around the world have registered to use Biocellion.

Biocellion is the only available technology to deliver both high performance and high scalability sufficient to simulate high fidelity biological systems at scale while providing high flexibility to implement various models for a range of biological systems: multiple cancer, skin, bacteria, and yeast models in different environments all have been developed using Biocellion. In 2014, Biocellion SPC was founded by a former PNNL staff member to commercialize the software and support future development of Biocellion and the ecosystem around the framework.
Actionable Visualization Tools for Power Grid Situation Awareness

Luke J. Gosink

*This project addresses the fundamental need for greater situation awareness (SA) within the grid domain through the design of actionable visualization strategies that increase inter-organizational communication and collaboration.*

A sustainable, efficient power grid operation relies heavily upon real-time information transparency and wide-area SA for all organizations in the grid. Without real-time system-wide awareness in the power grid, there is significant potential for small local power instabilities to escalate and cascade into large-scale blackout events. While many organizations have developed methods to support internal SA capabilities (i.e., awareness of state within the organization), there is little evidence of successful research that can help organizations to see across organizational seams to increase external SA.

This project will support the need for external SA by designing a new visual communication mechanism that will allow organizations to share information securely across organizational boundaries. We will extend this mechanism with new visual analytic strategies that incorporate information outside of the power domain (e.g., weather, political/social, cyber, etc.) so that organizations have a better awareness of events that can potentially impact grid stability. We will support access to these functionalities through a new application, Shared Perspectives, that will allow power system operators to achieve a more broad SA of events both within and outside of the power grid.

Project progress is based on two fundamental objectives: creation of a master specification document for fostering SA that identifies use-cases, challenges, and needs of operators when they attempt to share information during critical events; and the design and implementation of the Shared Perspectives visualization application that directly addresses challenges identified within the master specification document.

During our project start, significant progress was made in compiling the master specification document. We conducted numerous interviews with organizations (including representative cases of utilities, balancing authorities, and reliability coordinators) to identify the need for external SA. Also, we attended several workshops and seminars to identify current approaches used to generate this awareness. Based on this initial research, we identified that organizations are lacking in methods that support external SA. Operators communicating across organizations often depend exclusively on telephones to create a foundation of common understanding.

For non-critical situations, this communication medium is sufficient; however, growing evidence indicates that during critical, complex events, relying on phone communication alone creates significant opportunity for miscommunication that can result in disastrous consequences. To address this challenge, our research identifies the need to broaden the communication conduit through a common tool that supports both audio and a common visualization perspective where organizations can “push” and share various types of information to help build common understanding.

From our findings, we initiated the design work for Shared Perspectives based on the need to build a common understanding between organizations flexibly and securely through information sharing. The application is based on a scalable web architecture that supports a highly interactive collection of visualization components that enables the rapid design of custom applications for industry use-cases.

We completed the design and implementation of the Shared Perspectives application during FY 2013 and demonstrated the application to subject matter experts from several utilities. The demonstration depicted a use-case that involved four organizations that used Shared Perspectives to resolve conflicts caused by a downed intertie. The new components of Shared Perspective include a new visualization strategy for power data that depicts data streams as an interactive “theme river” view that consolidates data from different sources and highlights critical trends for interactive exploration and collaborative problem solving.

In FY 2014, Shared Perspectives was fully integrated with PNNL’s Grid Optics software suite. Additionally, we designed and conducted a large-scale user study that was conducted over 2 days. Results from this study helped confirm the effectiveness of Shared Perspectives to reduce time-to-resolution for various events and to identify important communication trends that are built when organizations are able to establish wide-area SA.
The Signature Discovery Workbench (or Workspace) provides a visualization of information where signatures can be created, used, and adapted.

The Signature Discovery Workspace provides a facing application to allow users to create multimedia signatures quickly and efficiently for classifying information from disparate data sources across multiple domains. The system will allow rapid comparisons between new and existing signatures as they are being developed, enabling informed decisions about multimedia content through user interaction and features extracted.

Our approach was to leverage prior work in semantic interaction to formalize signatures based on user interactions. Our project aimed to answer the following research questions:

- How can we infer the process of signature discovery from information synthesis through user interaction of the information?
- What is the tradeoff between explicit signature creation (using the radial decision tree) and implicit signature creation (using the spatial canvas)?
- How do user-defined spatial visualizations impact the signature discovery process when the process/workflow itself is abstracted?

To address these questions and accommodate for the user feedback into the signature creation process, we developed a new spatialization visualization of domain-specific data to steer and augment the signatures. Based on the user research across the three domain areas (Bio, Nuke, and Cyber), spatialization visualizations are leveraged as visual metaphors to gain an overview of classification and clustering of information as well as a means for exploring relationships that form between the information.

As part of this work, we added new algorithms and models into the LIFT architecture to support this research. Lighthouse is a proven image and video processing system previously leveraged in the Canopy application. Specifically, Lighthouse extracts features from images and videos that can be used to describe the content and create relationships based on those features. We also incorporated text analytics from InSpire to bridge multimedia content effectively from text, image, and video.

The new spatialization visualization allowed us to infer the analytical reasoning associated with specific interactions afforded in the visual metaphor, whereas workflows and signatures are implicitly created on behalf of the user. We shifted the focus of the users from actively building a workflow to analyzing and synthesizing information spatially while the workflow is inferred and implicitly adapted. Next, we introduced “attractors” for information based on individual signatures. These seed the clusters of information and drive the meaning behind areas of the spatialization. Finally, we provided support for multiple data types, including images, text, video, and sequence data as sustained by a related project. The user focus on the synthesis of this information will align this research with crucial work through the data types selected and the analytic steering of the signatures through the inferred reasoning of the user interaction.

Future work on this project will include developing a method for capturing the interaction of users in an effort to understand how that interaction effects the information theoretic feedback loop that will in turn facilitate the signature discovery process. This scenario will involve a new “crowdsourcing” semantic feature extraction from which we will create stronger, more meaningful classifiers of information. We will perform a user study to validate the new approach and demonstrate the utility of the innovation and research in multiple use cases. We plan to publish the research in conferences in our field.
Analytics Integration and Validation Framework

Ryan R. LaMothe

The goal of this project is to enable the integration of multidisciplinary research efforts and their products into a unified framework for the discovery and validation of complex signatures.

Software tools and infrastructures for the discovery of domain-specific signatures are in use and are well known. However, none has the flexibility and the reusable methodology that are required to be extended into multiple domains. These tools are typically applied ad hoc for the task at hand or they are integrated using workflow software, which provides a graphical interface to integrate disparate software tools. For either case, the methodology is not made explicit, in that it is tied only to a particular scientific domain or not documented systematically. This situation makes it difficult for signature development tasks to be repeated and applied in other contexts. Further, although the workflow tools help to automate and integrate distributed computing resources, they are often challenging to apply in practice and cannot individually maximize the high performance computing resources that are required to solve many of these problems.

Our research leverages multiple developed capabilities, including analytic framework architecture, signature quality metrics, and signature processing algorithms developed under multiple projects. To support the execution of commonly used signature discovery methods and algorithms, we created a flexible, lightweight integration platform able to incorporate existing and legacy tools into a single system known as the Laboratory Integration Framework and Toolset (LIFT).

LIFT adapts to client needs by allowing them to pick and choose the tools needed to address their particular signature development needs and deploy it to their environment of choice. These tools are made available via LIFT supplied web services, which are accessible from a wide range of client tools. LIFT achieves several core goals of the initiative by reducing trial and error, allowing users to reuse existing tools and approaches, and providing a reproducible mechanism for constructing and evaluating signatures. This methodology encourages reusability and reinvestment, and is actively being used to develop signatures in a wide variety of domains.

This enterprise-quality integration platform exhibits the following qualities:

- Modularity – The integration framework allows analytic services to be added and removed readily.
- Deployability – The system is able to be easily deployed and fielded through the use of flexible profiles that abstract away host-specific information.
- Interoperability – Web services are used to make analytic tools available to a wide range of client tools and programming languages.

In FY 2014, the analytic framework team partnered with challenge project teams across the internal group to encapsulate their algorithms and tools into LIFT web services available to other users. These collaborations resulted in the successful integration of capabilities and workflows from multiple projects, including Canvas, GraphScape, Inspire, and Lighthouse. Signature Quality Metric partitioning, classification, and accuracy calculations were also integrated as core LIFT services during this year. At an internal annual review, LIFT was used to lead multiple challenge project demonstrations.

The maturity of the system is exhibited by the fact that LIFT has been adopted as the integration framework for PNNL’s Analytics-in-Motion and Asymmetric Resilient Cybersecurity Initiatives, and external projects sponsored by DTRA, DHS, IAEA and Special Programs. Additionally, PNNL LDRD leadership has recognized LIFT’s crosscutting value to the laboratory and is considering supporting the framework for all applicable future research initiatives.

In FY 2015, the team will continue to support signature challenge projects through LIFT’s novel Analytics-as-a-Service (AaaS) platform, which will be also be an integral part of PNNL’s Research Cloud efforts in coming years.
Characterization of Anonymous Peer-to-Peer Networks

Curtis L. West

This project examines the content and technology behind the evolving social and technological movement surrounding anonymous peer-to-peer networks.

Anonymous peer-to-peer networks and related technology for the sharing of illicit materials and for non-attributable, encrypted communication are a worldwide movement that is growing in terms of impact and sophistication. FreeNet, GnuNet, Retroshare, Tor Hidden nodes, and I2P are all peer-to-peer networks that exist now and allow users to exchange data, chat, and blog anonymously. These networks are ideal for sharing illicit information, as they protect the identity of the source and recipient and also provide a distributed peer-to-peer cloud in which the content is stored. Radical decentralization appears to be an over-arching goal.

In this project, we are seeking to define rigorously the landscape of anonymous peer-to-peer (P2P) networks in terms of technology and content. Although there is a great deal of literature on various technologies that contribute to these networks’ capabilities, there is little on the evolution of the technology, its actual (not assumed) content, scale, and general use patterns, and its emerging future. We are striving to achieve the following: 1) develop the capability to characterize and assess the ongoing use of these networks in both scale and topical space; 2) develop capability and expertise in these technologies and report on the landscape in terms of maturity and technical capabilities; and 3) suggest future directions for technical and policy related work.

We have observed a wide variety of technologies that appear to be converging in the areas listed below:

- crypto-currencies
- peer-to-peer technologies
- the idea of the “block-chain” as a contracting mechanism and general public ledger
- alternative network technologies and protocols
- encryption.

This “radical decentralization” movement is aimed at replacing common elements of our current culture, such as central banks, fiat currencies, internet service providers, voting mechanisms, trade regulation, and other critical elements. If a phrase could represent such a movement, it would be: “There is no trusted third party; trust only the math.”

While the specific goals of each network, technology, currency, and other elements are quite varied, the effect of anonymity tends to support the proliferation of a wide variety of illicit content. These networks provide the basis for a current and future worldwide criminal services ecosystem. Conversely, they also provide a mechanism for the oppressed to share information and communicate with some degree of privacy. Our research takes a valuable neutral approach.

For FY 2015, we will be producing a primer for these networks and examining related technologies detailing the technology and content landscape.
Through this project, we are deepening understanding about how an organization relies on its cyber infrastructure to accomplish critical missions.

Cyber security is both an area of current concern and an area of immense opportunity for attackers. Any and all mechanisms that can turn the tide in favor of the defenders, especially against poorly defined attack vectors or insider threats, are of particular significance. To combat these threats, the Cyber RAM project will define a holistic risk assessment model incorporating risk, remediation, and cascading dependencies. We will create an architecture for and implementation of this holistic model suitable for near real-time adaptation of cyber assets during active events to minimize mission impacts from asset degradation or loss. During normal operations, the Cyber RAM technology will provide a means to assess risk, plan adaptation, and mitigation strategies to maximize threat reduction and mitigation. Further, the technology will account for mission impacts, restoration times/costs, and multi-enterprise interdependency analysis.

Specifically, our research is focused on two primary “soft” aspects of security: involvement/engagement and interorganizational communication. The project explicitly creates a technology model to capture and convey the inter-organizational dependencies on technology within an enterprise (information technology (IT) infrastructure mapping onto non-IT operational missions) and between enterprises/departments (sales department reliance on inventory management department), with a mapping of the missions to the underlying infrastructure providing the mission capabilities. The current and completeness of the data will be ensured by facilitating data integration capture to “hands-on” operators of the missions and infrastructure rather than relying on subject matter experts (SMEs) or IT staff to capture this information. This approach of distributed data capture is a variation on the theme of “crowdsourcing” to augment SME and instrumentation data that will be relevant in applications well beyond the cyber security domain.

The development of an approach to analytics over a distributed graph will provide significant improvement in the ability to scale cyber network/system topology-based (and any graph-based system) analytics in the operational setting without the need to resort to exotic technology and approaches. The Cyber RAM approach provides a distributed model which has direct implications to the efficiency and effectiveness of cyber security throughout the attack lifecycle by focusing the attention of defenders to areas of greatest weakness to infrastructure supporting operational missions rather than to operational infrastructure itself. This method acts as a force multiplier by providing a means of more effectively “moving the bottleneck” away from the most critical missions to mitigate impacts before and during attacks.

Cyber RAM will provide the implementation of a general concept that will scale and integrate with other infrastructures and hazard types to provide a foundation for enterprise-wide risk management across all infrastructures for failure and hazard modes, including multi-modal (cascading) hazards. While the current project does not focus on this area specifically, the technology implementation is directly transferrable to a more broad infrastructure. We began by conducting a background investigation on the state of the practice. Over the limited course of evaluation this year, we saw an alignment with operational need but to this point found no directly competing projects. There has been limited overlap with other products that capture a skeleton of information around assets and missions, but none has provided an analytic capability.

For FY 2015, we will focus on the specific model of cyber assets and organizational missions within and between organizations. The research will provide a set of patterns and practices for technology development (software and protocols) that enable multi-organizational (or multi-network) information fusion for connected (linked, graph, and relational) data. Given that a primary goal of Cyber RAM is to create a distributed graph model that supports distributed analysis over the sub-graphs in a limited trust environment using commodity hardware, research will entail the use of multiple compute nodes (simple desktop workstations) running the Cyber RAM software (on dedicated hardware or hardware host other services).
Cyber Security Testbed and Dataset Generation

Thomas E. Carroll

We are designing and implementing a common infrastructure shared by cyber security researchers with the aim of accelerating research and development, advancing the state of cyber security science, and eliminating the expense of operating redundant experimental platforms.

Cyber security suffers from the lack of scientific rigor, which slows the advancements made in the domain. Specifically, the science of cyber security is immature and often lacks necessary conditions of repeatability and reproducibility, attributes that inform scientific quality. A common research infrastructure—including an experimental platform, reasonably realistic models and simulation, tools to control experimentation, and the stewardship of datasets—shared by like investigators will advance the state of the science, accelerate research and development, and reduce costs associated with redundancies.

In FY 2013, our efforts were expended to understand the ways in which testbeds can be built and instrumented so that they provide a valuable platform on which to conduct experimentation. Desiring enterprise scale, we determined that virtualization was a must; thus, we investigated several different virtual machine monitors (VMMs), a hardware/software system for creating, executing, and managing virtual machines. Using the capabilities of virtualization to create an instance of a small business network, we generated synthetic datasets using a PNNL-developed cyber-user behavior modeling framework and made these sets freely available to researchers.

In FY 2014, we organized our efforts into three categories: standing up CyberNET, an enterprise computing experimental testbed; modeling and simulating; and gathering and stewarding datasets. In CyberNET, we consolidated the resources under OpenStack cloud computing platform. These changes provided central management of the resources and an abstraction that permits researchers to easily instantiate models.

For modeling and simulating, we evaluated cyber-user behavior modeling frameworks, designed and instantiated a network instance of a reference architecture, and designed a framework for modeling cyber-social behaviors. We evaluated the cyber-user framework that was used in the year prior. Specifically, we noted that the behaviors generated were often incomplete and demonstrated artifacts. One example was a temporal correlation of what should be independent behaviors. Additionally, the framework suffered from resource constraints and would halt unexpectedly. This challenge added complexities to generating datasets, as only after inspection of the resultant datasets could we detect defects. We began evaluating another framework late in the year, but the work will not be completed until FY 2015.

Also during this last year, our project designed a network model that fulfilled the requirements specified in the reference architecture. We used the three-tier “hierarchical internetworking model” as a guiding principal, and we incorporated fault-tolerant/redundant components at multiple OSI levels within the design. The model was then stood up within CyberNET. Several projects actively use the project to test assumptions and demonstrate proofs-of-concept. Finally, in our review of existing cyber-user behavior modeling frameworks, we observed that the frameworks ignored cyber-social interactions, activities within which an enterprise exist include email, web, and user applications. One way to model user behavior realistically is to analyze social interactions (first order and higher) among users. Our approach began with simple automated agents and added complexity as required to be consistent with observed data. Our primary data source for deriving and validating our approach is a set of connection records for emails and phone calls obtained from the PNNL enterprise. Our data-driven, agent-based modeling approach is infused with models of social interactions between agents, producing a prototype tool that demonstrates realistic email social behaviors.

We approach datasets differently in FY 2014, whereby we moved away from generating synthetic datasets to gathering and stewarding real, semi-synthetic datasets. We archived PNNL enterprise operational data (upon approval) as well as several exercise datasets. Additionally, we hosted a capture-the-flag exercise and recorded the resultant data. We also began data curation, which included organizing a meta-data catalog that explains the types of data within each set, and defining sufficient safeguard mechanisms to anonymize and sanitize data.

For FY 2015, we plan to complete the installation of CyberNET, which will include developing additional OpenStack modules to improve the support of CyberNET when used in cyber security research. After completing the evaluation of the final cyber-user behavior modeling, we plan to use the framework for designing generalized user behaviors that researchers can use on CyberNET. Finally, we hope to validate the reference architecture network model to determine its realistic potential.
Developing Signatures that Relate Fecal Microbiome Characteristics with Gastric Bypass Surgery Outcomes

Nancy G. Isern

The methods we are developing in this project will help us understand the biology of fecal microbial communities in relationship to human hosts. These data interrogation tools will be applicable to such diverse areas as biofuel and bioproduct production.

In collaboration with Arizona State University (ASU) and the Mayo Clinic, we are exploring fecal microbiome biomarker relationships using a combination of disparate data types for anticipating patient responses to gastric bypass surgery. Our broad project goal is to advance the understanding of microbiome conditions as they relate to energy regulation and patient responses to the most commonly performed bariatric surgery in the United States, the Roux-en-Y (RYGB) gastric bypass. We are exploring the relationship between the patient fecal microbiomes and gastric bypass health outcomes and searching for biomarkers or clusters of biomarkers that relate both to the composition of the fecal microbiome and to patient health status. We intend to apply the unique tools established at PNNL (Trelliscope, Fishing for Features [FFF], PILgram, and software quality management [SQM]) to develop composite biosignatures that will allow us to discriminate patient groups, providing predictive indicators of surgical success while also offering insight into host-microbiome metabolic interrelationships.

Our effort differs from related research in three fundamental ways. First, we will use novel tools and statistical methods developed recently that have not been used previously in metabolomic studies. Second, we will leverage five different data types, where previous studies have used only a subset. Finally, we possess robust datasets with at least 10 biological replicates per subject group. We believe that our project represents a unique opportunity to apply these contemporary methodologies to a rich, combined dataset consisting of multiple data types, thus facilitating predictive systems biology not only for our immediate application but also for other systems biology research.

In preliminary work, NMR metabolomics data has been visualized in Trelliscope, which has provided quick and easy assessment of data outliers, allowing us to re-examine the data analysis and correct errors as well as assess variability among biological, process, and technical replicates. Sham data to represent 16S RNA data and MS data have been provided to the team to develop data handling strategies, and work is commencing in this area at the start of FY 2015.

The major portion of the work will occur in FY 2015. The original study includes four patient groups: 10 normal controls, 10 obese controls, 10—15 successful RYGB, and between 10—15 unsuccessful RYGB. We generated nuclear magnetic resonance (NMR) metabolomics data for most of these subjects. Shortly, we plan to acquire liquid chromatography (LC)—mass spectrometry (MS) fecal bile acids, gas chromatography (GC)—MS fecal metabolomics, and NMR fecal metabolomics on three matched aliquots prepared contemporaneously from each individual sample. In total, we will have 10 biological replicates for each of the four patient groups, giving a grand total of 40 matched samples for each of the three detection methods. Once we have the matched datasets, we will move into full-scale analysis using the integration of up to five specific, discrete datastreams: NMR 1D and 2D metabolomics; GC–MS metabolomics; LC–MS bile acids determinations; parent grant 16S rDNA sequencing data; and parent grant patient metadata.

