CHEMICAL ENGINEERING & MATERIALS SCIENCE RESEARCH HIGHLIGHTS 2014

MICHIGAN STATE UNIVERSITY

LETTER FROM THE DEPARTMENT CHAIR

Reflecting back on the 2013–2014 academic year, I am reminded of the many exciting developments in the Department. First, congratulations to our three young assistant professors who are recipients of prestigious National Science Foundation CAREER Awards. These faculty members—Richard Lunt, Tim Whitehead, and Jason Nicholas—are branching out into new research areas that are keeping our department on the cutting edge.

I also am very pleased that Bruce Dale was named a University Distinguished Professor, MSU's highest honor for a professor, in recognition of his achievements both in the classroom and in research. Bruce is a pioneer in cellulosic ethanol and has spent his career in developing sustainable biofuels. Congratulations are also in order to faculty members who have recently received University-wide recognition—Dennis Miller for a Distinguished Faculty Award and Jeff Sakamoto for an MSU Teacher-Scholar Award. Congratulations again to Dennis Miller for receiving the Department's Withrow Teaching Excellence Award.

The Department also welcomed two new faculty members in August. Philip Eisenlohr has extensive expertise on microstructure-property relation with a focus on metal plasticity. He comes to us from the prestigious Max Planck Institute in Düsseldorf, Germany. Yue Qi specializes in integrating material failure models with battery life prediction. She brings 12 years of experience working for General Motors at the Chemical Sciences and Materials Processes Lab in Warren, Mich. These faculty hires and faculty accomplishments help the Department expand its research portfolio and attract outstanding graduate and undergraduate students.

Our students' accomplishments were also noteworthy. Logan Matthews, ChE '13, took top honors in the American Institute of Chemical Engineers 2013 National Student Design Competition, the fourth consecutive year the honor has been won by an MSU chemical engineering student. John Suddard-Bangsund, MSE Junior, was awarded a Goldwater Scholarship. To recognizing an outstanding ChEMS alumnus, the 2013 Red Cedar Award was presented to Morris C. Place Jr., celebrating his achievements during more than 50 years in the oil and gas industry.

I believe that our focus on three research themes — energy and sustainability, nanotechnology and materials, and biotechnology and biomedical engineering — has helped propel the Department's momentum, and I look forward to the Department's continued growth and future successes.

Martin C. Hawley
Chairperson and Professor

DEPARTMENT OF CHEMICAL ENGINEERING & MATERIALS SCIENCE

The Department of Chemical Engineering and Materials Science at Michigan State University has vibrant research programs in both Chemical Engineering and Materials Science and Engineering. The current faculty count stands at 32, including four University Distinguished Professors. The faculty have received numerous awards and honors, including: the NSF CAREER Award, the University Distinguished Faculty Award, the Withrow Teaching Excellence Award, and the Withrow Research Scholar Award. Also included among the faculty ranks are multiple society Fellows (of the American Institute of Chemical Engineers, the American Institute of Chemists, the Society of Plastics Engineers, ASTM International, the American Ceramic Society, ASM International, ABET, and the American Physical Society).

Among the Department's achievements are

- Total research expenditures are about $8,000,000
- Approximately 155 refereed publications and 8 patents per year
- Growth of the total undergraduate student population to 633
- Current graduate enrollments of 93 Ph.D. students and 14 Master's students.
- Several major research centers, including the Composite Materials and Structures Center; the Center for Revolutionary Materials for Solid State Energy Conversion (Department of Energy); and the Great Lakes Bioenergy Research Center (Department of Energy).

The mission of the MSU CHEMS Department is to be nationally recognized for excellence in research, teaching, and service. In support of this mission four goals have been targeted:

- Provide leadership and excellence in conducting nationally recognized, innovative, and cutting-edge research
- Recruit high performing students and deliver modern, high-quality graduate and undergraduate programs that produce top-notch graduates serving the needs of industry, government, and academia
- Offer outstanding professional and outreach services
- Conduct fundraising from the private sector, state, and federal sources, and provide stewardship in support of research, instruction, and service

As we look to the next decade, the Department has established strategic initiatives to ensure our continued ascension in productivity and prominence:

- Addition of new faculty to complement and supplement our research priorities
- Recruitment of a higher number and quality of PhD students
- Increase in the number of highly qualified undergraduate students and bachelor's degree graduates prepared to solve the problems of both today and tomorrow
- Enhanced support of endowments for fellowships, scholarships, professorships, and the discretionary excellence fund.

The department has positioned itself and established its research priorities to address critical 21st Century challenges such **as energy and sustainability, nanotechnology and materials, and biotechnology and biomedical engineering.**

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Kris Berglund

Kris Berglund's work is directed at using non-fossil fuel raw materials to make foods, chemicals, and food ingredients. All of the sources are either from agricultural products or forest raw materials. There are two main objectives to this approach. In the first case the goal is to produce sustainable production, while the second is production of products with a lower potential for containing harmful impurities. The main approach is to use fermentation processes followed by purification to create complete processes for the final product.