Trelliscope will be used to explore the datasets interactively in order to search for relationships and patterns between the patient fecal microbiomes and gastric bypass health outcomes. We will also search for biomarkers or clusters of biomarkers that relate both to the composition of the fecal microbiome and to patient health status. FFF and PILGrams will be used to identify the set of analytes that can be used to optimally classify the each patient into one of the four known patient groups. SQM may be used to develop an objective function that PILGram (and perhaps FFF) would use in searching for the features. SQM will then be used to assess and compare the various combinations of features and classifiers (i.e., the candidate signature systems) used to construct an optimal model for predicting obesity in RYGB patients and controls.
Discrete Mathematical Foundations for Cyber Systems Analysis

Cliff A. Joslyn

Our goal is to develop a modeling formalism for representing state and change of state in general cyber systems with hierarchically interacting discrete mathematical models.

Cyber systems are currently modeled piecemeal and ad hoc, and unifying methodologies are elusive. Traditional modeling methods are inappropriate because in digital systems, there is the absence of space, ordinal time, energy, conservation laws, and natural metrics involving continuity or contiguity. Thus, the Asymmetric Resilient Cybersecurity (ARC) group needs to advance a comprehensive formal framework for cyber analytics built on sound modeling methods founded in discrete mathematics. The repertoire of state variables validated as significant will form the foundation for robust multi-scale models to serve analysts and decision-makers.

We seek to represent cyber systems as discrete mathematical objects interacting across hierarchically scalar levels, each distinctly validated but interacting. Expressible as complex attributed graphs and networks, our approach draws on broad techniques from combinatorics and discrete mathematics to develop metrics for resiliency in scalar levels of cyber systems. All discrete math objects are representable as binary relation systems and thus (because the most general binary relation is an arbitrary directed graph) can be reduced to graphs. Though appearing to be merely graphs, they are decidedly complex, arbitrary objects involving structured attributes, features, and constraints. While discrete representations for cyber are graph-based, they have special mathematical properties appropriate for constraints represented. In turn, these images imply novel metrics based on those mathematics.

Our focus is on Netflow traffic data structured as a graph with complex IP:Port labels, time interval edge attributes, and payload information. This inherently multi-scalar position allows drill-down to packets or roll-up to whole-network representations. We prove our approach over the VAST test data set of 69M simulated flow edges, addressing four distinct capabilities.

High performance graph exploratory data analysis. Using the Netezza platform for HPC graph management and Tableau for interactive EDA, we identify the known test threat patterns in the complex relations between flows’ IPs, ports, times, protocols, sizes, and combinations in VAST data.

Graph cubes. The complex node attributes support the ability to do hierarchical roll-up over different aspects of node structure, port numbers and IP octets. The resulting graph contractions provide reduced network views and the ability to find patterns at multi-scalar coarsened levels.

Time interval analysis. Netflow records are attributed with [begin,end] time intervals that can be ordered in three different ways by measuring the presence, kind, and amount of overlap. Series connections demand certain order relations, while edge contractions supplied by the graph cubes require and respect different orderings. Interval orders and statistics provide temporal analysis of attack patterns.

Labeled degree distributions. Each IP:Port node maps to a set of downstream IP:Ports in a Netflow graph, and the grouping of that distribution determines an integer partition. Statistical information measures on those partitions allow us to gauge the amount of grouping among IP:Port node pairs, identifying outliers and unusual patterns. Information theoretical combinatorial measures of the compression and steepness of labeled degree distributions are complemented by appropriate correlation and rank correlation measures to identify unusual structures.
Current research has explored defender roles and responsibilities; however, it has been conducted without the introduction of resilient infrastructures. What is required is to provide a foundation of understanding roles, responsibilities, and needs of cyber network defenders in resilient infrastructures. In turn, that foundation can be leveraged by new and existing research in resilient infrastructures to increase utility to defenders, minimize complexity, and assist with adoption of the technologies.

The object of this work is to advance the knowledge of how to enable defenders to manage resilient cyber infrastructures without increasing their cost (resources) to do so. As architectures, algorithms, and methods are developed to make networks resilient to attack, the network becomes more complex to manage for the defender. If resilient cyber security research is to tip the asymmetric advantage toward the defenders, it must not increase the burden on those defenders to understand and manage the network.

As Dorci is an early FY 2015 start project, we have had only a couple of months to begin investigating the impact of resilient infrastructures on cyber network defenders. During that time, we devoted our tasks primarily to designing a study that can be conducted to inform the research. A key component of the study design is finding a mechanism to have users provide feedback on systems that may or may not actually exist in the real world. From this preliminary exploration, we have had the results that are explained below.

**Importance of an initial “current state” study.** While research has been performed to evaluate the role of defenders in cyber network defense, the research does not explore resilient infrastructures. We need a study to provide a basis for further readings; therefore, an initial study will be designed to evaluate what defenders currently view as resilient infrastructures in order to help provide context for future work. In addition, questions to help the correlation between previous research will be leveraged.

**Initial resilient infrastructures study design.** Having participants provide answers and reasons about an environment that does not exist is a challenging problem. We initially planned on a scenario based semi-structured interview process to help users imagine their environment. While still a potential solution, we feel this mechanism may still be too difficult for users to place themselves in that type of environment.

Leveraging study designs typically used in emergency management and pandemic research, we are exploring the use of a table top excursive within which users will be given roles and responsibilities, activities will occur, and users will have various options for actions that they can take. By adapting the actions and the activities, we can explore various aspects of resilient infrastructures. Specifically, table-top study designs have the distinct advantage that they allow a participant to immerse themselves into the activity, which is helpful in assessing the impact of technologies that may be fictional. We are still evaluating what conclusions can be drawn from these types of exercises and whether they are a good fit for what we are trying to accomplish.

**Grounding in reality.** As part of the study design exploration process, the concept of being “far enough” into the future has been raised for the primary user study. In essence, the study should explore resilient infrastructures but needs to be believable and reasonable to defenders today. While the implementation and adoption of resilient infrastructures is not widespread, making technologies difficult to map, we do have support from other projects to help ground research in the plausible domain.

To assist with the study design, we will be looking at existing projects for insight into their research and examining what types of technologies might be built from them. Additionally, we will leverage the reference architecture and scenarios in our study design to help with a common thread across various projects in order to increase the reality of the study.

For FY 2015, we will be finalizing study designs for both the initial survey and the primary resiliency study. In addition, we will be conducting studies across several organizations, compiling results from the studies, and reporting on the findings.
Effective Representations and Optimizations for Recursive Parallel Programming Systems

Sriram Krishnamoorthy

This project studies novel approaches to represent and optimize the key characteristics of applications written as recursive parallel programs.

The era of periodic improvements in computing performance through increases in frequency has come to an end due to the constraints imposed by power density, heat dissipation, and energy utilization. This situation has led to multicore processors that exploit advances in silicon manufacturing technology by incorporating multiple processing cores within a single chip. In addition, the resulting ubiquitous parallelism has prompted an urgent search for effective parallel programming approaches. This challenge impacts all computing platforms from commodity systems with a small number of cores (such as laptops and cell phones) to supercomputers with anticipated billion degrees of parallelism.

Recursive parallel programming systems provide a natural approach to partitioning the work into subcomponents and specifying opportunities where such components can be processed in parallel. Thus, recursive parallel programming models are increasingly being considered as the solution to the parallel programming challenge faced in this multicore era. While widely studied in the broader computer science community, the adaptability of these models to various architectures and computing domains has been only preliminarily investigated.

Recursive parallel programs consist of concurrent recursive function invocations. Several useful properties such as optimal space bounds, optimal time bounds, and deadlock freedom have been proven for recursive parallel computations scheduled using work stealing. Such specifications also map well to locality domains when optimizing for data movement or mapping to streaming architectures. Despite these properties, recursive specification of parallelism, especially in terms of strict computations, imposes certain limitations in terms of the nature of dependences that can be specified. This scenario has motivated the renewed study of various additional synchronization constructs. Constructs often considered do not simultaneously extend the class of computations supported while retaining the provably optimal space and time bounds of strict computations.

During FY 2014, we studied novel approaches to represent and optimize the key characteristics of applications written as recursive parallel programs. In particular, we investigated various specifications of concurrency and program transformations to schedule such specifications. These algorithms and associated evaluation will have a fundamental impact on the design of parallel programming models for future parallel systems of all forms.

The specific tasks undertaken in FY 2014 and their outcomes for this project are described below.

Evaluation of constraints imposed by dependence specification typically supported in strict computations. We observed that strict cache-oblivious representations of certain classes of computations typically impose much greater synchronization constraints that those required by the true dependences in the computation. We benchmarked these applications in order to quantify the overheads due to the additional constraints.

Design and implementation of algorithms and abstractions to expose greater concurrency. We developed preliminary implementations of enhanced work stealing schedulers that can extract a greater concurrency from such over-constrained computations. As of the end of FY 2014, results from this work are being prepared for publication.

Evaluation of the limitations of mapping recursive parallel programs on GPUs and vector processors. We performed preliminary studies of the vector utilization achievable by recursive programs. While the straightforward vectorization yields limited benefits, we observed that a combination of algorithms can in many cases effectively vectorize such programs. The algorithms developed and the associated observations are also being prepared for publication.
Establishing a Strategic Goods Testbed to Disrupt Illicit Nuclear Trafficking

Jennifer B. Webster

This project focuses on establishing a strategic goods testbed for the disruption of illicit nuclear trafficking.

PNNL has a laboratory objective to advance the state-of-the-art in disrupting illicit nuclear trafficking. Accessing data and understanding the modern methods have proven to be challenges for researchers in this domain. One of the most promising approaches has been to leverage the current and pending investments in analytics into this complex, data-rich domain. It is believed that applying advanced analytical approaches would improve the robustness of the daily tactical analysis frequently conducted at PNNL and other national laboratories. In addition, there is good reason to expect that analytical tools could empower analysts to operate more strategically, either by assisting in new analyses or streamlining routine tasks. For the aforementioned reasons, the success or failure of the prospective work associated with the laboratory objective explicitly depends on the access to relevant data.

The overall goal of this project is intended to provide easy and appropriate access to data, schema, examples, exercises, and domain summaries.

To meet project needs and challenges specifically, we established a strategic goods testbed focused on analysis for illicit nuclear trafficking. This system is intended to include a framework that is representative of the real world operational resources used today for non-proliferation tasks at PNNL and other locations. An accurate framework is critical, as an array of policy, security, and logistical issues present in this domain are a challenge to many of the traditional analytical approaches. Aside from the framework, a cache of realistic data (either sampled from actual data sources or accurate proxies) would be required to provide accurate analysis challenges. Additionally, the success or failure of the work associated with this and related projects depends explicitly on access to relevant data.

Following discussions with analysts, sector contacts, and researchers in one-on-one discussions and a short group meeting, our project identified important data needs and took measures to provide the data in both quantity and quality. Specifically, our project grew into a PNNL-wide capability and filled a major gap in data collection. The current iteration of the testbed consists of several data sources categorized into three types: raw data from which researchers can build models, regulatory documents for the U.S. export control process, and analysis and background documents based on subject matter expert interactions and searches for ground truth examples for export control violations. We collected shipping data in the form of PIERS records, judicial information about export control cases, NAC data on the nuclear fuel industry, and financial data from Dun & Bradstreet, Inc. Our data sets continue to expand.

Throughout the year, we responded to 39 information requests for access to the testbed services from 14 active users. The majority of data requests came from challenge projects related to the laboratory objective, but we also provided information to technical specialists in export control. We also attended the International Nuclear Materials Management (INMM) conference to present on the strategic goods testbed concept. Our demonstration was well received, and we had several requests for more information and offers of collaboration.

Project plans for FY 2015 include identifying additional data sources relevant to disrupting the illicit trafficking of strategic goods and their owners (including open and access restricted sources) and access requirements or restrictions. We will obtain representative data samples using proxy data, as required. Using sample data, we will also research the suitable models and data structures, with particular attention to the distributed analytics needs specific to this domain. Additionally, we will continue to raise awareness of the testbed and the models, data structures, and sample datasets available to researchers. These domain specific models and sample datasets are likely to be a critical resource and would be of particular interest to the wider non-proliferation community for developing new analytical approaches.
Family of Resilience Metrics for Cyber Security Operations

Mary J. Lancaster

The development of operational resilience metrics will enable informed, objective cyber security decisions, cost-benefit analyses, and the development of both system resilience requirements and automated approaches to optimize system resilience.

Defining metrics for resilience in cyber systems has gained a considerable amount of recent attention. MITRE enumerates some 272 cyber resiliency metrics, including a subset that would be selected by an organization for use in a resilience assessment process. Some research provides a qualitative cyber-resilience assessment process, while others offer a hierarchical value modeling methodology for quantifying the resilience index in critical infrastructure. Although these metrics have been proposed, none has been widely adopted or made operational. An objective, reliable, repeatable basis for evaluating cybersecurity resilience is required: it facilitates discussion and decision making among stakeholders and cybersecurity practitioners, allows comparisons between system configurations, and enables the creation of minimum acceptable performance thresholds.

The resilience framework outlined in this project enables strategic, tactical approaches to enterprise resilience and facilitates discussion among stakeholders and cybersecurity practitioners regarding the necessary features and measures of enterprise resilience. The framework fills an identified gap in the literature between high-level process management and low-level control systems. The development of a resilience taxonomy also continues to foster a healthy discussion about and harmonization of terminology.

We propose the term “resilience posture” to describe the relatively persistent state of an entire IT enterprise system. Resilience posture is a high-level quantifiable system attribute that remains consistent within policy and management decision cycles. The degree to which the enterprise is configured to be resilient considers its intended purpose, its known hazard environment, its assessment of the future, and its values.

The evaluation of cybersecurity enterprise resilience requires two types of measurements. First, the system must monitor various operational conditions, which are critical to identify and respond to disruptions as well as enable a robust system. These measurements are also part of one or more observation, orientation, decision, and action (OODA) loops that fall under a spectrum of autonomy from fully automated to human-supervised. The second type of measurements include how well the OODA processes cover the critical enterprise functions and hazards to which the enterprise is exposed. The measurements allow an assessment about how well enterprise management processes anticipate, mitigate, and adapt to a changing environment. The assessment, decision, and change processes loop exists outside of this OODA control loop.

During FY 2014, we developed a theoretical framework in the form of definitions, a model, and a syntax to provide a mechanism for bridging resilience management process models (e.g., CERT-RMM) and the many enumerations of cyber-defense metrics that have been proposed [MITRE, CIS]. We also developed an initial list of measures of resilience from the literature and subject matter expert elicitation. A test plan and procedures to implement the measures within the cybersecurity testbed have also been completed.

In FY 2015, we will continue to implement measures into the testbed, evaluate their quality and combining them to develop metrics for cybersecurity resilience. A three-pronged approach will be used for evaluation: descriptive case study, low-resolution descriptive modeling and simulation, and high resolution implementation in the testbed. The resilience framework will be submitted to peer-reviewed literature. Finally, we will work closely with related projects to integrate metrics and measures into our framework that they have discovered or found useful and will share measures and metrics that may be relevant to their projects.
Fishing for Features: Discovering Signatures When the Underlying Phenomenon is Poorly Understood

Kristin H. Jarman

We are uncovering methods for finding and validating signature features for high dimensional, poorly understood phenomena that can be applied to practical areas of interest. This work is relevant to high throughput and big data applications.

We live in an age of big data that touches virtually every aspect of our lives. Scientists can quickly collect terabytes of information on everything from a single atom to a complex living organism. Search engines and social media contain volumes of individual personal data. Online databases contain scientific information, consumer preferences, business performance, economic indicators, and more. As data availability increases, researchers continue looking for ways to use this information to gain insights into increasingly complex phenomena. In this project, we are developing signatures when the underlying physical or conceptual model is weak or not completely understood while working with datasets that are too large to search exhaustively and too complex for traditional optimization methods.

During FY 2014, we focused our efforts on two projects. First, we worked on optimizing an individual re-identification modeling process using biometric features, in which we developed a methodology to re-create a biometric signature for an individual using only the features available in a probe dataset. Our second task was searching and developing spectroscopic and chromatographic signatures that can help predict important properties of bio-fuels and unconventional fuels, an area of interest to government agencies and private sector companies. In both projects, we employed a genetic algorithm (GA) to explore a vast problem spaces and created objective functions that helped the algorithm find reliable and informative solutions.

For the re-identification process, we explored a problem space with more than $8.8 \times 10^{12}$ feasible solutions, where the features are models predicting body measurements that can be used to interrogate a gallery database. The models can use only a secondary, or probe, dataset that contains features different from those in the gallery database. Our approach is able to narrow the search space using models for less than half of the body measures available in the gallery data and information from only 16% of the individuals to train the models. Our results produce better re-identification rates than other approaches that use information from all the features and all individuals available.

Our second focus area was signature discovery and development in fuels and oils. Fossil, renewable, and unconventional fuels and oils may be comprised of thousands of molecules, of which some important characteristics are related to the molecular sub-structures of their components. Structural attributes of unconventional and biomass-based fuels manifest themselves as features in high-resolution spectroscopic data. Of the thousands of spectroscopic features we can obtain, we want to understand which ones are important and how they affect the properties of interest. A methodology that can help predict physical and chemical properties of fuels based on characteristics of their components would help streamline their development.

In searching for spectroscopic and chromatographic signatures for properties of bio-fuels and alternative fuels, we implemented a greedy search algorithm to discover features that may be employed to model properties like viscosity, lubricity, and cetane number. Using a dataset for nine biofuels each with around 800 2D-nuclear magnetic
resonance (NMR) features and another with a $2^3$ factorial array containing data for nine research diesel fuels, we produced an initial set of models to use for validation. Our methodology is not deterred by the hundreds of spectroscopic features we have available, and the objective function we developed produces relatively simple models while employing less than half of the number of features available.

During FY 2015, we will expand the use of our approach to datasets with new features and new biomass and research diesel fuels. The features will include high-resolution spectroscopic data like 2D-NMR, 2D-gas chromatography ($GC \times GC$), and Fourier transform ion cyclotron resonance mass spectrometry. We will iteratively select features, quantify performance of our methodology, and evaluate the applicability of our models. This setup will allow us to establish the strengths and weaknesses of both our models and our modeling approach, enabling us to achieve a better understanding of how spectroscopic features are related to the favorable properties we seek.
Many phenomena of interest are detectable only by measuring large hierarchical systems of distributed multi-type data. As these systems continue to grow in both size and complexity, the rates of data generation are likewise accelerating. This combination of system size and complexity, along with accelerated data-generation rates, presents a significant and compelling disruption for signature detection tasks. More specifically, these types of tasks in hierarchical systems are increasingly failing, not because of a signature’s inability to detect an event accurately, but because of the inability to process data and detect the event within the critical time requirements. Conventional analytic systems fail to address this problem because they use algorithms that require data to be collected, aggregated, and then processed at a central location. In this context, data bandwidth limitations become a bottleneck that increase the time it takes to process and detect events of interest.

This project presents a statistical framework for signature detection based on three methodologies that will readily scale to hierarchical systems. First, we use genetic classifiers to detect precursor events in data at individual nodes in the hierarchical system. These precursor events are the key processes or activities likely to (or must) occur prior to the primary event. Second, we extend these classifiers with information fusion approaches that can combine and propagate the evidence generated by these classifiers to higher level nodes in the hierarchy. Finally, we use this evidence to drive a predictive capability based on conditional random fields (CRFs). With this new framework, our work presents a method to be performed in parallel as a set of smaller, intermediate detection tasks. This predictive component leverages all existing evidence to assess the probability that the primary event will occur, thereby creating early situation awareness that will cue contingency and mitigation actions in the hierarchy.

In FY 2013, we completed the design and implementation of all three components in our statistical framework, including the realization of the theory as working code. Both the framework and its implementation were validated with tests that used synthetic data to assess the ability of our approach to: 1) detect precursor events across nodes in the hierarchy based on genetic classification; 2) aggregate and propagate classifier-based evidence throughout the hierarchical system; and 3) leverage propagated evidence to predict successfully that an event will (or is beginning to) occur. The test results indicate that the framework can detect events much faster than conventional systems: the framework reduced the mean detection time for events by approximately 86%, compared to conventional detection methods.

In FY 2014, we applied our detection framework to simulators modeling the Belle II experiment’s iTOP detector. Our results improved classification accuracy for particle identification tasks by 20% compared with state-of-the-art approaches. Additionally, we tested our methods on simulated network data to detect hidden networks in social communication. In these tests, we showed that the Hierarchical Signature Detection framework reduced the amount of data needed to detect the hidden networks by six orders of magnitude.

The Hierarchical Signature Detection Framework is now being considered for detection tasks across a wide array of application spaces, including early disease detection in animals, detection of SNM-shielding material, and hidden networks in social media.
High Speed, High Volume Data Acquisition and Annotation System for TEM Instruments

Kerstin Kleese van Dam

This research seeks to improve the data acquisition process currently used by transmission electron microscope (TEM) systems to support improved analysis capabilities and the higher data volumes expected to be produced by systems such as the dynamic TEM (DTEM) currently under development at PNNL.

The DTEM enables a large pulse of electrons to be generated by photoemission and then manipulated in the microscope to form high-resolution images. It is the generation and manipulation of this short pulse containing a large number of electrons that enables the transient process being studied to be imaged in a single shot, permitting very fast, irreversible phenomena to be studied in detail for the first time. Current TEM systems create around 1000 images/day; however, the new TEM systems are expected to rise to 100–1000/sec (~ up to 2 GB/s) images/sec in the coming year, with a further increase to 20,000 images/sec (40 GB/s 1K × 1K images) expected in the next 2–3 years. Today’s data acquisition systems for TEM instruments such as SerialEM or Leginon were designed with much lower data rates in mind, generally working in serial on single PCs on one data stream at a time. As a result, they are unable to cope with the increasing data volumes, so a new data acquisition architecture is required. The fastest cameras currently using the Leginon system collect data at a rate of (4 × 4 k images) 40 frames/sec.

Other experimental communities have addressed high-speed data acquisition over the years, chief amongst them is the high energy physics (HEP) community. These HEP data acquisition architectures consist of custom built hardware and software, including complex event trigger systems to filter selected data; high performance, high throughput data systems; distributed storage systems designed for big data; and a distributed compute grid for post-processing and analysis.

This project will build on experiences gained with high data rate acquisition in single science instruments such as the Large Hadron Collider experiments and moderately high multi-science instruments such as those currently being developed for the Linac Coherent Light Source, which is the first of its kind X-ray Free Electron Laser facility, to design an improved data acquisition system for the DTEM. While the initial demonstration will be for TEM instruments, it is envisaged that the resulting system could be customized for other instrument types with high data rate requirements.

In an initial step, we investigated the inherent limitations of the existing in approaches in software (Leginon) and hardware. In this approach, we found that the software is bound by hardware bottlenecks that limit the data transfer rate. Existing systems cannot support more than ~ 4 frames/sec. Possible solutions include implementing a faster networking solutions: 10 Gbps, 100 Gbps, or 10 × 100 Gbps = 1 Tbps. In our tests, we successfully deployed a working instance of the Leginon system with a simulated data flow between a Windows computer (representing the microscope computer) and a Linux box (representing the server for data processing, storage and database). The simulations were also implemented between the same Linux box and two computers, one controlling an actual Jeol JEM-200F microscope and the other controlling two cameras (Gatan Orius and Gatan GIF). Leginon provides an ideal platform for customizing the metadata captured from the instruments.

Further research focused on software and hardware approaches to reduce the actual data volume that is collected, transferred, and stored without reducing the accuracy of the experimental results. For this situation, we initially investigated the benefits of applying zero-suppression and clustering algorithms to reduce the outgoing data volume. Based on available simulated images, we determined that the images can be reduce by one to two orders of magnitudes. In addition, the data rates can be further reduced by using the zero-suppressed results as a trigger to record the data. Using the same simulated samples, we were able to trigger clearly on each image and reject images that did not change. This scenario would allow to automate data acquisition, reducing data volume before and after interesting events.

A common hardware platform used for real-time data processing in the HEP community are field-programmable gate arrays (FPGA). These programmable hardware devices are capable of accepting and processing high-rate data streams by handling the data in a highly parallel fashion. For example, a 40 Gb Ethernet receiver as implemented in a high-end Altera FPGA presents the high-speed serial data stream to the FPGA logic as a 256-bit wide pipe at 320 MHz. In the FPGA, that 256-bit pipe can be subdivided into separate blocks of data and independent zero-suppression operations applied in parallel, meaning that each processing block needs to run at only a fraction of the incoming data rate. Greater subdivision of the data pipe could allow greater manipulation of the data, although there is a tradeoff with available resources in the FPGA.

As a proof-of-concept test, a zero-suppression routine that calculates differences between adjacent 10-bit pixels was converted to a pipelined version that performs operations in...
parallel, allowing 1 pixel per clock operation. This design was then synthesized for a high-end FPGA device, and an expected maximum data rate of ~ 750 MB/sec was reported. This finding implies that the zero-suppression routine could easily keep up with the data rate from the 40 GbE pipe described above. More importantly, increasing the data width in the zero-suppression routine will not directly affect the processing rate in an FPGA for smaller data sizes, meaning that larger multi-pixel chunks of data could be processed without slowing down the process, which would require fewer zero-suppression blocks.
High-Level Modeling Specification for Simulation of Control Systems

David Callahan

We are accelerating the development of next generation tools by evolving control theory and applications and working with control theorists and simulation developers to capture novel elements of successful control of complex systems.

A key aspect of effective tool design is to understand what is required for the user to be successful. In many areas of design and engineering, such an understanding is captured in a pattern language that captures good design practices. While broadly used to teach design skills and communicate successful design, we capture pattern languages directly into tools, frameworks, and literally in high-level specification languages in computer science. When appropriately designed, these specification languages guide their users to successful solutions as well as lead tool designers to features that reduce the cost and improve the reliability of designs even when made by comparatively novice users.

Prosser, the project name assigned to this project, is a language to support specification of complex systems of interacting components. The primary use case is to support experimentation with control mechanisms. In the development of new control mechanisms for complex systems, it is common to use simulators or emulators to run experiments to evaluate the behavior of the control mechanism. While there is a range of strategies, Prosser focuses on the scenarios in which the following situations occur:

- A system is described as a collection of components where each component has internal state, consumes input signals, and produces output signals.
- Once elaborated, a system may be simulated to determine how the state of the system evolves over time.
- Each component is implemented by an execution host, typically a discrete event simulator or possibly a hardware emulator or hardware embodiment.
- Assumes a coordination framework of some sort exists that mediates the global notion of time and implements inter-host communication.

We anticipate the need to generate hundreds of thousands to millions of components to form a system with multiple experiments that vary the structure of the system. Today, such experiments are often run by using a programming environment such as MATLAB or Python to generate input configurations for discrete simulators. Prosser will subsume this step in the workflow and provide stronger design-time validation for the elaborated system.

A Prosser script is a program that elaborates system components, their communication interconnections, the set of execution hosts, and the mapping of a component to a host. After this elaboration, the implementation of Prosser generates suitable configuration information for each execution host and for the coordination framework. We refer to this step in the workflow as system elaboration to distinguish from simulation. Components may be specified as external components (those coming from the existing tool libraries) or Prosser components (those components defined directly in the Prosser language).

In addition to describing components, the Prosser program includes an explicit portion that algorithmically elaborates the system graph. This portion involves a sequence of primitive operations which instantiate execution environments, components, and performs arithmetic to determine properties of components and to govern control flow in the elaboration. The set of statement types is typical for imperative programming languages and should be easy to learn for anyone familiar with programming.

The Prosser team took the initial steps in developing this ambitious domain-specific language. Our first year goals were accomplished. The basic domain-specific language concepts were developed, and a prototype tool was created. Use cases, including a representation of the AEP gridSMART Real-Time Pricing Demonstration project, were identified, and basic components and methodologies were extracted. A basic Xtext-derived editor was created to manipulate the models and provide early type checking and structural validation. GridLAB-D library components were added to the language to bootstrap using prior experience and extending this to new test bed.

A key outcome of this work will be to understand the new design patterns and requirements that they place on the evolution of existing tools or the creation of new tools, plus to capture these new design patterns in a high-level specification language. The life-cycle of this specification involves an iterative process of design, experimentation, and evaluation. As confidence is gained, the test environment will evolve to include greater accuracy or support more sophisticated scenarios including scenarios with large numbers of components. Each change will impact various elements of the specification, which introduces additional complexity to ensure various cooperative elements continue to have consistent views of interaction protocols.
KRITIKOS: Identifying Cyber Assets and Assessing Criticality in Terms of Business Processes

Thomas E. Carroll

KRITIKOS provide continuous, (near) real-time enterprise introspection for discovering cyber assets, identifying the functional relationships and dependencies between assets, and assessing the importance of the assets to business processes that they serve.

Computer and network operations and cyber security focus on information communication and technology are largely naive of an enterprise’s manifold business objectives and processes. The lack of business operations information hinders the defenders’ sense making, assessment, and management of situations. Current practices for identifying assets and mapping functional relationships are generally characterized by laborious, time-consuming, and error-prone processes that are difficult and expensive to deploy in large, dynamic enterprise environments. By linking business processes with their supporting cyber assets, KRITIKOS enhances cyber defenders’ awareness and improves the quality and speed of situation assessment and management that align cyber security with the objectives of the enterprise.

KRITIKOS functions as follows. A network model of the functional associations between services is constructed by discovering recurring spatio-temporal patterns in the NetFlow record set which, with its derivatives, are embedded instrumentation for the collection, characterization, and export of network traffic flow information and statistics. These recurring patterns arise from human-initiated machine-to-machine interactions that occur in the everyday operation of the enterprise. A business model that has processes annotated with essential services is correlated to the network model to identify other process essential assets. Asset criticality is then measured as a function of business process importance.

Our work in FY 2013 focused on developing a self-organizing map (SOM)-based algorithm to discovery recurrent temporal patterns within NetFlow. These patterns indicate functional associations. A functional association between a service A and service B arises whenever A and B are accessed. These associations arise because of graph associations observed as paths in a graph (a service A depends on a service B and communication is observed) or as temporal associations in which the graph of communication does not provide for a path between entities but does recur in time (services A and B perform function in time). SOM is a cognitive-inspired, unsupervised neural network machine learning algorithm that “clusters” and “generalizes” by spatially organizing similar data in neighborhoods and dissimilar data in different neighborhoods. Limited testing on the CyberNET testbed showed promise.

During FY 2014, we began exploring recurrent spatio pattern properties of the NetFlow data. We designed a deep learning workflow to extract the patterns that coordinate multiple machine learning algorithms. The work flow begins with NetFlow data windowed and discretized. The input is provided to a SOM, which identifies potential patterns. After labeling landmarks within the SOM output, hierarchal clustering, and decision support trees are used to robustly extract association patterns. Limited evaluation of the approach demonstrated greater applicability on the datasets generated in the previous year. We noted in the results that the output of SOM can suffer from low signal-to-noise ratio. To improve on the quality of results, we introduced in the pre-processing a method to compute the co-occurrence (or co-existence) of flows contained within the datasets. Instead of presenting individual flows to the SOM, co-occurrence combines flows with close temporal proximity together and creates a new “alphabet” with greater abstraction. Evaluation for this new step is planned for FY 2015.

Another effort from FY 2014 was investigating business modeling and business operations methods to assess criticality of business processes. Networks exist to serve business; thus, business should inform the criticality of the network and its constitutes. We elicited the support of internal business operations and modeling experts, and examined the business processes of PNNL. We discovered that a universally agreed upon measure of criticality does not exist and, furthermore, the measures that do exist are largely nominal and ordinal level of scales. While the measures can be ordered, they do not support basic algebraic operations such as addition and subtraction. Given the limits of measurements, we developed an algorithm that can compute criticality over the structures computed by the functional association discovery phase. Once criticality is assigned to a node, criticality then flows to the dependents.

Our plan for next year is to investigate multi-scale dependencies, which those expressed through the business model such as employees, customers, or users of the services. Much work already exists based on knowledge elicitation. We would investigate methods to discover automatically without explicit elicitation. Additionally, we plan to implement a proof-of-concept of the dependency method and demonstrate its applicability within the CyberNET testbed environment.
Leveraging Power Grid Contingency Analysis Techniques for More Resilient Cyber Networks

Patrick S. Mackey

Our aim is to leverage the contingency analysis concept as it has been developed for power grids and apply the technique to cyber networks so that the technique is practical in real world situations.

Although many metrics have been proposed to quantify the current “health” of a cyber system, few examine how resilient that health remains when one or more potential contingencies were to occur. Because computers and accounts are often compromised (many times without the operators’ knowledge), it is important to know if the system remains healthy despite these compromises. Power grid operators use a technique called “contingency analysis” to deal with this. Our goal has been to apply this basic concept to the cyber domain to determine whether systems can be made to be resilient against potential contingencies before they occur, giving a potential asymmetric advantage to the defender.

Our research began with building an availability approach to cyber contingency analysis that was highly influenced by the practice of power grid contingency analysis. The cyber system was treated as a graph, where nodes are computer, servers, routers, software, and resources; and edges are data connections between nodes. Nodes were assigned a value based on the importance of their functionality to the enterprise. Additionally we developed a concept called the “mission critical path.” Each business has many mission critical paths which are defined as pairs of nodes in which a path must exist to support a mission need. Each of these paths was assigned a value based on its importance. Lastly, each system had a list of contingencies, which in our case were nodes that might become compromised. Each of these contingencies also had a probability assigned to it.

To perform this availability contingency analysis, we iterate over each contingency node and remove it from the graph. We then check to see which mission critical paths can no longer be made in the network. We add the value of the node removed and the paths broken to determine a severity score for that contingency. Likewise, we multiply the probability of the contingency by the severity score to yield the risk score. The sum of all the severity scores becomes the collective severity score, which represents the resiliency (or lack thereof) of the entire system. The sum of all risk scores likewise becomes a collective risk score. These values can then be used to compare against hypothetical alternative configurations of the system to see if there is improvement, allowing for a similar type of contingency analysis to what is currently done for power grids.

We implemented the algorithm to perform this contingency analysis in C++ on a standard Windows PC. Input is CSV files containing the pertinent information. Each possible combination of contingencies can be performed to see if removing two (or more) nodes at a time causes different issues than simple single node failures. Our initial implementation had a time complexity of \(O(n^{k+2})\), where \(k\) is the number of simultaneous contingency combinations. By developing a faster algorithm, we reduced the time to \(O(n^{k+1})\), which allowed for dramatic speed up. Additionally, the new approach allowed for greater parallelism than our original method.

In addition to our availability contingency analysis, we developed approaches for confidentiality and integrity. For this kind of analysis, we treated user accounts as the contingencies. Files containing information that would be sensitive to confidentiality concerns are marked as confidential, while files containing information that would be sensitive to integrity concerns are marked as integral. Each user account is calculated to see which confidential files they have read access to and which integral files they have write access to. The number of sensitive files is summed up for their respective confidentiality or integrity severity score. Likewise, a probability of account compromise can be used to calculate a confidentiality or integrity risk score by multiplying it by the respective severity scores. As before, collective severity and risk scores are calculated by the sums of the scores for individual contingencies. By experimenting with user and group permissions, an operator can reduce the collective severity scores for confidentiality and integrity concerns to improve resiliency of the system against one of its accounts becoming compromised. The less damage that any particular account might provide, the more resilient the system should be against attacks.

A version of our confidentiality and integrity approach was implemented that can be used by users on their own personal systems. This system looks at all the users who have...
logged in as well as all the groups that exist on it. It can then provide the risk and severity of each account as well as the risk and severity of the groups to which the users belong. An analyst can use this information to discover why a particular account is more risky than others and determine the best mitigation. The tool features a user friendly interface to make it easier for staff members wishing to test this system. Our hope is to see whether this tool can be used to prevent real confidentiality and integrity concerns at PNNL by the users who test the software.

Finally, we began creating a scientific experimentation plan. We composed a document with our initial experiments to show that the severity scores for our availability approach really do correspond with negative state of the network under stress, utilizing Chimera’s CORE simulation tool, as well as some of the measures being catalogued by a related project. We anticipate commencing experimentation in early FY 2015; if successful, we will begin creating methods that will help to validate our confidentiality and integrity approaches.
M&Ms4Graphs: A Multi-Scale, Multi-Dimensional Graph Analytics Framework for Cyber Security

Sutanay Choudhury

This project is delivering a set of scalable, uncertainty-aware, multi-scale graph analytics tools for cyber analysts and mission defenders.

The current approach toward mission assurance and cyber defense is primarily reactive. Automatic discovery of critical missions and their relationships with users, applications, and the physical infrastructure is a major challenge. Thus, chartering the response to a security incident is a manual process with high complexity and uncertainty. Also, a cyber system is constantly evolving and generates prodigious amounts of data. Thus, a scalable framework to provide continuous updates of the system state in terms of important security metrics is absolutely critical.

This project is taking a graph theoretic, data-driven approach toward modeling the dynamic behavior of a cyber system at multiple scales that range from a single machine to an entire enterprise. The models will provide continuous metric based updates to provide situational awareness and enable a system that is resilient by design. Specifically, we are modeling the key behavioral aspects of an enterprise by studying the information flow across hosts as large-scale, dynamic graphs. We adapted a novel, multi-scale approach for continuously updating the graph-based model with local information and enable very fast computation of essential security postures and cost/benefit metrics. By accounting for both the connectivity structure of the graph (who talks to whom) and the attributes of the communication (using which protocol, how often, and for how long), we are able to create a comprehensive model that describes the behavior ranging from micro- (host level) to macro-scale (enterprise level).

We developed a network-of-networks model to represent heterogeneous cyber datasets and motivated a multi-scale approach for cyber modeling. We also established our formal foundations for multi-scale graph models, a variant an existing algorithm, and created specific algorithms on probabilistic methods for reachability. Our preliminary data structures and the test suite were developed and included simple synthetic test cases and examples. We established our build framework, which consists of the unit test framework, preliminary test cases, and code scaffolding.

Additionally, we developed a graph analytics framework for multi-scale modeling of cyber systems. This software was demonstrated at a high visibility conference mid-year. Our presentation received particular interest from the financial security domain, including representatives of a venture capital company and strategists from the Federal Reserve System.

Our OpenMSG version 0.5, an alpha version of the software framework for multi-scale and -dimensional graph analytics of cyber data, was released. Functionality included basic data structures and preliminary algorithms for reachability or the shortest path. We demonstrated simple functionality on a limited use case set after specific cases were identified. Over the last year, we have presented at four conferences and have had our work published in both the SIAM Journal on Discrete Mathematics and a special issue of the international Journal of Machine Learning Research.

For FY 2015, we will strive for validation of graph models with respect to domain use cases. We will also work toward validating the utility of our metrics with respect to asymmetric resilience. Finally, we will integrate our analytics framework into the reference architecture being developed internally.
Making MLSTONES Cyber Ready by Completing ScalaBLAST 3.0

Elena Peterson

The MLSTONES project has already applied bioinformatics techniques to solve cyber security problems. MADBLAST provides the means to apply these techniques at scales that will enable MLSTONES to become truly effective in an operational environment.

ScalaBLAST was at the core of the MLSTONES project. Cyber data is quite a bit larger than regular protein data, and its processing can be resource intensive. ScalaBLAST allows users to maximize high performance computing to enhance the process of running thousand to millions of protein comparisons. However, ScalaBLAST is still constrained by the current open-source legacy BLAST code distribution. In the cyber arena, we have refactored that code to handle different constraints (scoring matrices), bigger alphabets, and different underlying statistics while maintaining robustness and performance. Internal work has provided the start to creating a more generic BLAST tool now called MADBLAST. However, testing on non-biological data revealed that our refactored implementation requires performance optimization, thorough testing, and a thorough set of documentation and installation tools on non-biological data to be deployable to potential clients.

Completing and optimizing refactored BLAST and parallelizing it will provide the MLSTONES project with the ability to control the BLAST algorithm in key areas. It would provide a totally transparent, PNNL-developed plug and play architecture for using new scoring matrices, offer a much larger alphabet (~100), be optimized for non-biological cases, and perform and scale as necessary for cyber security data. Once we have a fully functional and optimized version of MAD-BLAST, we can apply the MLSTONES tool suite to numerous cyber domains. This update to a critical piece of software will offer backbone to deploy the MLSTONES tools into external enterprises. Current interest from commercialization partners would also be bolstered by this development. The resulting documentation, testing, and installation tools will enable us to market the MLSTONES tool suite as a set of deployable tools ready for piloting and/or operation.

We began with the refactored BLAST code that removes dependence on biology-based statistics. We extended our base to use the open source messaging platform ZeroMQ to parallelize the code and created new algorithms for managing data, distributing jobs efficiently, and wrapping up the output to a usable form. The code now works on any slurm based cluster or other Linux-based machine (i.e., Macintosh). The scaleup is linear based on the number of processors, an improvement over previous attempts in ScalaBLAST 2.0. The overhead is negligible in all cases, providing the scalability needed to deploy MLSTONES successfully in a cyber environment and could benefit bioinformatics, as they need to handle additional data.

We successfully augmented the MADBLAST tool to perform well on many types of data sets. Through our testing process, we found a number of issues with the current implementation that prevented the code from running optimally as well as small implementation bugs to fix. Specifically, we discovered a problem that can occur when most of the work is complete but a number of long running jobs are open, causing idle resources that remain allocated but not used. To avoid this waste of resource allocation and time, we created a new algorithm that can detect this problem and re-distribute the remaining work effectively. Additionally, we optimized memory management to support the large-scale parallel processing, resulting in more reliability because it allows for any length of sequence to be processed. In previous implementation, long sequences would fail; this approach improved reliability for cyber because the data are usually much longer than in biology.

In FY 2015, we plan to develop and implement our deployment strategy. We will provide easy to install software and a full documentation suite based on various possible hardware architectures. We will also publish our findings to both bioinformatics and cyber audiences.

A visualization of how the cores are used to help inform our analysis of performance. The top graph shows that the process starts executing tasks and engaging more cores to complete them; as the tasks complete, the usage of the cores decreases. The bottom graph shows example usage of two individual compute nodes.
Manifold Learning for Accurate Search and Locate Tasks

Elizabeth R. Jurrus

We are developing an improved method for classifying images from a data set given a set of example images, a challenging problem due to the changes in lighting, shape, and scale of natural images.

The community at large is experiencing a rapid growth of data from airborne motion imagery and full motion video. The most accurate method for detecting objects of interest in these immense datasets is through human analysis. However, real-time detection of events in large image datasets is impossible. Therefore, there exists a significant need for automated methods to help analysts perform accurate, content-based image retrieval in large image datasets. Techniques for video analysis and image retrieval can vary depending on the task. Most algorithms in video analysis focus on continuous visual event recognition in realistic scenes, which is difficult with the changing nature of individual's poses, appearance, and size. In addition, backgrounds for objects under surveillance can change along with lighting and occlusion. Similarly, image retrieval problems suffer from the same constraints without the time component.

We are developing a set of algorithms that will create models of image data, enabling classification of objects in image datasets (e.g., video surveillance data). Given a set of images that can be used to train our algorithms, we will build a description of the data in the images. This scenario becomes our object model and enables searching for similar models in unseen images. Collectively, we will create an image processing pipeline with the following components: feature detection, selection of appropriate feature vectors (to describe the data), correspondence selection (to align shapes), shape modeling, and classification (with a manifold learning algorithm).

We believe that analyzing the data using a shape-based manifold learning algorithms to learn a low-dimensional subspace or manifold of the original feature space will better capture the variability inherent in these datasets. This learned manifold may be nonlinear, providing greater flexibility to explain complex data variations. Additionally in this framework, the image retrieval issue is reduced to a lower-dimensional search within the learned manifold rather a search in the original high-dimensional data space. We are testing our method on the Caltech bird dataset that contains 200 different classes of birds, and we plan to demonstrate this idea by learning a model that better distinguishes bird species.

The most progress was made on feature detection, feature extraction, shape analysis, and the correspondence problem parts of our pipeline. With these tools, we are in a good position to generate improved classification rates over what is found in the literature. The following sections describe these areas in more detail.

Feature detection. We experimented with many of the current commonly used feature detection algorithms reported in the literature, including SIFT, SURF, Kadir-Brady, and Harris corner detectors. These computer vision feature detectors are based on responses to some type of image filters (typically gradients or second derivatives). We found that these techniques tend to return points of interest that contain high amounts of clutter, and we hypothesize that these contribute to the low accuracy rates in the literature. Alternatively, there has been recent work on learning features directly from images themselves, with the idea that such features will be a better match to the data. However, the features suffer from a deficiency, as they are not invariant to simple image transformations such as rotation. To address this issue, we formulated a dictionary learning algorithm that is invariant to rotations and scale, which showed improved classification rates for the Caltech bird dataset: no rotations (16%), with rotations (27.6%), and rotations and scaling (33.8%).

Correspondence assignment. We additionally investigated a novel approach to handle correspondence between unordered features in images. Rather than find optimal correspondences between features, we are treating correspondence as a latent random variable that should be integrated out. A naive approach to solving this issue requires summation over all possible permutations, which is intractable. Finally, we are developing an algorithm for learning models from “scrambled” data (i.e., features in arbitrary order), a common property that comes as output of an image feature detector (e.g., SIFT). Another property of such computer vision feature detectors is that they return false positives or clutter that is not part of the object of interest. Our method handles this problem by probabilistically assigning features as foreground or clutter. The algorithm is scalable to large numbers of features by efficiently sampling high-probability correspondences instead of solving the exact combinatorial matching problem. Our current tests on simulated data show that our method can produce promising results, and we are exploring ways to apply this to real image data.
Shape classification. We added shape to our model for bird classification by computing the distance kernel of the given segmentations in the Caltech birds dataset followed by classification using relevance vector machine. Using nine classes and 36 pairwise comparisons, we obtained the following results: dictionary features alone (39%), global shape alone (38%), combined (51%). The combination of using local features (dictionary elements) with shape indicate an improvement over using only local.

Unsupervised image clustering. We experimented with two types of clustering algorithms to evaluate the usefulness of texture and shape features for unsupervised clustering. First, using the features from the dictionary learning, we experimented with K-means, the Gaussian mixture model and spectral clustering to group images based on texture. Separately, we used isomap to project images using texture and shape into a 2D plot. We found that clustering based on texture and shape produced promising results, and we are considering the combination of these techniques with an active learning algorithm.

Over the last 2 years, we developed a suite of tools for the classification of image data. These techniques can be extended to video frames or natural image datasets to automatically classify objects. We anticipate extending this work by incorporating our learned image features into an active learning framework to leverage applications in which training data is limited to broaden our impact.
Multiscale Modeling and Uncertainty Quantification for Complex Non-Linear Systems

Alexandre M. Tartakovsky

Our research is creating novel dimension reduction methods for large-size, non-linear systems of deterministic and stochastic equations, leading to an explosion of results in mathematics and various engineering and science applications.

The accurate modeling of most natural systems is still beyond our computational capacity. At the same time, we have witnessed a tremendous increase in our ability to obtain accurate and detailed measurements for many phenomena (from the very large to the very small). Data assimilation for the improvement of predictions is a subject of intense research, and it will remain so. However, it is not the only way in which our capability to obtain vast amounts of data can be used. There are two connecting concepts between the simulation and data disciplines: scale dependence, which postulates that the strength of interactions depends on the scale at which we probe a system; and renormalization, which allows us to use scale dependence to estimate the strength of interactions in our models so that they reproduce certain experimental results. Both concepts have served the high-energy physics community well by providing the backbone for many striking achievements. Our hypothesis is that a similar approach will be equally effective in the field of scientific computing.

We will develop several multiscale models for complex non-linear systems. Our general idea is that one needs to exploit as much as possible the inherent structure of a problem before engaging in computations. Features such as time and/or scale separation, variable and component dependencies and randomness should be used as guides in order to reduce the actual computational work. At the same time, the need and usefulness of the elegant formulations that encompass many different cases should not be ignored: they allow us to view the big picture, make connections between seemingly unrelated subjects, and serve as starting points for controlled approximations. Specifically, we will use a data-driven renormalization analysis to derive reduced models for the problems described by non-linear partial differential equations (PDEs, such as the Navier-Stokes flow equations). We will use the data-enhanced model estimation techniques to construct models for complex biological systems. Additionally, we will develop a multiscale Lagrangian model for multiphase flow. Finally, we will use the large eddy diffusivity closure to obtain reduced closed-form equations for the probability density function of the stochastic advection-diffusion-reaction-equations.

Previously, we used the concepts of scale dependence and renormalization for detection and tracking of singularities of time-dependent PDEs. For most real-world problems, however, one is interested in tracking solutions that exhibit high complexity but are not necessarily singular, such as vortices in turbulent flows. These highly complex structures are characterized by spatial and temporal intermittency. To follow these ideas accurately, we need to focus our computational resources on different parts of the domain at different instances. In short, this situation requires a model that is flexible and easily adapted to the evolving conditions. Thus, we expect the relevant renormalized coefficients to be time-dependent, though it may be a challenge for where are we will obtain information needed to adapt the renormalized coefficients. We propose to use experimental data as the source of this information.

The theoretical challenges in modeling multiphase flow are the presence of non-physical singularities near the fluid-fluid-solid interfaces and the dynamic behavior of the contact angle, which is a result of fluid-fluid and fluid-solid molecular interactions. While the fluid-fluid interactions can be represented in terms of hydrodynamic variables such as fluid density, pressure, and velocity, there is no accurate description of fluid-fluid-solid interactions on the hydrodynamic scale. Therefore, constitutive relationships are required to describe the dynamic contact angle as a function of the magnitude and direction of contact line velocity. Existing empirical models are accurate only for a small range of flow conditions such as small Capillary numbers. For complex systems (i.e., multiphase flow in natural or engineered chemically heterogeneous porous materials), the dynamic behavior of contact angle is unknown; therefore, phenomenological models for these issues cannot be constructed.

To combat the above issues, we are developing a predictive model for complex flows that does not require prior knowledge of the contact line dynamics. The second objective is to develop a model that is computationally efficient, accurate, and avoids the stress singularity. To achieve these objectives, we will develop a multiscale model by combining Lagrangian grid-based (e.g., Lagrange Finite Elements) or particle-based (smoothed particle hydrodynamics [SPH]) discretization of the Navier-Stokes equations with molecular type interactions. We will also incorporate random (thermal) fluctuations into a multiscale model, which will make the multiscale model applicable to study the behavior of complex fluids (e.g., colloidal suspensions), thin wetting films, and contact line dynamics. The research in this task will be separated in five subtasks.
Previously, we proposed a multiphase model based on the SPH discretization of the Navier-Stokes equations. The boundary conditions, prescribing surface tension at the fluid-fluid boundaries, and contact angle at the fluid-fluid-solid interfaces are replaced with pair-wise molecular-like forces. Through numerical experimentation, we demonstrated the accuracy and efficiency of the model. The main (and fundamental) deficiency has been the need to calibrate the model with respect to macroscopic parameters such as surface tension and contact angle. Also, the effect of the added forces on the solution of the Navier-Stokes equations away from the interface has not been well understood. To eliminate these deficiencies, we will develop theoretical relationships between molecular type forces and macroscopic fluid properties such as pressure, surface tension, viscosity, and contact angle with and without thermal fluctuations. Expressions of this type have already been derived for the molecular dynamics method, and these expressions will be extended to the multiscale SPH method.

Our preliminary results show that due to the smoothness of SPH forces, many of these expressions can be estimated analytically, resulting in the closed-form relationships between the pair-wise forces and the surface tension and contact angle. The relationships between the pair-wise forces and pressure and viscous stress will be used to guarantee that far from interfaces the simulations reproduce the appropriate single-phase hydrodynamic behavior. In addition to the SPH discretization, we will investigate alternative Lagrangian grid-based discretizations of the Navier-Stokes equations, including Lagrangian finite volume and finite element methods, which may increase numerical accuracy of the proposed multiscale approach.
Network Analysis and Modeling of Illicit Nuclear Trafficking

Steven F. Bradley

The illicit nuclear trafficking threat faces every nation and the mission to counter this threat spans international and domestic agencies. This project developed a general framework to understand how illicit nuclear trafficking can occur, identify the essential activities that non-state groups must undergo to develop improvised nuclear devices, and assess the progress by any group toward that goal.

The threat of illicit nuclear trafficking is an issue faced by every nation, and the mission to counter this threat spans international and domestic agencies. Current international and domestic programs exist to secure nuclear material at its source as well as detect and support interdiction of illicit materials in transit. Illicit nuclear trafficking networks can lead to nuclear proliferation as state or non-state actors expand their ability to identify and acquire expertise, technologies, components, and materials related to nuclear weapons. The ability to characterize and anticipate the key nodes, transit routes, and exchange mechanisms associated with and utilized by these networks is essential to influence, interdict, and disrupt the functions and business processes of these networks.

Complex paths hide transaction networks and individual perpetrator's identities and make detecting an illicit trafficking activity very difficult. These transactions may individually look normal, but when linked together indicate evidence of malicious activity. In this way, illicit trafficking activity paths are easily hidden among vast transaction records.

During FY 2013, we developed a conceptual model for illicit nuclear trafficking to decompose the problem into concrete activities that could be performed to conduct trafficking and enable an adversary to construct an improvised weapon. The model was used to construct three scenarios for adversary activities, which collectively formed an initial set of task sequences. The vision for this model was supporting estimates of future activities and directing information-gathering resources to improve the estimates and support the disruption of adversary activities. In addition, an inference model was developed based on the activities defined in the conceptual model, which uses evidence-based reasoning (e.g., the Dempster-Shafer decision theory) to connect hypotheses with evidence to assess group “readiness.” This information is then fused through hypothesis weights and confidence of existing evidence. In addition to the conceptual model, an object model was developed to support future analysis efforts of illicit nuclear trafficking. This object model specifies the individual entities and relationships that are meaningful for the illicit nuclear trafficking problem.

Existing work on non-state illicit nuclear trafficking is limited. Historical incidents are scarce, and the information surrounding these incidents is equally rare. This problem requires a systems approach—this viewpoint frames our entire approach to the problem. We developed a method to integrate direct and indirect information about the problem to estimate the degree of activity and identify sources of additional information that can be used to strengthen these activity estimates in the future.

Our objective for FY 2014 was to develop mechanisms that enable early detection of illicit nuclear trafficking in order to thwart adversary goals of developing an improvised nuclear device. The models help identify plausible methods of material and
component acquisition and device development. Signatures can be constructed from indicators and observables to detect and identify nascent illicit nuclear trafficking activities. This scenario allows earlier detection of emerging or ongoing threats by non-state groups. We used subject matter experts (SMEs) and historical case studies to decompose the problem and characterize activities. Specific activities were documented in a conceptual model, and generalized into a task network that exposes the sequence of steps, which enables the interagency to identify related activities that can help thwart an adversary from successfully accomplishing the development of an improvised weapon.

Prior to project close out, we developed a conceptual model, task network, process models, and detailed scenarios for illicit nuclear trafficking. The results advance the state of the art beyond tacit SME knowledge to a set of codified, shared models. This situation is rooted in a methodology that connects observables and indicators through an analytical framework that integrates expert-driven and data-driven reasoning to detect and understand the complex threats that straddle multiple measurement domains and signature types.

Formal knowledge representation and an analytic framework are required to apply new algorithms and methods that build on expert judgment and meet emerging analytic needs. Our approach provides a foundation for analysts to organize and preserve information from multi-source, heterogeneous perspectives using modular knowledge representation. The models described provide the foundation to store historical knowledge products and develop innovative signatures that can be used to explore and uncover complex patterns and relationships and yield new insights.
Network Chimera

William Hutton

Our network simulation environment will be used as a proof-of-concept for various theories of resiliency, including temporal diversity. In addition, our simulation environment will be used to investigate higher order effects of resiliency theories.

The Chimera is a mythical beast composed of a lion, dragon, goat, eagle, and snake. At times, modern enterprise infrastructures similarly consist of hodgepodge pieces combined, often in unplanned ways – a wifi hotspot here, administrative access for the high level professional there – and very quickly this structure (or lack thereof) creates a system where robustness is lost.

This project will apply the theories of robustness to evaluate infrastructures and use those results to create new, more robust infrastructures. When attempting to design robustness into an infrastructure, there is no high level logical method. Low level robustness (policies, limitations, and the like) are implemented, but the high level architecture and design fail to consider robustness, and a majority of other work looks at specific threats and vulnerabilities. Our focus is more comprehensive, looking at the overall architecture of the infrastructure, as well as how components alter this big picture. We attempt to identify robustness-positive vs. robustness-negative factors, in which those factors could include specific components policies and network architectures. Our approach breaks down the research into two parts – testing of prior work/existing architecture styles and then testing newly created network architecture models based on the prior work results – to evaluate the various factors, their interactions, and how these affect robustness.

Originally, Network Chimera proposed to discover how properties like redundancy, diversity, and independence could improve availability in various network topologies. Redundancy is the obvious way to improve resiliency, but most organizations cannot afford to buy two of everything. Environmental threats like the Baltimore Tunnel fire and Hurricane Sandy showed how the diameter of an event could impact redundant components. For example, if components can be rank-ordered, selecting an inferior component for the sake of diversity could actually reduce resilience instead of improve it. By conducting experiments to identify properties of resilience, measure those properties, and analyzing the higher order effects of changing those properties, we hope to improve network resiliency.

After a change of principal investigator on this project, it took our team some time to adjust and be relevant without the original leadership. We had Network Chimera establish a simulation environment using the Common Open Research Environment (CORE) from the Naval Research Laboratory. We implemented the “reference architecture” in CORE and conducted some rudimentary experiments to educate the team on the mechanics of conducting simulations using CORE.

One of our most important findings this year was the realization that concurrent diversity of components will likely negatively impact the overall resiliency of a network, but temporal diversity or diversity over time will likely positively impact network resiliency. As of FY 2014 end, a paper documenting this idea is in progress and nearing ready for peer review.

For FY 2015, we will focus our Network Chimera efforts on helping other projects to use our simulation environment as a proof-of-concept for validating individual elements of resilience theory. This situation will include continued collaboration with the science committee and the measurements and metrics projects. Our team will help other projects to design repeatable scientific experiments to be run in CORE. Promising theories will move on to the testbed project or become prototypes. In addition to helping validate other projects theories, we will continue to advance our own research, specifically the theory of temporal diversity and how it can be used be used to improve resiliency.
Next Generation Network Simulations for Power System Applications

Jeff Daily

We are developing a next-generation modeling tool that captures the interaction of communication technologies with the power grid, enabling systems engineers to understand and address the challenges of communication quality of service on the control, monitoring, and operations of future power systems.

New smart grid technologies and concepts such as dynamic pricing and state estimation, demand response, or wide-area monitoring, protection, and control are expected to require considerable communication resources. As the cost of retrofit is too high, future power grids will require the integration of high speed, secure connections with legacy communication systems while providing adequate system control and security. Considerable work has been performed to co-simulate the power domain with load models and market operations, but limited efforts have examined integrating communications directly into a power domain solver.

We are developing a scalable, high performance simulation infrastructure for data communication networks for power transmission and distribution power grids. Our goal is to develop a unique infrastructure that will position PNNL as the leader in modeling and planning power grid communication networks. This project will yield a general scalable high performance computing (HPC) communication network simulation, modeling, and planning infrastructure. We will investigate bottlenecks and limitations in state-of-the-art simulation infrastructures, proposing new approaches, parallelization methods, and high level algorithms to enhance performance. We will map and optimize existing simulations to state-of-the-art HPC computers, proposing new engines for integration with current simulation infrastructures. We will also interface existing power grid simulation infrastructures with the new proposed network simulation, identifying network properties and requirements representative of the power grid network domain.

In FY 2013, we chose to use federated co-simulation as the basis of our scalable simulation platform. By the end of the year, we successfully demonstrated the co-simulation of the communications network simulator ns-3, the power distribution simulator GridLAB-D, and the transmission simulator MCA. The choice to use a federated co-simulation approach directly resulted in new publications, approaches, and a reduced time to solution for simulating the future power grid in FY 2014. The two primary requirements for integrating simulators in a federated co-simulation are reuse and separation. The goal is to make the modules of any one simulator available for integrated simulations and, where necessary, allow the different simulators to pass information into or out of one another. In this way, users can implement and experiment with different power and communication hardware/protocol combinations.

It is possible to integrate simulators by adapting the modules of one simulator for use with the other one. Unfortunately, such adaptations can complicate the code base of the simulators, introduce errors, and often recreates work than has already been done. It is thus important to keep the code bases of simulators separate, allowing for independent but parallel development. For example, modules of ns-3 could be adapted to work with GridLAB-D by linking the ns-3 functionality through the core operations of GridLAB-D. However, this complicates the code base of GridLAB-D, as developers must maintain these modules. The adaptations can also introduce errors into the existing code, leading to crashes or incorrect results. Considering the requirements, a federated co-simulation middleware was developed in FY 2013 to facilitate information exchange via messages between federated simulators and time synchronization, a critical operation to coordinate the exchanges. For example, a message sent by a GridLAB-D module at time $t$ should also be forwarded to the communication network at time $t$. If ns-3’s internal time is less than $t$, the message can be forwarded back to GridLAB-D at $t$, which may result in errors during calculations.

It is possible for the communication network to “lose” packets (e.g., by simulating network errors). In such case, the counters for sent and receive messages would never be equal; therefore, the synchronization algorithm described above would force the simulators to progress one step until completion, severely impacting performance. To prevent this situation, the time synchronization module was programmed to declare packets as lost when the sent and received counters do not stabilize after $n$ time steps after it is sent, and the user can set the value for $n$. The source code for the message exchange and time synchronization middleware was released in FY 2014 as the Framework for Network Co-Simulation (FNCS, pronounced “phoenix”) to our GitHub account. The maturation and public release of our FNCS software was a direct result of our focused efforts after FY 2013.

With the availability of a mature platform, we integrated the MATPOWER software as a new, feature-rich replacement of
the previous MCA software we were using for transmission simulation. Using MATPOWER added the ability to simulate wholesale markets in addition to the retail markets at the distribution level in GridLAB-D.

The FNCS software was publically unveiled as part of a PNNL-hosted “bootcamp,” which included an overview presentation, a detailed use case example demonstrating cutting-edge results from our transactive control use case, and an in-depth tutorial and walkthrough of our programming interface and software architecture. We hosted both internal and external collaborators, showcasing the broad impact FNCS was already making and its interest beyond internal research and development. The FNCS release also allowed us to reach new simulation domains, including building management using the EnergyPlus software. We successfully integrated EnergyPlus with GridLAB-D using FNCS, which allows any house work to be modeled with greater fidelity by replacing them with an equivalent EnergyPlus model. Research is ongoing to use this new capability; however, initial prototype results has led to important results in energy sustainability.

Finally, we proposed three additional algorithms for time synchronization of federated co-simulations that complete the story of what types of synchronization is capable in federated co-simulations using advanced computing techniques. Co-simulations can now run many times faster using our new algorithms than previously reported without any special user intervention or a priori information about the simulators being used.

Although our project will end under its current state, its software products will continue under new funding sources for 3 more years. With the ease of integration of new simulator software and from the success of our synchronization algorithms, the FNCS software will be adapted to run in a real-time environment, including the incorporation of hardware-in-the-loop. The additional work will be funded by other sources in the following fiscal years. With this new funding, FNCS will continue to make a broad impact on the types of simulations that can be integrated.
Online Predictive Analytics on Streaming Data

Bobbie-Jo Webb-Robertson

Many real-world applications involve aspects of dynamic control, data mining, and classification in feature spaces that are drifting over time. The goal of this project is to develop a methodology for event detection and characterization that achieves high accuracy and speed in dynamic and high volume domain spaces.

Current technologies provide the ability to collect large amounts of data in real-time, offering the potential for major advances in dynamic data-driven decision making. In these cases, ideally training examples are incrementally generated, made available, and then fed into evolving models. The benefit of such an approach is that it mirrors how humans assimilate knowledge in a piecemeal fashion over time. However, current predictive models are limited in their capacities to ingest large-scale and/or high velocity data, effectively deal with missing or incomplete data, and detect rare events.

This project aims to locate events of interest in a set of data that is changing over time. It will do so by using a time-evolving method that can also describe and localize changes to the underlying dynamics of the system, which will be exploited to provide enhanced knowledge of complex systems. To provide the functionality, this project will explore the use of automated structure learning with incremental machine learning in a time-varying method, the use of variations in behavioral models to establish indicators of changing dynamics, and the use of missing or hidden variable methods to drive future data collection. We also aim to close the gap between the potential and realization of incremental machine learning, allowing for in situ decision-making on streaming data.

In FY 2014, we conceptualized the Dynamic Incremental Machine Learning Model for Evolution (DIMME). Within DIMME, we evaluated multiple machine learning algorithms for potential to deal with non-stationary data in the framework of a spectral processing use-case. In this context, algorithms were evaluated based on the capability to classify chemicals correctly with known characteristics occurring simultaneously within a single spectrum and with overlapping peaks and unknown shifts and concentrations. Several machine learning algorithms, some of which were integrated with inductive models, demonstrated perfect classification in initial experiments involving a small number (between 3 and 10) simultaneously occurring chemicals. Identification of algorithms with the most potential to scale for use in a streaming spectral context was then completed on data involving 50 to 100 simultaneously occurring chemicals. Results showed that traditional machine learning algorithms were not sufficient to classify many chemicals effectively in this more realistic context, demonstrating the need for an incremental learning method integrated with spectral processing algorithms. Preliminary steps were taken to couple a support vector machine algorithm with a functional data smoothing spline algorithm to develop a potential incremental machine learning methodology. Initial results showed better classification performance for the incremental learning algorithm compared with the non-incremental method. Additionally, the incremental method has the potential to allow for the identification of evolving data and/or unknown entities.

In FY 2015, we will focus the DIMME framework on demonstrating that the incremental learning paradigm can regenerate models in near real-time, even when the underlying dynamics of the system are changing. In particular, because the machine learning development has been completed, the methods will focus on three key developments. First, explicitly measuring of model drift will be used to quantify and characterize model evolution. The second task is the interrogation of latent variables and missing data from the model structure to aid the analyst and help steer data collection. Lastly, we will incorporate anomaly detection into the incremental machine learning approach to identify unusual behavior in the system.
Scalable High-Level Programming

David Callahan

*We will enable a broad spectrum of scientists, engineers, and analysts to apply modern parallel computing systems effectively to their everyday tasks – and to the ever larger data sets they examine – to free them from the limitations of desktop computers and to improve the pace of scientific discovery.*

Scientific programming for the bulk of practitioners is dominated by tools such as MATLAB, Python, or R, developed before the major architectural change from single- to multi-thread processors. Their key designs inhibit them from implicitly maximizing modern architectures. While there have been several attempts to extract parallelism automatically, key design choices have limited the practical impact. We believe that with the design for parallelism as a central goal, we can overcome these shortcomings and provide a new language with a comparable ease of use and extensibility but with far greater applicability to modern problems.

The focus of this research is to prototype such a language design and its key implementation techniques. Core contributions will include the following:

- The demonstration of an automatic parallel evaluation of a high-level modeling language suitable for use by scientists and engineers.
- Reusable design patterns for evaluator/compiler interactions to support effective, efficient optimization of high-level modeling languages.
- Optimization techniques for specialization and optimization of dynamically typed language in an on-the-fly context.
- A description of type-system and compilation interaction to support extensibility of high-level modeling languages with system-level support packages.

The first year of this project focused on building out the initial prototype infrastructure. We identified key features and syntax elements to handle the range of patterns common in scientific programming. This activity also focused on examination of existing practice and a survey of emerging patterns particularly those around structured data that has become a common metaphor for “big data” problems. These patterns converted to the basis for design of both data concepts and syntax of the language.

During FY 2014, we built prototype parser, compiler, and interpreter for a large subset of the language. As is common for this community, the language is dynamically typed, and the great bulk of functionality is ultimately provided through libraries. The implementation aspects that impact library design were fundamental to establish and provided a baseline for understanding the analysis challenges. We co-designed with the type system the interfaces for the library with a particular focus on the boundary between the core language and libraries written in foreign languages such as C.

A key design aspect of the language is controlling the features that lead to loss of effectiveness for parallel execution. This situation includes basic call semantics and data structure properties. The library interface design is particularly rich to enable accurate analysis in the presence of foreign functions and to guide developers of such libraries to exclude parallel-unsafe patterns. We established these interfaces and validated them with sample libraries, which include core array support and multi-precision math libraries.

Another key feature is the patterns around iteration over data structures, which are both extensible to new data structures and not part of the core language that support parallelism. The design is novel in its support for a number of distinct iteration patterns, and the late binding of these patterns is supported by on-the-fly compilation. This structure was validated on core array-based patterns but is also shown effective for supporting high-level, multi-dimensional loop constructs.

Another achievement in the last year was prototyping the interfaces between the reference interpreter used to validate the semantics of the language and the on-the-fly optimizer which is ultimately responsible for extraction of a parallelism as well as eliminating various overheads of dynamic type checking where possible. Key responsibility for the optimizer is recognition of parallel algorithm patterns and analysis of array use — common techniques in mainstream languages.

The goal of this project is to validate through demonstration that those techniques will be applicable in this dynamic, extensible language and that automatic-storage management techniques would not inhibit them. This part of the work is ongoing but progress has been very encouraging, with the most basic patterns already demonstrated as analyzable.

In FY 2015, we will focus on expanding analyzable patterns and adding capability to translate those patterns into code suitable for parallel execution. We will identify compelling problems and expand the library support as needed to demonstrate the feasibility of this language and implementation strategy.
Scalable Techniques for Resilient Reconstruction and Robust Reconfiguration (ST4R)

William Moeglein

Application of the theory of resilience inspired ST4R to develop decentralized methods for network reconstruction and reconfiguration that focused on determining real-time optimal strategies for adjusting and reinitializing services and topology while the network is under attack.

Our approach leveraged ideas from decentralized control theory to develop a variety of reconstruction and reconfiguration algorithms that will be empirically tested through automated methods and theoretically validated. Further, they will be stress-tested, especially for scalability. The algorithms will be deployed and exploratory testing (attacks against the system by domain experts) will be conducted by the ARC validation center. Based on feedback validation and testing, we will evolve our algorithms. Part of this work will include devising appropriate test procedures. After an initial literature review, we determined that the project would focus on virtualization as an enabling framework to address reconstruction and reconfiguration. It would provide the necessary framework to enable investigation into enhanced capabilities not addressed by technology out of the box.

First, we determined that commercial solutions could address sought-after fundamental capabilities to enable reconstruction and reconfiguration of a system under attack. Research was initiated by investigating existing frameworks that could potentially be leveraged to solve engineering challenges such as communication, security, and high level management.

Initially, we researched grid computing technologies, namely Globus, which addressed a number of issues, but the implementation was not as robust as described and was difficult to work with.

After determining that Globus and grid computing platforms were not the right fit for our problem, the team shifted focus to virtualization technology, which would solve a number of our problems but are typically better supported and more widely adopted. In particular, high availability virtualization features address a number of the major problems the project aims to solve, although the maturity of these features varies across vendors. Understanding the potential value that virtualization solutions offer, research focused on identifying candidate virtualization frameworks based on functionality, extensibility, popularity, and ease of integration. We needed to determine the state-of-the-art for current technology and features that support the need for resilience in the face of attack. Included in our consideration was market share and solution robustness for each vendor offering.

We engaged local virtualization experts to inform on current technology and capabilities and leveraged their understanding of technology and experience implementing solutions. We began to understand that much of what we plan to accomplish is enabled by technology through various forms and combinations of products. Each solution will likely be application and organization specific, version-dependent, and difficult to maintain. If this situation is similar to what other organizations do to achieve resilience, there remains room for improvement. Virtualization and commercial products appear to be good candidate frameworks to support and enable advanced capability to support resilience. Before we identify technology gaps, we should acquire and establish a sandbox within which we evaluate and develop a next generation capability using current technology as an enabler. We leveraged resources from the ARC test bed and resources provided to us by PNNL Institutional Computing (PIC).

From our discussions with virtualization experts, we created a list of technical tasks, acquired time from key staff, and established a timeline to have our baseline system fully functional. The engineering tasks behind setting up our system not only benefit our project but are also useful to PNNL. This work can be treated as a skills reinforcement exercise to enable functional documentation needed for the organization. We then began preparations for technical discussions with Microsoft. Our focus centered on their ability to enable a better understanding of what the real state-of-the-art is in this area, as many technical details are proprietary.

The team continued efforts to document, deploy, and configure the virtualization platform for our purposes. To deploy the technology, the team worked to provision computing resources on PIC. These resources play host to the virtualization and management software that the team will use as the underlying framework to enable reconstruction and reconfiguration. In addition to these resources, we identified physical resources from CyberNet to serve as hypervisors for our virtualization. We completed installation of the underlying management software but identified a challenge with interconnectivity with CyberNet from firewall restrictions between the two enclaves. We focused efforts to identify timely resolution to the technical challenges to enable communication and support research progress.
A cornerstone of visual analytics is fostering sense-making, a cognitive process of gaining understanding into data by testing one’s own assertions and domain expertise against data. Science of Interaction aims to maximize the roles of the human and computation for reasoning at scale and speed to enable faster, more meaningful insights.

Current approaches to incorporating the user’s domain expertise into the visual and mathematical system is through user interaction explicitly steering the computation. This direct manipulation approach for user interaction has been successful for interactive information visualizations. However, a new paradigm for user interaction is needed; hence, we present Science of Interaction. We base this work on the user interaction paradigm called Semantic Interaction that suggests a connection between the embodiment of the process through the user interaction and the cognitive discourse users have with the information. As a result, capturing that tacit knowledge associated with the user interaction in a mathematically structured form can lead to a more fluid cognitive process of discover, and thus faster and more meaningful insights.

The project objective is to improve human insight from data by making complex algorithms and models more accessible and adaptive through inference over user interaction data. To make progress towards this objective, we are implementing new user interfaces from which we can gather user interaction, develop new inference strategies, understand sense-making, and explore mixed-initiative visual analytic systems.

In FY 2014, the Science of Interaction project instrumented a spatial visualization called the Discovery Canvas to capture user interactions such as movement, grouping, and labeling of multi-dimensional data. The Discovery Canvas was adapted to handle both multi-dimensional representations of documents records or spectral data such as those produced by nuclear magnetic resonance or mass spectrometry instruments. The Discovery Canvas functionality was extended to support a more complete analytic task, thus providing a richer set of interactions.

Several feature weight inference strategies were designed and implemented within the Discovery Canvas system. As the user incrementally explores and analyzes the data, the machine learns feature weights to reflect the current understanding of the user’s interests. The evolution of these feature weights is logged and visualized over time; alas, the evolution visualization process seems to reveal the cognitive processes of the user.

A two-day Science of Interaction workshop was conducted at PNNL to establish leadership in the community of interest, better define the Science of Interaction concept, and outline future research directions. Participants included leaders in visual analytics and data mining from both academia and industry. The workshop results and several other Science of Interaction related publications were presented outside of PNNL at three conferences (two of which were IEEE) and two workshops.

Thus far, the Science of Interaction has developed foundational software with the capabilities to gather and study user interaction. The implemented inference strategies for feature weighting allow the machine to model what is important to the user and gives us insight into the sense-making process. As the project continues into FY 2015, we aim to accomplish modeling aspects of the sense-making process observable in user interaction data. We will also develop a more diverse set of visual analytic interfaces to couple humans with algorithms over streaming data. Finally, we wish to achieve a broadening of interest within the Science of Interaction community.
We are developing and exercising a methodology for verification and validation when performing modeling and simulation, experimentation and studies, and theoretical research.

Older, more established fields have generated foundational laws and theories upon which to base their engineered systems. However, cyber security still lacks necessary fundamental understanding of cyber space to engineer effective solutions. Cyber security needs to move beyond tradecraft and building interesting systems to include scientifically rigorous knowledge gathering and engineering based on science. For example, before chemistry became scientific, people believed that alchemy was possible. Without instituting a scientific approach, the status quo will remain; we will continue to be unable to differentiate fear, uncertainty, and doubt-derived mysticism from real solutions; and we will slide further down an asymmetric slope of attacker advantage.

To address the scientific rigor within the cyber security field, we are developing scientific tools that researchers will leverage to exercise their research questions and operating a science council to assist other projects in applying scientific approaches developed last year. Two of the scientific challenges found in the first year were the lack of a common reproducible approach to threat modeling and implementation for experimentation and the lack of adequate human initiated network traffic models to mimic human users in an experimental cyber environment.

The first task performed under this project was to develop a cyber conflict taxonomy that enables the generation of threat models for testing in experimental environments. This taxonomy provides coverage of the general possible motivations and targets that a cyber threat might have such that sets of threat models from the taxonomy provide test cases for evaluating different cyber security and resilience solutions. While the taxonomy provides a repeatable method of defining models of threats, it is still required to exemplify the threat model in some fashion. A survey of the methods of performing threat activities in research was provided to gather a set of possible methods that represent the defined threat models to be studied in different ways depending on the type of research performed. For instance, a theoretical evaluation of resiliency could generate functions from the threat model to explore fundamentally what would happen in the presence of different threats, during which a red team could be given the threat model to direct its actions in trying to achieve an objective in experimental research.

The second task was to perform cluster analysis on real network datasets to derive human network behavior models. Experimental cyber security research must be performed within fabricated environments. One major gap in experimental research using these synthetic environments is the lack of realistic simulated users. Statistical cluster analysis was performed on anonymized PNNL network data to generate general models of human network behavior. These clusters define mean behavior across a 24-hr period with variance bounds. From these models, simulated users could be studied that stochastically generate traffic within the bounds defined by the model. The method and models from this task provide a more realistic set of users that will enable more rigorous experimental cyber security research.

Finally, to apply the knowledge gained in the first year of the project, a science council was formed from experienced experimental scientists across many fields of study. This council developed a process by which it interacts with other projects to review their scientific questions and experimental
designs to provide feedback and recommendations to improve rigor and effectiveness. The process includes a subset of the guidance document developed in the first year with a set of questions that projects must answer in preparation for meeting the council. Next, the group critiques the scientific questions, the measurements being taken to answer the question, and the experimental design. The end goal is to have a solid research plan that has confidence in answering the appropriate research questions. The science council trialed the process with two projects this year, with the intent of working with the full research group next year.

Next year, the science council will leverage the tools and techniques generated in this project to this point to interact with the projects to improve their research processes and procedures to yield more impactful results.
Testing a hypothesis involves significant investigative effort, whether it is scientists performing experiments in a lab or detectives working to uncover illicit behavior. We aim to answer the query of what happens when hypothesis testing is automated to occur automatically as new information becomes known.

At the core of hypothesis testing is deductive reasoning: a gathering of relevant facts which, when combined with established background knowledge, leads to useful conclusions. Although deductive reasoning is an established field in artificial intelligence, only recently has interest greatly shifted toward performing deduction at the time new information is received, which is termed stream reasoning. Information can be accumulated and then processed later (off-line), but this situation implies a significant delay between the reception of the information and the act of reasoning. Many works have focused on deduction over only the most recently received information, but this approach has limitations because related information may not co-occur within the same window of availability. A new approach is to employ so-called data-aware eviction, in which we actually try to remember (or forget) information selectively based on its semantic content.

We are seeking to answer the following questions regarding data-aware eviction for stream reasoning and assessing how the information can be used in collaboration with other reasoning approaches:

- How is the quality of deduction impacted by changes in stream parameters (e.g., how quickly information arrives) and choice of eviction policy?
- How can deduction collaborate with other kinds of reasoning in a streaming environment to improve results further?
- How can deduction be used to quicken the investigative cycle of “human-in-the-loop” users?

In FY 2014, we laid the groundwork for answering these questions. We captured the use cases for two domains: nuclear magnetic resonance (NMR) and disrupting illicit nuclear trafficking (DINT). Specifically, we obtained relevant background knowledge to support reasoning for problems in those domains and implemented a prototype stream reasoner using a custom cache data structure and COTS reasoners. We performed experiments on benchmark reasoning datasets, and we demonstrated the efficacy of combining induction and deduction to produce better results.

Using the Lehigh University Benchmark dataset of 103,410 triples (statements, propositions), we sought to find all the professors in the dataset as the data was streamed through our prototype stream reasoner. The stream presented 50 new triples every 2 milliseconds, and only the last 1,000 triples were visible at any given time. The cache was configured to hold 5,000 triples; when overflowed, 1,000 triples would be removed according to the chosen eviction policy. The Jena RDFS reasoner was used internally, and recall was measured as the fraction of all professors found when performing RDFS reasoning on the entire dataset standing still. Using a simple FIFO eviction policy, 0.0761 of the professors were found. If we gave preference to terminological triples (i.e., let triples stay in the cache longer if they make universal statements about the world), we found 0.145 of the professors. Combining established background knowledge with RDFS rules, we established an eviction policy that gave preference to triples that were more likely to lead to the conclusion that a person was a professor, which enabled us to find 0.899 of the professors. This result indicates that data-aware eviction policies can substantially improve results.

Next, we performed the same experiment with different cache sizes: 10,000 and 15,000 triples. One might expect that more professors would be found when using larger caches. For the simple FIFO policy, recall indeed improved to 0.141 and 0.264, respectively. For the terminological policy, the recall again improved to 0.277 and 0.676, respectively. However, for the data-aware eviction policy, recall dropped to 0.508 and 0.450, respectively, due to the computational burden of performing eviction. Because the cache size is larger, more complex eviction policies take longer, and the stream reasoner begins to overlook data in the stream because it is preoccupied with performing eviction. This result indicates that there is a tradeoff; e.g., it is not always better to have a larger cache size or a more complex eviction policy. Further investigation is required to understand this tradeoff.

Outside of a streaming scenario, we demonstrated the ability to use deductive reasoning as a “veto” mechanism with machine learning approaches. In the NMR use case, an SVM approach was used to predict the chemical compounds reflected in NMR spectra. The F1-measure using only SVM ranged from 0.481 to 1.00. Using deduction, we determined that some predictions were wrong (false positives); removing those predictions from the result improve the F1-measure. In the best case, the F1-measure increased by 0.398; in the
worst, the F1-measure remained unchanged. This result reveals that there is the potential for significant improvement in reasoning by combining induction and deduction.

The results of FY 2014 indicate our direction for FY 2015. We will continue to investigate various data-aware cache eviction policies to see how they impact deduction. We will also increase work in how we can augment induction with deduction not only as a “veto” mechanism but also as a corroboration mechanism; i.e., if we can come to any certain conclusion (a determination of whether the induced prediction is correct or incorrect), we can feed back these conclusions to the induction-based approaches to act as “on-the-fly” training data, which is essential for dynamic model evolution. Additionally, we will explore how we can use deductive reasoning to discover connections between things of interest established by users, thus helping to quicken the investigative process.
Signatures of Community and Change

Alan R. Chappell

This research aims to identify and validate a novel set of computationally tractable signatures for social media data that signal the presence of significant community events such as dissolution, schism, conflict periods, and ideological change.

A community is a set of individuals that interact in a shared environment around a set of shared interests, values, or problems. Historically, this shared environment has been a physical area, but it more recently includes a cyber or virtual space defined by a common communication fabric. Being made up of independent individuals also means that communities are dynamic in many ways. Community membership can change over time, member’s interests and degree of participation in the shared environment can evolve, and the central pattern of shared interests and values can itself evolve. The advent of online social networks has dramatically increased the quantity and quality of the data available to study such communities, and many of the necessary computational tools have now been developed. PNNL has previously explored the use of behavior-based features as well as features extracted from message content as a way to identify abstract groups. However, the underlying models for understanding this data are typically rooted in topological approaches and static analysis. We still have a very limited understanding of how social media communities evolve over time, and because of this situation, we still do not have reliable signatures that indicate interesting points in a community’s evolution.

This project addresses the above-noted technical gap, focusing on the intersection of two techniques: PNNL’s work on computationally understanding the content of individual social media postings, and a new approach to modeling social network propagation effects pioneered by the University of Washington. Our overall objective is to use these techniques to identify and validate a novel set of computationally tractable signatures for social media data that signal the presence of significant community events such as dissolution, schism, conflict periods, and ideological change.

An important principle in analyzing general community behavior is that not all members are equal in their influence over other members. Certain members (“influencers”) have superior knowledge, authority, or rhetorical skills around particular topics, and their contributions to the community carry more weight, propagate further, and more powerfully affect the contributions of others. Consequently, we focused our research on approaches for three aspects critical for understanding social network evolution: detection of topic of conversation, community, and influence.

A leader or influencer in one topic often is not a leader or influencer in another topic. Hence, any influencer-based algorithms for community dynamics must be sensitive to topic flows. Topic detection in text is a technical strength at PNNL; however, the textual style of social media presents many unique challenges. We applied the outcomes of other PNNL research to segment conversations based on broad topics to focus assessment on coherent communities.

Identification of communities in social media is a distinct research area and is not our area of focus. For our initial work, we selected a known algorithm (Louvain) based on its high-quality results and good computational characteristics. However, Louvain and other related algorithms require the user to identify connections between individuals prior to identifying communities. This situation is not possible for many classes of real social network data such as Twitter. Our team has proposed several approaches to addressing this limitation, including the use of analyses based on transfer entropy and other information-theoretic concepts and will continue to test such mechanisms as the research progresses.

Several techniques have been developed to identify influencers in social media and online social networks. We collaborated closely with University of Washington researchers on the PHYSENSE system that they developed to analyze topic propagation in communities using physics-based algorithms derived from the analysis of fields. PHYSENSE can also be understood as a computational instantiation of a simple sociological model of influence propagation, giving it an independent plausibility. By adapting PHYSENSE to run on the PNNL Institutional Computing (PIC) system, we were able to validate previous results independently and assess computational requirements in the face of the large scales of social media. PIC also provided an effective mechanism to test the impact of multicore architectures on this performance. Building on the PHYSENSE system provides a sociologically grounded and computationally tractable approach to assessing influence in social media.

Ultimately, these three aspects — topic, community, and influence — form the basis of understanding community behavior. In the next year, we will combine these techniques to build signatures for a variety of important characteristics of dynamic communities, including polarization and changes in level of engagement, precursors of schism, dissolution or merger, and the emergence of new leaders and directions.
Signatures of Illicit Nuclear Trafficking for Strategic Goods (SINTS)

Zoe N. Gastelum

This project is identifying, comparing, and characterizing procurement networks within large international commerce datasets to integrate data and knowledge from various domains and subject matter experts. Our outcomes will support expedited, reproducible, holistic foundations for nonproliferation analysts to examine countries and sensitive commodities and procure networks that connect them.

The international spread of sensitive nuclear technologies poses a serious threat to the nonproliferation community. Analysts currently addressing the challenge tend to focus on one of two problem spaces. First, they assess export control license applications for dual-use nuclear commodities for the validity of export, primarily through verification of the end-user of the commodity and its declared end use. Second, they examine country’s nuclear fuel cycle assessments for a state’s current and planned nuclear activities. However, the two analytical communities tend to work in isolation from each other, which results in a lack of holistic understanding regarding the context of a commodity and company or a country.

To provide some of the above context, the SINT project is utilizing tools and methodology to automate the identification and characterization of procurement networks consisting of commodity and company pairs. While the ultimate goal is to apply the tools and methods to procurement networks of strategic nuclear goods, we are focusing on non-sensitive proxy case studies such as the automotive and housewares industries in FY 2014 to develop and test our approach while we work to acquire the necessary data for strategic nuclear good procurement network analysis.

First, our team focused on understanding the procurement network and illicit nuclear trafficking problem space to determine our analytical questions and approaches. The team conducted an extensive literature review covering illicit nuclear trafficking networks, proliferation financing, supply chain management, constraint based reasoning, and competitive intelligence. The team also conducted a survey of expert knowledge regarding the export control license application assessment process and state-level nonproliferation analysis captured in Bayesian network models by previous projects.

Team members also conducted job shadowing with PNNL analysts to understand their processes, data sources, and use of analytical tools.

To analyze a procurement network, the analyst must first recognize that the network exists. In the current analytical workflow, analysts build networks manually as they come across new information linking entities (individuals, companies, countries) with commodities (materials, equipment, finished goods). Analysts use their knowledge of companies, entities, or commodities to search databases for various spellings and abbreviations of names or addresses, and develop these networks in an iterative fashion. Building these networks can be a time-consuming, monotonous process.

To support network detection, the project implemented an edge-betweenness community detection algorithm. In graph analytics, an edge with high betweenness has a high degree of influence over the transfer of items through a network. If one considers a network of streets on a map, those roads connecting houses within a single neighborhood have relatively low betweenness, while highways that serve as the only direct route between cities have high degrees of betweenness. The edge-betweenness community detection algorithm defines a threshold of betweenness, and breaks a large graph into smaller graphs or “communities” by removing the “highways.” To validate that the edge-betweenness community detection algorithm was identifying similar networks to an analyst, the team compared several analyst- and algorithm-defined graphs. While not completely identical, we found that the algorithm-generated graphs were similar to the analysts graphs via visual inspection as well as by using the edit distance similarity metric defined below.

Once a network has been identified, we want to understand its characteristics. Our team investigated two ways to comprehend a network: through similarity (to determine quantitatively how similar one network is to another) and anomalies (to understand normal patterns of behavior and attempt to determine what derivations from those patterns could indicate). In FY 2014, the project used edit distance and subgraph comparisons for network similarity assessments. Edit distance (modified for computational optimization) reflects the number of changes (additions or subtractions of graph nodes and edges) required to make one graph identical to a second graph. While edit distance does provide a telling story about the similarity of two networks, it is highly influenced by graph sizes.
Sub-graph comparison identifies the most common set of nodes between two graphs and calculates the edit distance between them. Specifically, the comparison attempts to correct for graph size issues of the edit distance measure. However, the identification of the most similar sub-graphs within two networks may obfuscate the broader activities of a network and focus instead on a common supplier or shipment company that does not have high impact on the network as a whole. As such, methods for graph comparison are still being investigated.

We explored anomalies within a network from two different angles: commodity and time-series. The team conducted statistical analyses on shipment manifest data and tariff codes to identify shipment records that were “out of the norm.” We identified example anomalies such as differences in the use of tariff codes for explosives by country and potential misunderstanding of the meaning of some tariff codes, with users confounding the petroleum product “coke” and the Coca-Cola beverage in one example, and the electrical fuses for domestic appliances and those required for explosive charges in another. In the preliminary time series analysis, we used transaction visualization techniques in the PNNL-developed T.Rex software to identify companies’ import patterns over specified series of time (monthly, quarterly, annually). Using these patterns, we compared networks across an industry for an understanding of the general import patterns of companies working in a specific industry. This type of analysis could be codified into formal patterns and used as templates for determining the industry of a new, unidentified network.

In FY 2015, the team will move from a data mining to a constructive approach for network identification, defining the necessary and sufficient characteristics of a network to classify it into a particular industry, and assessing our methods’ impact against current practice by export control and nuclear fuel cycle analysts. In addition, the team will assess our approach on dual-use networks identified in our current data and assess the utility of new datasets as they become available.
Streaming Data Characterization

Mark T. Greaves

We are creating an integrated resource of high speed, streaming data characterization and analysis algorithms upon which future projects can build.

Initial processing of streaming data sources is an area in which there is substantial previous work. We planned out a set of related projects that will survey the scientific literature on initial stream processing algorithms for co-design domains, implementing the promising projects and tasks as well as evaluating their performance. We will use these studies to qualify potential university partners for their suitability within longer-term cooperative research and development relationships. There is currently no repository that gathers together the state-of-the-art in powerful online analytic algorithms that can process data on the fly, and such a repository will not only be critical for success but will also be a lasting resource for PNNL.

In FY 2014, we directed four exploratory projects within different organizations as described in detail below.

**Foundational streaming data preparation methods.** This work was performed by a student at Rensselaer Polytechnic Institute and carried many initial research tasks for AIM, including a categorization, survey, and component listing for popular open-source and COTS streaming frameworks; an analysis of the specific uses of the selected frameworks that identified the overall strengths and any breakthroughs in these frameworks; and a new formal ontological classification of the chosen frameworks based on the technical approach.

**Visualization of hypotheses about streaming data.** This work was performed by a student at the University of Utah's Scientific Computing Institute and addressed statistical hypothesis testing as a visual tool for quantifying and understanding complex phenomena. The student developed an approach that relies on simultaneously leveraging the analytic capabilities of both humans and computers, using visualization as a knowledge sharing interface between the two. For example, computers are good at extracting linear models, dealing in high dimensional spaces, and processing large quantities of data. On the other hand, humans tend to be much better at more abstract tasks such as identifying nonlinear models and classifying data. In this work, the human helps build the computer model while the computer simultaneously helps the user to build their mental model of the data. A prototype has been built.

**Data summarization for streaming scientific video.** At the University of Washington, this project supported initial architectural work to address the significantly growing scale of microscopy video data. The scale of imagery coming from new systems such as PNNL's DTEM requires developing new streaming algorithms even for common tasks such as retrieval, interactive browsing, or compressing video content. This project developed architectures and basic summarization algorithms in an attempt to identify the most important and pertinent scientific content from sequential imagery on the fly and produce a condensed version of video as an output. The techniques also meet single-pass and high throughput requirements. A paper that covers the progress of this work is planned.

**Event summarization in microscopy imagery.** At the University of Utah’s Scientific Computing Institute, we developed a collaboration with biologists that had streaming image analysis needs. For two selected bioimagery problems, we determined the best set of current nonstreaming algorithms and proposed modifications to current methods to adapt them for streaming image analysis in experimental settings. Expected impacts include techniques for automated analysis of image data from microscopes to drive experimental techniques as well as the development of new techniques for quickly post-processing acquired image data. A paper and further collaborations are planned.

We anticipate additional targeted stream processing studies to be carried out during FY 2015. For example, we expect to expand and formalize our collaboration with Rensselaer Polytechnic Institute to include studying algorithms to efficiently extracting semantic knowledge from different kinds of streams.
We are developing and evaluating a theoretical framework for resilience to provide the technical basis for evaluating cyber defense and reconstitution approaches.

Resilient cyber systems ensure mission critical functions of an organization continue operating in the face of ongoing detrimental events. Assuring resilience requires techniques for robust design, evaluating proposed solutions, and identifying optimal solutions to dynamic reconstitution of compromised cyber systems. The reconstitution response, including recovery and evolution, may require significant reconfiguration of the system at all levels to render the cyber system resilient to ongoing and future attacks or faults while maintaining continuity of operations.

The quest for resilient cyber-systems has seen a number of technical approaches (such as moving target defense) that attempt to add specific properties such as diversity, redundancy, deception, segmentation, and unpredictability to make the system more resilient to one or more attack vectors. However, the approaches cannot be applied readily after a system has been compromised. It is also difficult to ascertain whether such methods are applicable under any attack scenario or if limitations exist. The objective of this research is to develop and evaluate a theoretical framework that identify specific principles of resilience that may be applicable to cyber systems; develop a mathematical methodology that relates these principles to elements of a cyber system; and integrate decision making into the framework so that decisions in a compromised environment may be made with the goal of achieving continuity of operations (ideally to a safe state) in a fast, cost effective manner.

The resulting framework will enable the identification of key components of resilient cyber systems; decision making with uncertain information (i.e., the design and recovery decision-making methodologies may need to function with limited information); and asymmetric advantage (increased cost to the adversary should be a factor in the decision making). The results of this research will also provide insights into measurement needs and success criteria for asymmetric resilient cyber infrastructure.

Current frameworks for resilience encompass four basic concepts that collectively enable resilient design (anticipate, withstand) and dynamic reconstitution (recover, evolve). In FY 2013, a theoretical framework for dynamic reconstitution that applied principles of multi-objective optimization was developed and evaluated. Including recovery and adaptation, the reconstitution response may require significant reconfiguration of the system at all levels to render the cyber system resilient to ongoing and future attacks while attempting to maintain the continuity of operations. In FY 2014, the focus of the technical developments was on a theoretical framework for cyber resilience that also included reconstitution.

We hypothesized that resilience is achieved by a combination of specific cyber system design actions (during planning) and control actions (usually after an event). This notion of controllability enables a mathematically rigorous definition of resilience as the degree of stability of the cyber system at or near any operational state and defines conditions about system dynamics, connectivity, and control input locations. Given this definition of resilience, problems of robust system design and reconstitution are defined as a multi-objective optimization problem, and resulting solutions provide insights into tradeoffs between resilience, cost, risk, and other relevant metrics.

Challenges in this context include defining state of a cyber system relevant to mission, identifying relevant operational states that support mission, and developing methods for reconstituting compromised cyber-systems. We previously defined state C of a cyber system at time t as a representation of its key properties; this scenario could include configuration information directly or could be the result of mapping configuration to a metric of availability, integrity, or confidentiality. We also assume the existence of a well-defined notion of mission as well as measures of performance.

The theory of resilience is being evaluated using several abstractions of cyber-systems, including queues and small (30–40 node) graphs. Queueing models represent systems...
Example of simulation results. The system connectivity map (left) at time 0 shows a failure of multiple nodes due to some event that negatively impacts metrics measuring connectivity and continuity of operations (right). When applied after the failure, reconstitution methodology helps the network recover while improving continuity of operations.

that store and process requests from other entities (such as clients), and key properties include queue length, resource limits for processors, and number of queues. At a different level of abstraction, an \( n \)-node system with \( m \) critical services is described by a graph \( G \) that captures the connectivity structure of the cyber-system at one or more layers (network, services, data, etc.) in the system stack. Here, a node represents some computational resource, such as a computer or a server, that can run any subset of the \( m \) services.

Simulation studies consisted of changing the input conditions to the simulation, and evaluating the ability of the system to maintain mission as a function of the state variables. Initial results indicate viability of the theory of resilience, though this needs to be confirmed using additional studies. Specifically, the notion of resilience as an attribute of the system related to controllability, observability, and stability appears to be sound, and may be applied in an optimization approach to determine system states that are capable of continuing to meet mission.

Results of simulation studies also indicated that the proposed approach may be viable for reconstitution of compromised cyber systems. Applying the proposed approach to reconstitution, network services were able to be reconstituted quickly after a fault at time step zero. Unlike existing techniques, the proposed approach was seen to be viable even when disruptions occurred during the reconstitution process. Based on simulation results, the approach was capable of reconstituting systems and improving overall resilience in the presence of serial disruptions (i.e., as the system is recovering, a subsequent disruption occurs); however, the recovery may be somewhat slower as the approach needs to account for severe reductions in capacity. The formulation also provides a mechanism for evaluating performance of other approaches to reconstitution of compromised cyber systems. This formulation and its results were presented at an IEEE international conference.

To date, the simulation studies, particularly around evaluating the concept of resilience, were limited and included several assumptions that will need to be relaxed if the results are to be more generally applicable. This research is planned for FY 2015.
Our objective is to discover shapes, structures, and overall system behavior using topological data analysis of graphs derived from cyber system data with the overall goal of providing analysts with more robust information to determine the state of their cyber system.

Topological methods have been deployed in real-world problem domains with great success, as in signal processing and medical imaging. These methods were created to identify shapes and structures in data sets, discover average system behaviors, and combine information from different sources. As applied to cyber systems, dynamic objects are changing as elements sign on and off, as communications begin and end, and when interactions with other systems initialize and complete. In this project, analysis of these dynamic systems is accomplished through the application of topological methods that lead to new tools for cyber system operators to judge resiliency and make sure that system missions can still be completed.

We are taking these well-established methods to a new domain of cyber security and cyber resilience. We hypothesize that this analysis will provide a way to differentiate between resilient and non-resilient system states, possibly even identifying different types of causes of non-resilient states. Within the broad theory of topological data analysis, we are using two major techniques, both coupled with novel statistical graph analysis. The first technique, persistence, is for discovering graph structures that persist as the system evolves through time, within which dynamic graphs representing system processes will be tracked. Finding periods within which certain structures persist can indicate periods of network resilience, whereas degradation or loss of these features may be periods in which resilience is lost.

Our second technique is tracking dynamic graph evolution through the use of reduced dimensionality representations of graphs. We reduce a graph to a small vector of statistical measurements and use this vector of values as a proxy for the graph. Then, we are able to track how graphs evolve through a low-dimensional visualization and using machine learning classification to learn patterns of different types of behavior. Both of these techniques, along with statistical analysis of the dynamic graphs, are to be run side-by-side to correlate results.

In FY 2014, we created a prototype of the software to do graph dimensionality reduction, currently using top two or three eigenvalues of the graph adjacency matrix. We have been experimenting with different types of graph evolution on random graphs. For comparison, we started with a random graph and doing random edge shuffling. We expect this work not to be representative of any real-world graph evolution, but it can serve as a comparison baseline. We are also looking at starting with a regular random graph—one in which each vertex has the same number of neighbors—and still performing random edge shuffling while keeping the graph regular. Other random graph evolution methods are being experimented with, and we are writing a methods and comparative paper on our initial work in this technique. We discovered that different types of graph evolution exhibit different behaviors in this lower dimensional space, which is important going forward because it shows the first proof-of-concept: using a low-dimensional graph representation that can discern between different types of changes in the graph.

Additional work this year has been producing dynamic graphs from our collected data, which is NetFlow annotated with ground truth from a cyber competition. Each indicating source and destination IP and port for information flow, NetFlow records are annotated with information that includes a start/stop time of flow that we are using to create a sequence of time-windowed graphs, plus we are researching other techniques for creating dynamic graphs.

During FY 2015, we will work on our persistence technique. We will be developing algorithms to turn dynamic graphs into topological sequences on which will discover persistent structures. Our dimensionality reduction code will be enhanced with different types of mappings (beyond just eigenvalues) and machine learning techniques to begin learning patterns of behavior. Both of these activities will be accomplished alongside a statistical graph analysis so that when state changes and resilience changes are discovered using one technique, we can correlate that with discoveries using the others. All of our work will be with the benefits to cyber researchers in mind.
We are exploring tools to support verification of simulations to increase the quality of results and reduce the cost of enhancing simulators for emerging scenarios.

We are surrounded by complex systems – power, transportation, health, and the like – on which we rely. These systems’ safe and effective innovation and control crucially depends on accurate computer simulation before deployment. Our project seeks to create a reusable framework that will significantly raise the productivity and increase the impact of developers adding new features to simulators of complex systems. Additionally, this work seeks to adapt techniques from the broader software validation literature to build frameworks specific to the concerns around simulators used for testing control mechanisms. We are building a prototype framework to demonstrate its use and utility on simulators and simulation workloads of current interest to the laboratory and the industry. In conjunction with another project, we will explore high-level language support to expose the framework to users who do not need to make direct low-level modifications to simulators.

Explicit modeling of time is required to specify the behavioral constraints of a control system. Existing runtime verification approaches for simulators, however, require users to specify the intended behavior of the system as a temporal logic formula or a transition system. Such specifications do not allow explicit modeling of time and, hence, are not sufficient for verification of control systems. In addition, constraint specification languages for the existing approaches are tuned to modeling software execution, such as the order of method calls or variable updates. For control systems, however, the behavior is observed as the controller’s response to input. Hence, runtime verification for control systems requires a constraint specification language tailored for expressing input/output relations. Specifically for specifying the behavioral constraints, existing approaches require detailed knowledge of the implementation of the simulator. Generally, users extending the simulators do not have such detailed information on the implementation of the simulators.

To overcome these limitations, we developed a runtime verification framework called Con-V designed for low-level control system simulation verification. Con-V provides a specification language tailored to modeling the controller’s response to changes in its input and a second specification language to capture simulator specific constraints that hide the implementation details of the simulator from the control engineers. For the first of these languages we refer as the control tier, engineers specify the constraints of the control system using Con-V’s specification language based on timed automata to allow explicit modeling of time constraints. This language can be used to express constraints on relative changes to inputs and outputs with respect to time.

The second language addresses the need for detailed simulator knowledge: the developers of the simulator provide the mapping rules expressed in this language. The mapping rules are reusable transformation rules that encapsulate implementation-specific details of which variables correspond to the input/output of the control system and when the simulator updates the value of these variables.

Con-V automatically transforms the “design-level” specifications of the control system into simulator-specific runtime verification specifications. Con-V also uses this information to generate the runtime monitors. These monitors observe the input and output variables of the control system and report changes to Con-V’s runtime verifier. Concurrently, the runtime verifier evaluates whether the updates move the simulator into a next state in the specification. If the next state is a reject state or if the system stays at a state longer than the specified timing constraint, the runtime verifier reports verification failure with the current state of the monitored input/output variables.

We successfully demonstrated Con-V use in enforcing behavioral constraints of an HVAC control system implemented in a power grid simulator. We modified the implementation of the controller so that it successfully executes but does not respect the behavioral constraints. Con-V successfully detected that the implementation violated all the constraints. This application shows that even if the implementation of a control system within the simulator executes without errors, it might not follow the behavioral constraints. In addition, Con-V can be used for verifying the implementation of a control system within the simulator against the control system’s behavioral constraints. The specification language has been shown to hide the implementation details of the underlying simulator. In this way, the control engineers can model “design-level” constraints of the control system.
Nuclear Science and Engineering
Atomic Mass Separation for Enhanced Radiation Detection Measurements

Gregory C. Eiden

This project is seeking to improve the measurement and detection of radionuclides of interest in nuclear security.

Sensitive measurement of radionuclides requires both high fidelity chemical separation of isotopes of interest from the sample matrix and state-of-the-art radiometric counting of the nuclide decay events in the separated sample. Previously, the only option for preparing samples for counting was chemical separation. While most elements have distinct chemical behavior that can be leveraged for separations, there are enough similarities that these separations are never complete. There are only a few exceptions, such as with lanthanides, which are notoriously difficult to separate from each other.

This research seeks to develop separations based on radionuclide atomic mass. With modern mass spectrometers (MS), such separations can be many orders of magnitude more effective than chemical separations. Our novel approach is expected to create a paradigm shift in the way radiochemical separations are considered by experts in the field. The technique that we are developing will lead to improved methods in both fixed laboratories and field deployed instrumentation, especially in nuclear accident and terrorist incident response. Our objective is to explore the analytical performance of the prototype instrument, develop follow-on modifications to this prototype, and obtain proof-of-concept data for key beta and gamma emitters. We are developing a prototype instrument, preliminary method, and a demonstrated ability to capture single unit mass wide (1 atomic mass unit) ion beams efficiently from a mass spectrometric-based separator.

During FY 2013, we developed a prototype instrument with which individual atomic masses can be implanted into a solid target, thereby enabling isotopes of a given atomic mass to be characterized radiometrically. Initial experiments sought to address several analytical or method issues; i.e., ion beam capture efficiency, spatial distribution of captured ions on the target, and ion scattering on mass separation efficacy. We also developed a computer program that calculates decay rates as a function of time as well as for the beta, gamma, and alpha radiation for each fission product.

In FY 2014, we developed an experiment involving overlapping beta emitters. We worked with PNNL’s Cat II Facility staff to quantify stock pure solutions of both $^{137}$Cs and $^{90}$Sr isotopes based on a $\beta/\gamma$ ratio using HPGe and LSC counting. After mixing the stock solution to equal activities, the two MS-RAD implants were radiometrically counted with HPGe. Preliminary results indicate better than ppt level isotope removal. Following this result, we will perform a similar experiment with two isotopes of the same element (e.g., $^{137,134}$Cs), which will be a more thorough test of the mass-based separation method.

We applied MS-RAD to a mixed sample of plutonium isotopes, i.e., a $^{244}$Pu standard. Even if chemically purified, the $^{241}$Pu will over this time decay to $^{241}$Am, as it has an alpha energy overlap with $^{239}$Pu. We demonstrated the successful removal of all other plutonium isotopes and $^{237}$Am by alpha spectroscopy of a mass 238 implant, as shown in the figure. We also created an electrodeposited sample of the $^{244}$Pu standard for comparison and are currently awaiting results.

In FY 2015, the focus will shift to beta and gamma emitters, as these are the main decay modes for the isotopes of interest in the analysis of fission products. The prototype instrument will be modified to enable multiple implants to be accomplished during a single pump down of the instrument. Analytical issues, including methods for calibration of specific activity determinations, will be addressed such that analyses can be compared with conventional radiochemical methods. Calibration and yield determinations will also be addressed.

Comparison of alpha spectrum of MS-RAD separated Pu standard ($^{238}$Pu was implanted) with alpha spectrum of the un-separated standard electrodeposited (ED). All plutonium isotopes have been removed in the MS-RAD spectrum. There is no sign of alpha peak contributions caused by $^{241}$Am.
This project is developing a high-resolution ionizing radiation imaging detector technology for specialized use in medical imaging, nuclear science, and national security applications.

During the last several years, BazookaSPECT, a new class of gamma-ray detector, has been developed that combines columnar scintillators, image intensifiers, and charge coupled device/complementary metal oxide semiconductor (CCD/CMOS) sensors for high-resolution imaging. This detector has been employed primarily in pre-clinical medical imaging applications such as single-photon emission computed tomography (SPECT), which monitors level of biological activity (instead of just taking a picture) in a 3D region of anatomical structures. We are interested in exploring and characterizing the use of BazookaSPECT for detecting additional forms of ionizing radiation (e.g., neutrons, alpha particles, fission fragments, betas, and conversion electrons) for use in national security and nuclear science applications.

Our objective in this project is to establish a detector capability at PNNL and investigate, demonstrate, characterize, and improve the detection response to ionizing radiation. We are building a high-resolution position-sensitive neutron detector (~100 μm resolution, 10–16 cm diameter) that will be used in a variety of imaging experiments such as neutron radiography, diffraction, and neutron coded aperture imaging. In addition, we will seek to develop applications that are enabled or improved upon by the technology. After establishing the capability, we aim to expand BazookaSPECT in terms of hardware, software, and applications.

As noted above, our focus was evaluating the response of the detector to other forms of ionizing radiation, including fission fragments, alpha, neutron, and beta particles. Results have been successful and, as a result, the detector has been renamed the ionizing-radiation Quantum Imaging Detector (iQID) to represent its broad response to ionizing radiation.

During FY 2014, we focused on characterizing iQID performance for single-particle digital autoradiography with alpha particles and broadening its utility by establishing additional collaborations. The iQID spatial resolution was characterized at various imaging configurations by acquiring line spread functions and modular transfer functions. We found that spatial resolutions as high as 20 μm FWHM can be obtained when imaging alpha particles. We showed that a background rate ~2.5 × 10⁻⁴ cpm/cm² can be obtained using spatial features to separate background events from alpha particles. For short-lived isotopes like ²¹¹At with a 7.214 h half-life, we showed that activity concentrations as low as mBq/μg-levels were obtained and μBq/μg-levels for long-lived isotopes.

Our collaboration with the Fred Hutchinson Cancer Research Center continued to grow during the last year with inclusion of the detector for imaging tasks in multiple National Institutes of Health proposals. We commenced a collaboration with the University of Mainz in Germany, which is interested in using alpha-particle digital autoradiography to correlate cancer types resulting from Thorotrast injections using radioactivity biodistributions and histology. Another collaboration has been established with the U.S. Transuranium and Uranium Registries (USTUR), a DOE-funded research program operated by Washington State University that studies actinide elements deposited within the human body in persons with measurable, documented exposures to those elements. USTUR is interested in applying single-particle, digital autoradiography to its studies, as it offers vastly superior performance over the traditional autoradiography techniques that it has used previously.

In FY 2015, we will continue developing iQID. A specific task will be to characterize and improve iQID spatial resolution with beta particles. We will also focus on developing microdosimetry methods, where the dose (amount of grays) to a small clusters of cells will estimated. In addition, we will continue to develop PNNL internal collaborations that can utilize iQID for nuclear science- and national security-related applications.
Measurement of Solubility Curves for Light Lanthanide Elements in Ammonium Carbonate Solution

Chuck Z. Soderquist

This project will provide a data set that will be used in the design of a chemical process for eliminating the U.S. inventory of used nuclear fuel.

The largest single impediment to the expansion of commercial nuclear power is the disposal of used fuel. Currently, the United States has neither a repository nor a formal interim storage plan. Our group at PNNL has developed and demonstrated a process for chemically separating commercial spent fuel into its components on a 10-gram scale to shrink its volume and eliminate much of the risk, giving the fuel a disposal pathway that did not previously exist. Our development is chemically very different from other fuel processes such as PUREX and is intended to separate the fuel into many different fission products and actinides, not merely recover the uranium and plutonium as PUREX does.

The ultimate goal of this work is to eliminate the U.S. inventory of used commercial nuclear fuel by chemically separating it into its components, which yields a much safer, easier-to-handle material. Part of the fuel can be returned to the reactor, where it will be irrevocably burned up and permanently eliminated; another part must be stored for ~400 years for radioactive decay. The remainder, which is nearly all of the original bulk of the fuel, is not very dangerous and can be handled easily with gloved hands, which will make a technically and politically viable disposal pathway for used nuclear fuel. Although the process has been demonstrated at PNNL on a 10-gram scale using actual commercial spent fuel, a number of measurements of solubilities must be made before the process can be scaled up to a multi-kilogram level. The data acquired in this project will fill in one large gap.

Solubility curves were measured for the first six rare earths in ammonium carbonate solution. These particular rare earths were used because they appear in fuel as fission products. At low carbonate concentration, the measured rare earth solubility was low as expected. At high ammonium carbonate concentration, however, the measured solubility was surprisingly high and was a complicated function of temperature, ammonium carbonate concentration, and time. The solubility of the fission product rare earths is easily high enough for used fuel processing. Ammonium carbonate is volatile and can be expelled from aqueous solution by warming. The ammonium carbonate will be gone before the water reaches its normal boiling point, allowing carbonate to be added and later removed without providing any non-volatile components to the solution.

In used nuclear fuel processing, the fuel is dissolved in strong ammonium carbonate solution. Along with the rare earths, most of the fuel dissolves, but insoluble strontium and barium carbonates remain and require filtering, after which the rare earths are re-precipitated by evaporating away the ammonium carbonate. This process causes the rare earths to precipitate, leaving other fission products such as cesium and iodine in solution. The entire progression will separate the used fuel into several components without adding bulk. The products have about the same mass and volume as the starting fuel. No secondary waste stream is produced, and only simple chemical operations are required.

In this project, we were able to show that the fission products have very high solubility in strong ammonium carbonate solution and can be easily manipulated in solution using this process. In addition to solubility curves, we also demonstrated that the ammonium carbonate concentration can be directly monitored using Raman spectroscopy. Ammonium carbonate is never pure; it is always a mixture of ammonium carbonate, ammonium bicarbonate, and ammonium carbamate. The kinetics and equilibria of these three components involve several variables and are moderately complex, so the actual carbonate concentration is hard to know without stopping to measure. Raman spectroscopy allows the simultaneous measurement of carbonate, bicarbonate, and carbamate in solution in a single operation. Using Raman, a shift in equilibrium can be monitored in real time.

The Raman spectra of bicarbonate, carbamate, and carbonate. The composite spectrum can be deconvoluted, and the individual peaks heights can be converted to concentration in solution.
Signatures of Underground Explosions (SUE)

Tim White

We are in search of non-traditional signatures that indicate a chemical explosion rather than rely on the absence of nuclear debris to indicate that an event was chemical in nature.

Should the International Monitoring System detect an apparent underground explosion that lacks the necessary radionuclide signatures necessary to confirm a nuclear event, the question will be which signatures should be exploited to determine whether the event was a chemical rather than nuclear explosion. Discovery of signatures and development of tools that can be used to discriminate underground chemical from nuclear explosions will provide government agencies with the tools to enhance national and international security. Investigations and experiments into these potential signatures will also leverage the science and discovery base at PNNL and enhance our capabilities and expertise.

Identification of signatures used to discriminate underground nuclear from chemical explosions will be a demonstration of the signature discovery process that is

- more efficient by carefully defining the proposition, specifying the scenarios, and developing a process to use limited resources of subject matter experts (SMEs) efficiently
- more economical by documenting a method for exploring the discovery process that will be applicable to other problems, and
- more rigorous as we work potential signatures down through the process to demonstrate developed tools for measuring signature quality and experimental design.

The process for investigating signatures of underground explosions began with brainstorming by a breadth of SMEs and a parallel investigation at the Defense Threat Reduction Information Analysis Center for prior work (primarily nuclear testing) that could be used to guide or impact our investigation. The brainstorming results were followed by a distillation of key ideas to a list of eight categories of observables, which are phenomena that could rise to the level of signature but require investigation in order to explore the order-of-magnitude effects and potential for discrimination. The categories were addressed in targeted white papers by “signature champions.” These documents were used to choose small projects for the characterization of specific potential signatures.

Categories of observables to determine either chemical or nuclear explosions

<table>
<thead>
<tr>
<th>Category</th>
<th>Chemical Explosion Observable</th>
<th>Nuclear Explosion Observable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical degradation products</td>
<td>Hundreds of tons of CO₂, NOₓ, and unique products</td>
<td>Very little</td>
</tr>
<tr>
<td>Thermal</td>
<td>Thousands of degrees</td>
<td>Hotter than the sun</td>
</tr>
<tr>
<td>Post-test ground effects</td>
<td>Extended source, “pushing” force</td>
<td>Point source, sharp force</td>
</tr>
<tr>
<td>Stable-isotope ratios</td>
<td>Introduce C, N, O from external source</td>
<td>Produce 14C, 13H</td>
</tr>
<tr>
<td>Electromagnetic pulse/radio frequency</td>
<td>Small signal, larger if decoupled</td>
<td>Large signal</td>
</tr>
<tr>
<td>Patterns of life</td>
<td>Infrastructure for kilotons of chemical explosive</td>
<td>VIP activity</td>
</tr>
<tr>
<td>Biological</td>
<td>Poisonous CO₂ levels</td>
<td>Uptake of 3H</td>
</tr>
<tr>
<td>Classic test signatures</td>
<td>Seismic, infrasound, hydroacoustic</td>
<td>Radiological, seismic, infrasound, hydroacoustic</td>
</tr>
</tbody>
</table>

Investigations were initialized in the chemical degradation products and patterns of life categories. The chemical degradation work is focused on cataloging the gases released from detonation of ammonium nitrate and fuel oil, concentrating on less ubiquitous chemicals. The patterns of life group examines a variety of observational data in the pre- and post-detonation time frames that may differ between the types of events. These are both small-scale studies that may expand in scope in FY 2015, depending on the initial results. Specifically, we anticipate that preliminary investigations in the biological, stable-isotope ratios, and post-test ground effects categories will begin in our work for next year.
This project is a viability study of non-invasive techniques to measure the gas density and mass flow rate in cooperative verification scenarios.

Expanding global uranium enrichment capacity under international safeguards presents challenges to the International Atomic Energy Agency (IAEA) and regional safeguard authorities (e.g., Euratom) to safeguard gaseous centrifuge enrichment plants effectively while working within budgetary constraints. A key enabling capability in the safeguards approaches that are being considered by the IAEA for the international nuclear safeguards regime is high-accuracy, non-invasive, unattended measurement of UF₆ gas density and mass flow rate in gaseous centrifuge enrichment plants. At present, however, the IAEA has no unattended technology to meet this critical need.

This project is a viability study on the use of acoustic technologies to measure UF₆ gas density and mass flow rate non-invasively in the header pipes of enrichment plants. Acoustic techniques rely on the interaction of applied acoustic energy with the flowing gas to enable assay of gas parameters (e.g., density). Transmit-receive methods have been used in other fields for measurement of flowing gas, but the enrichment-plant UF₆ scenario presents significant challenges for accurate acoustic assay. Primary among them is that the very low nominal gas pressure – approximately 100 times lower than commercially available acoustic measurement systems typically operate – creates a large acoustic impedance mismatch between the metal pipe and the gas. This mismatch means that the transmission of acoustic power directly through the pipe walls into the gas and then to the receiver is very low. This relatively weak interrogating signal must be discriminated from a relatively high background noise produced by the acoustic energy that propagates directly to the receiver through the walls of the pipe. The enrichment-plant scenario is further complicated by temporal variations in gas pressure and density as a part of normal plant operations.

An extensive review of published research activities and commercially available acoustic flow measurement systems was performed in order to understand the state-of-the art, focus the study, and collect the UF₆ acoustic parameters needed to support the simulation, measurements, and analysis.

A simulation framework was developed to explore methods systematically for increasing the signal and discriminating the background; e.g., the careful placement of transducers to enhance signal collection while reducing noise collection as well as damping materials to reduce the noise component selectively. Other options to be considered include encoded transmitter signals and phased-array transmitters to focus the transmitted energy in the gas region. Two-dimensional simulations support rapid, preliminary exploration of design options; more computationally intensive 3D modeling as shown provides high-fidelity insight into the strengths and weaknesses of realistic instrument designs.

To complement the predictive modeling, a laboratory test bed was developed. A combination of commercially available transducers, custom mounting fixtures, and flexible noise-reduction provisions allow the exploration of innovative system designs and benchmarking of the predictive modeling results.

In FY 2015, the systematic investigation of signal enhancement and noise-reduction approaches will continue via simulation and laboratory measurement. Analysis of the assay uncertainty budget for the measurement of both UF₆ density and mass flow rate will inform the viability for the enrichment-plant safeguards scenario.
This project leverages PNNL’s surface science expertise in order to quantify material production at a uranium enrichment facility.

Currently, there are a number of countries with uranium enrichment technology that are either not signatories to the Nuclear Non-Proliferation Treaty or have dubious nonproliferation credentials. Though a robust measurement technique for determining throughput and operational history of a uranium centrifuge enrichment facility does not exist, this technology would be valuable for resolving international concerns associated with these facilities. The nonproliferation community has recognized that an ability to assess past enrichment facility operations is a “holy grail” of nonproliferation verification. To this end, our project will maximize signatures inside of a centrifuge and use PNNL’s ultra-trace analysis capability to provide a unique method for estimating past enrichment plant operations. We will furnish a scientific basis for assessing the ability of various archeological techniques to predict the throughput and enrichment level of uranium processed in the facility.

To develop the capability for validating operations of a uranium enrichment facility, four objectives must be achieved: identify a possible discriminating signature present in an enrichment centrifuge, develop the means to acquire a physical sample that contains the signature, develop the ability to measure the signature accurately, and create a model that translates the data into an assessment of fissile material production. In FY 2014, the potential signatures in uranium enrichment facilities from this work were included in the *Journal of Science & Global Security*.

In FY 2012, we formed collaborations with Oak Ridge National Laboratory, the University of Virginia, and the UK Department of Energy and Climate Change. We completed modeling of centrifuge walls in FY 2013 to estimate the UF₆ corrosion/passivation layer growth rate on the surface of the centrifuge for all materials of interest. Having a good prediction of this growth rate will enable us to interpret the surface analysis and determine the length of the operation.

In FY 2014, handling procedures and samples preparation protocols were developed for the uranium enrichment components. A subset of samples was obtained from the components to test the procedures and protocols. Extreme caution was taken not to damage or disturb the surface of interest or to damage the remaining material for use in future measurement campaigns. Initial measurements were conducted using the 4F-SIMS on samples from the relatively radiological clean uranium enrichment component. Analysis indicated that the equipment had been exposed to a single enrichment of UF₆. Although the sample was analyzed for 13.5 hours, the component substrate was never reached, an unexpected result that demonstrated the large quantity of signature present even on a relatively clean piece of equipment. To deal with this magnitude of signature, sample preparation and analysis methodology will be modified.

A significant effort was made in FY 2014 to prepare and analyze samples containing Pa-231 and Th-230 using TIMS analysis, which is a possible method for measuring a signature to estimate the cumulative mass throughput of a centrifuge. TIMS analysis requires the chemical separation of elements of interest from the substrate. Laboratory testing was conducted to determine the separation efficiency and determine the range of etchant composition over which the procedure was valid. To complete the testing, known quantities of protactinium, thorium, and uranium were added to various quantities of etched Monel to determine the range over which the chemistry process is effective. Initial TIMS measurements were conducted to confirm the separation efficiency of the chemistry process.

To test the chemistry on more prototypic conditions, a surrogate to an enrichment centrifuge was required to be composed of similar materials and exposed to a known uranium enrichment for a significant period to build in the decay products of interest. Small UF₆ containers with known exposure histories to a variety of uranium enrichments were acquired for follow-on work to validate the proposed TIMS analysis method.

SIMS analysis of “clean” valve used in a uranium enrichment facility. Analysis shows consistent isotopic enrichment over the depth of analysis.
To support nuclear materials analysis, we are developing new tools and techniques for analyzing uranium chemically and isotopically on the nanometer spatial scale.

Each year, a considerable amount of research is conducted to detect and analyze anthropogenic uranium, often in a natural uranium background. Most of these studies ignore the chemical form of the sample and rely on mass spectroscopy to gain isotopic information. Unfortunately, this oversight leads to wasted efforts analyzing natural uranium minerals. Recently, researchers at synchrotron facilities have developed and employed sophisticated techniques for analyzing samples with X-rays. These experiments yield valuable information about electronic structure and chemical bonding.

The objective of this research is to determine the utility of X-ray microscopy for enhanced analysis of anthropogenic uranium. We are employing advanced X-ray tools developed at synchrotron light sources for identification of different anthropogenic and natural chemical forms of uranium. We will analyze relevant natural and industrial uranium compounds for fingerprinting purposes. Given the proper signatures, spatially resolved X-ray absorption spectroscopy could efficiently and non-destructively screen samples for anthropogenic uranium, allowing for subsequent isotopic determination. The results of our research will be of great interest to DOE and could fundamentally improve anthropogenic uranium analysis.

FY 2013 focused on obtaining preliminary X-ray absorption data on a test set of uranium minerals and developing methods for preparing the anthropogenic uranium samples. We restricted our time to collecting spectra at the oxygen K-edge, as this region promises the most chemical information. Indeed, the pre-edge peak position correlated with the chemical environment or uranyl species; i.e., oxygen K-edge spectra exhibit potential to differentiate various chemical forms of uranium.

Our FY 2014 goal was creating a library of reference spectra over bulk compounds to compare to future scanning transmission X-ray microscopy (STXM) measurements. We measured the oxygen K-edge absorption of a variety of uranyl minerals, including uranyl silicates (bolwoodite, soddyite, uranophane, sklodowskite, and cuprosklodowskite), oxyhydroxides (compreignacite, becquerelite, and schoepite), carbonates (zellerite, liebigite, and sodium uranyl carbonate), and phosphates (phosphuranylite, metatorbernite, and meta-autunite), and some anthropogenic uranium compounds (uranil fluoride, uranyl chloride, and uranyl nitrate). We also collected fluorine K-edge absorption spectra of uranyl fluoride and uranium tetrafluoride data at the Synchrotron Radiation Center with supplemental data from the Canadian Light Source and Stanford Synchrotron Radiation Lightsource.

We find that the general classes of uranyl compounds (silicate, oxyhydroxide, carbonate, or phosphate) can be reliably distinguished on the basis of their X-ray absorption spectra. In all cases, X-ray spectra derived from uranyl minerals were distinct from the spectra obtained from uranyl fluoride and uranyl chloride. Comparison to the X-ray absorption spectra of appropriate model compounds (e.g., sodium bicarbonate for the uranyl carbonates) allowed the assignment of particular transitions to either the counterion or the uranyl moiety.

After establishing bulk spectroscopy and proving the ability of ligand near edge X-ray absorption fine structure (NEXAFS) to chemically distinguish uranyl samples, we worked to confirm the spectral integrity on the nanoscale. For this purpose, we collected STXM data at the Advanced Light Source over a schoepite particle sample. These results show excellent correspondence with the bulk schoepite spectra. In addition, the spatial resolution of the instrument can distinguish schoepite from a nearby contaminant.

In FY 2015, we will continue STXM measurements on chemical reaction interfaces, developing a method for depositing uranyl fluoride particles onto silicon nitride STXM windows aged under various temperature and humidity conditions and analyzed for chemical changes across the particles. By comparing our STXM measurements with our spectral library, we hope to elucidate reaction intermediates and correlate the extent of reaction with the storage environment.
The nature of the matter in our universe is currently unknown. Cosmological observations on scales of galaxies to galaxy clusters to the thermal photon relic of the Big Bang suggest that the standard model of particle physics accounts for a mere 15% of the matter content of the universe. Baryonic matter has largely been ruled out as a candidate for dark matter, which leaves new, stable fundamental particles as the favored possibility for dark matter. Weakly interacting massive particles (WIMPs) are a broad class of new, fundamental particles similar to the neutrino that have been proposed as a solution to the dark matter issue. Fundamentally, if there is a new symmetry of nature, then there could be massive, stable particles filling the universe with limited interactions with normal matter.

Through this project, scientists at PNNL have established critical roles in the community effort to make progress in dark matter. PNNL is now a member of a number of large collaboration dedicated to searching for WIMP dark matter, MiniCLEAN, DarkSide, SuperCDMS, and PICO. SuperCDMS uses unique germanium detectors to search for dark matter interactions. SuperCDMS uses cryogenic bolometry to identify background events. PNNL scientists have recently published SuperCDMS data using a novel, high-voltage technique to search for light (< 5 GeV) WIMPs. DarkSide and MiniCLEAN approach dark matter detection using 500 kg of liquid argon as the target material. The scintillation light of liquid argon fundamentally contains information on the nature of the particle interaction. Although MiniCLEAN is a large dark matter detector, it is a small but critical demonstration for the envisioned third-generation experiment, a high priority for the long-term strategy of the high energy physics community.

PNNL's expertise in ultra-low-background materials helps to reduce the natural and cosmically induced background that could overwhelm the extremely rare dark matter events, which is the common challenge for all these experiments. PNNL's expertise in copper electroforming, uranium and thorium assay and detector assembly are helping these experiments make order of magnitude improvements in sensitivity.

In addition to participation in the planning, execution, and analysis of large, complex experiments to detect dark matter, PNNL is involved in detailed calculations to determine the ultimate sensitivity of specific approaches to WIMP detection. Scientists are using modern computation techniques to estimate the backgrounds produced in unavoidable high energy, cosmic ray interactions. Additionally, scientists are calculating the signals that are expected from the lowest energy interactions in semi-conductor detectors, a crucial detail that has no data and no theoretical predictions. With these two calculations, both the signal and the backgrounds will have better predictions, leading to a better understanding of the ultimate sensitivity of future experiments.

From a recent Physical Review Letters article, this figure illustrates the scientific impact of recent SuperCDMS data. The black line shows the sensitivity of the data to the blue region of interest; the red shows the low-mass WIMP sensitivity of the high-voltage operational mode proposed and led by scientists at PNNL.
Resolving the Reactor Neutrino Anomaly by Precision Beta Spectrometry

Kim A. Burns

We are developing a new technique that will reduce the uncertainty associated the beta spectra and subsequent unfolded neutrino spectra.

The observed antineutrino rates at reactors, currently vital to the study of neutrino oscillations, are typically lower than model expectations. An experimental approach may provide a new understanding of neutrino physics to explain this deficit, though model estimation uncertainties may also play a role in the apparent discrepancy. Reactor neutrino spectra have been used in conjunction with neutrino detector measurements in the search for evidence of neutrino oscillations and in applications investigating nonproliferation surveillance methods. Next generation experiments aimed at measuring the last unknown mixing angle $\theta_{13}$ would also benefit from an accurate description of neutrino spectra. The absolute precision and the energy spectrum of the neutrinos released by fissions are the primary constraints in the interpretation of the reactor neutrino data.

Through the fission process, four isotopes, $^{235}$U, $^{239}$Pu, $^{241}$Pu, and $^{238}$U contribute more than 99% of all reactor neutrinos with energies above the inverse beta decay threshold (neutrino energy $\geq 1.8$ MeV). Reactor neutrino fluxes from the thermal fission of $^{235}$U, $^{239}$Pu, and $^{241}$Pu are currently obtained by inverting measured total beta spectra obtained in the 1980s at a beam port at the High Flux Reactor of the Institut Laue-Langevin (ILL). The objective of this project is to design an experimental technique that promises reduced uncertainties for measured data using precision measurements of the beta energy spectrum from neutron induced fission using an accelerator.

A major advantage of an accelerator neutron source over a neutron beam from a thermal reactor like the one used at ILL is that the fast neutrons can be slowed or tailored to approximate various power reactor spectra. The ability to measure fission betas produced using a prototypic reactor spectrum provides two potential methods for quantifying the uncertainty with the existing measurements: quantifying the contribution from the $^{238}$U fission betas and quantifying the difference between the reactor neutrino fluxes from the thermal fission and prototypic reactor fission of $^{235}$U, $^{239}$Pu, and $^{241}$Pu.

During FY 2013, we completed a thorough literature search and completed a statistical analysis of the previous experimental setup and spectral unfolding methodology. Initial stages of an accelerator target design were completed to demonstrate feasibility of completing a fission-based experiment using a proton accelerator. Preliminary results indicated that it is possible to generate an appropriate neutron spectrum and neutron flux to support the experiment.

In FY 2014, the accelerator target design was completed. The material composition and layout of the target were determined based on nuclear physics, fabricability, mechanical requirements, and thermal analysis. The target consists primarily of a neutron production region, neutron spectral tailoring region, and the reflector/shield. We determined that the spectrometer would be a simple dipole with a time projection chamber to provide active tracking of the betas and ultimately a different set of systematic uncertainties compared to previous measurements, ideally providing an “independent” test. Fission foil targets containing a small (mg) isotopic fission target of the primary reactor isotopes $^{235}$U, $^{238}$U, $^{239}$Pu, or $^{241}$Pu will be irradiated using the tailored neutron spectra produced by the accelerator target.

We completed a more detailed analysis to determine the fission product retention rate vs. fission beta release rate from the foils. Two potential encapsulation materials, nickel foil and sputtered graphite, were identified. The final choice of...
encapsulation material will depend on several factors, including ease of fabricability, minimum wall thickness achievable, and cost. Analysis of the beta spectra for various foils showed that a thickness of 7.85 μm can be tolerated without significantly worsening the energy resolution of the entire system, and we added a gamma spectral analysis capability to constrain the fission products. By measuring the gammas produced by the decay of many of the fission daughters, a maximum likelihood fit in energy and time can be performed to extract the yields of the various fission products. To accomplish this measurement, a single high relative efficiency high-purity germanium (HPGe) detector will be situated some distance from the fission foil for measuring gamma rays emitted from the fission foil. In FY 2014, the details of the target design were presented at the international Conference on Application of Accelerators in Research and Industry and submitted to a journal focusing on conference proceedings.

For FY 2015, alternative targets for the production of neutrons that are tailored to produce a range of different neutron spectra will be investigated. In addition to applications associated with the reactor neutrino anomaly experiment, developing alternative tailored neutron spectra targets has many potential applications. Other potential missions for tailored neutron spectra include Cf-252 replacement, prototypic fast fission irradiation testing for fast reactor materials testing with high dpa rate, a standard neutron field for fissionable material detector development, nuclear data testing, neutron tomography systems for radiologic diagnostic imagining, and development of isotope production methods. The broad applicability of tailored neutron spectra represents a potential future funding avenue, but work will be required to define acceptable target configurations that produce a variety of neutron spectra.
Smartphone Enabled Transmission and Backscatter Radiography

Tim White

The goal of this project is to demonstrate a novel approach to X-ray imaging specifically leveraging the spatial information, computational power, and image display capabilities of a smartphone.

Transmission-imaging geometry is a variant of a lens-coupled radiography-system design that has been used for decades. Typically, the optical detector in the design is a high-end charge-coupled device (CCD) camera, although certainly inexpensive cameras have been used. In addition, cone-beam CT is a well-established practice, and laboratory-scale systems using lens-coupled detectors are ubiquitous. The novelty of our approach leverages the integrated detector, processing, and display of the mobile device to provide a more compact, modular, and portable unit.

Two possible imaging geometries are envisioned: a transmission radiography with CT capability, and a backscatter geometry. Common to both geometries is a compact, low-energy X-ray generator and a smartphone. The phone is used for detection as well as the display and computation needed for image creation. The two geometries use different components to convert X-ray photons to optical photons that can be sensed by the camera on the phone and, of course, different processing to create images. As noted, the geometry is a variant of the well-established lens-coupled radiography-system design.

Our project demonstrated the feasibility of a lens-coupled X-ray imager using a smartphone as the detector, processing, and display unit. The novelty in the approach is marrying the components and imaging techniques into a modular, stand-alone, hand-held capability for nondestructive-evaluation applications. An Apple iPhone 5S was used as the smartphone platform; available resources and budget drove this choice, and it may be that other smartphones would work as well or better. A prototype application was developed to control camera parameters, accumulate images into a sum, display, and save the data. A high-sensitivity phosphor was used as the X-ray-optical-photon conversion element. For demonstration purposes, a compact rigid assembly holding the phosphor, smartphone, and optical-path-folding mirror was constructed on an assembly that was approximately $12 \times 12 \times 12$ cm$^3$.

An X-ray generator was obtained for imaging experiments in which contrast and spatial resolution are functions of the source geometry and energy and the phosphor response. Images of modulation-transfer function test objects were obtained for quantitative analysis, and images of small objects obtained for qualitative analysis. A spatial resolution of about 2.5 line-pairs/mm was demonstrated. Although computed tomography was not demonstrated, the software hooks for coordinating and recording spatial position as data are collected are available in the application.

Backscatter-imaging experiments were not as promising. Thin (0.25 in) samples of polyvinyltolulene (PVT) phosphors were obtained for the backscatter experiment. These were optically coupled to the camera with index-matching pads. Experiments with low-activity isotopic sources (used to mimic the small signal from the backscattered radiation) demonstrated very little light collection by the camera, likely due to the low efficiency of the individual pixels on the camera or to the poor optical coupling.
Ultra-Precise Electron Spectroscopy to Measure the Neutrino Mass

Brent A. VanDevender

A precise measurement of neutrino mass is critical to our understanding of the gravitational evolution of the universe; thus, we worked to demonstrate that cyclotron radiation is detectable with sufficient frequency precision.

A fundamentally new electron spectroscopy technique has been developed to be applied in the search for the absolute mass of the neutrino. The conversion electron spectrum of $^{83m}$Kr was measured as a proof-of-principle demonstration for a tritium beta-decay endpoint measurement, which can be sensitive to neutrino mass. In the process, the cyclotron radiation from individual electrons in a magnetic field has been observed. Though predicted by Maxwell’s Equations for Electricity and Magnetism over a century ago, it had never been observed for individual charges before. Neutrino mass has far-reaching implications from theories beyond the standard model of particle physics to the evolution of large-scale structures in the universe. The DOE Office of Science and the physics community at large therefore rate measurement of neutrino mass as one of the top priorities in basic nuclear science.

We developed and demonstrated a new technique in this field: specifically, we detected the cyclotron radiation emitted by magnetically trapped electrons. The energy of a trapped electron is encoded in the radiation frequency, which is measured with extreme precision. Our method promises energy resolution superior to existing techniques. The goal is to measure the neutrino mass $m$ involved in tritium beta decay by observing a small reduction in electron energy $E$ attributed to neutrino mass by Einstein’s relation $E = mc^2$. Experiments based on existing techniques have reached their ultimate neutrino mass sensitivity and may still not be sufficient to weigh the neutrino, which could be up to 100 times lighter still.

A proof-of-principle demonstration of our technique was made by measuring the conversion electron spectrum of $^{83m}$Kr. Individual electron events all have the same general features: a sudden onset of power at the cyclotron frequency, a slow chirp towards higher frequency (lower energy) as the electron loses energy by cyclotron radiation, and a series of discrete jumps corresponding to energy lost in collisions with residual H$_2$ molecules in the high-vacuum environment. The initial kinetic energy of the electron is also related to the start frequency by basic relativistic kinematics. The desired spectrum is just a histogram of initial kinetic energies. At the time of this writing, a report of these results is being peer reviewed for the journal Nature.

PNNL played critical leading roles in three major aspects of the experiment, which was performed in collaboration with MIT, the University of Washington, and the University of California, Santa Barbara: manufacture of strong radioactive $^{83m}$Kr sources, electrical engineering of microwave receiver structures and electronics, and hosting of high-performance computing resources. The success of this prototype demonstration is the basis of a pending proposal for a base grant to PNNL from the DOE Office of Science, Office of Nuclear Physics.

This project laid the foundation for this research that will now continue for many years. The next step is to explore the instrumental effects and systematic uncertainties on measured electron energies with more data from $^{83m}$Kr. First measurements with molecular tritium gas will determine the mass difference between tritium and $^3$He in the same prototype instrument. A limit on neutrino mass comparable to present limits will follow. The ultimate neutrino mass sensitivity will be obtained after the technique is scaled to larger volume sources, and techniques for maintaining the tritium source gas in atomic (vs. molecular) form.

Upper image: Individual electron events are shown as having the same general features. Lower image: The desired spectrum is just a histogram of initial kinetic energies.
**ON THE COVER:**

**PNNL Scientists Study the Role of Soil Microbes in the Soil-Mineral Weathering Process**

PNNL scientists are studying the mineral/biological associations in the rhizosphere, plant root systems, to better understand the role of the soil microbes in the soil-mineral weathering process. Pictured are conidia (spores) of *Penicillium sp.*, an ubiquitous soil fungus that lives mainly on organic biodegradable substances. The spores were imaged using instrumentation at EMSL, a DOE user facility at PNNL. Research for this project was supported by the U.S. Department of Energy’s Office of Biological and Environmental Research.

**PNNL Scientists Design Novel Structured Metal Alloy Anodes for Na-Ion Batteries**

At Pacific Northwest National Laboratory, researchers are designing novel metal alloy anodes that improve the effectiveness of sodium-ion batteries. Within these anodes, nanofibers, created through an electrospin technique, serve as key components. The tiny fibers, shown in this colorized image, were captured with a helium ion microscope. The research is based upon a design material synthesis approach that achieves targeted nanoarchitectures by controlling chemical reactivity at interfaces. The goal is to create a low-cost storage technology that makes it possible to more effectively capture energy and manage the nation’s power grid. This research was funded by the U.S. Department of Energy’s Office of Basic Energy Sciences.

**PNNL Scientists Search for a Rare Form of Radioactive Decay, Never Detected Before**

Drawing upon the Lab’s signature capability in ultra-low-level counting, research in the field of high energy physics is helping to determine the mass and properties of neutrinos, one of Nature’s fundamental sub-atomic particles. The raw copper pictured here, is used to build and shield the experiment and will be manufactured underground in an ultra-pure form using a PNNL-developed process to protect against naturally occurring radioactive impurities. This research is supported by the U.S. Department of Energy, Office of Nuclear Physics.

**PNNL’s Advanced Computing Capabilities Resolve National Scientific Challenges**

PNNL is creating new computational capabilities and providing multifaceted mathematical solutions to address and resolve significant problems of national interest to missions in science, energy, environment, and national security. PNNL’s graph-theory research is helping to characterize the power grid using a “network-of-networks” approach and developing stochastic models to match these characteristics. This computational research is supported in part by the U.S. Department of Energy’s Office of Advanced Scientific Computing Research.