Thomas Bieler

Thomas Bieler examines deformation and heating effects on evolution of microstructure details in structural metals and alloys using electron microscopy and synchrotron x-ray diffraction. Analysis of spatially resolved crystal orientation and misorientation relationships is used to identify mechanistic details for models useful for prediction of properties and long term reliability. These skills are used to examine damage nucleation in titanium alloys, lifetime prediction of solder joints, and identification of processing strategies to obtain optimal properties in refractory body centered cubic metals such pure tantalum and niobium (in support of advanced superconducting cavity design for particle accelerators).

Carl Boehlert

Carl Boehlert's research group is concentrating on understanding the deformation behavior of hexagonal close packed metals, in particular titanium and magnesium alloys, under extreme environments. The environments include a combination of both elevated temperatures and irradiation, and a variety of loading conditions are being used to mimic component use in commercial applications. In-situ testing methods have been developed which allow for characterizing the surface deformation behavior during deformation in order to understand the deformation evolution. The work is being sponsored by the National Science Foundation and the Department of Energy.

Scott Calabrese Barton

Electrochemistry dramatically impacts numerous technologies for energy and chemical production, including modern electric and hybrid vehicles. A key enabler of these technologies are electrocatalysts. Scott Calabrese Barton's research group studies new electrocatalysts, materials, and electrode design for fuel cells and chemical conversion. Transition metal electrocatalysts are being studied as replacements for high-cost platinum. These catalysts could potentially lower the cost of fuel cell systems and enable practical fuel cell vehicles. Bioconversion involving enzyme electrocatalysts may lead to conversion of renewable resources to value-added chemicals. Professor Barton's group is developing electrodes to achieve such bioconversion, including catalysts for regeneration of enzyme cofactors, and high-surface carbon materials for immobilization of enzymes, catalysts, and cofactors. Throughout this work, mathematical models are incorporated to build understanding of electrochemical kinetics and transport, leading to tools for analysis and optimization of novel electrode architectures.

Eldon Case

The reliability of brittle materials, such as thermoelectric materials for waste heat energy conversion, depends very critically on their mechanical properties. The mechanical properties, in turn, depend on how the materials are processed. Eldon Case conducts research on the mechanical properties and processing of brittle materials. In collaboration with other professors in the Department of Chemical Engineering and Materials Science, Professor Case is processing thermoelectric materials with nanoparticle and nanoplatelet additions and then characterizing the resulting mechanical properties in an effort to utilize the nanophases to slow the growth of cracks. Also, Professor Case is exploring the use of porosity to help blunt crack growth in thermoelectrics while still maintaining the thermal and electrical properties needed for efficient energy harvesting. In a related area, he is characterizing the scatter in strength in highly porous ceramics that have the potential for applications as sensors, filters and biomedical materials.

Christina Chan

Christina Chan is a Professor of Chemical Engineering at Michigan State University. She has appointments also in the Biochemistry and Molecular Biology Department as well as the Computer Science and Engineering Department. Currently, her laboratory focuses on understanding the pathways that are altered in diseases, such as obesity, Alzheimer's disease and cancer. Her group develops and applies bioinformatics and systems biology approaches in combination with biochemical, biophysical, and molecular biology measurements and animal studies to identify targets and disease biomarkers. Her group also is developing polymeric-based drug delivery and tissue engineering platforms to modulate these pathways for treating these diseases.

Martin Crimp

Martin Crimp's research group uses advanced experimental techniques, including scanning electron microscopy, transmission electron microscopy, nano-indentation, and atomic force microscopy to characterize the details of how materials react to mechanical loads. Understanding these deformation and fracture mechanisms is critical to optimizing the performance of materials in a wide variety of application environments, including energy generation, transportation systems, and medical applications. The optimization of performance facilitated by an understanding of the mechanisms involved in mechanical performance leads to enhanced reliability and lifetimes. In turn, enhanced structural performance can lead to significantly lower raw materials consumption, enhanced fuel efficiencies, and beneficial life cycle costs.

Bruce Dale

The mission of the Biomass Conversion Research Laboratory (BCRL), led by Bruce Dale, is to help catalyze the transition of the modern industrial society to a sustainable society. The BCRL strives to develop the conceptual and experimental foundation for large scale, economical, environmentally sustainable systems to produce fuels, animal feeds and chemicals from cellulosic (non-food) plant biomass. Experimentally, Professor Dale's team focuses on pretreatment and enzyme systems to produce low cost sugars and aromatics from biomass. Our conceptual work uses life cycle assessment and techno-economic analysis to design and evaluate integrated systems by which cellulosic biomass is grown, harvested, transported and processed in ways that are economically and environmentally sustainable.

Lawrence Drzal

Lawrence Drzal conducts research on the synthesis, functionalization, processing and manufacturing of multifunctional nanomaterials such as graphene, nano-cellulose and boron nitride with a wide range of physical properties, morphology and economics. Research from Professor Drzal's Group has led to a commercially viable method for manufacturing graphene nanoplatelets which have multiple desirable intrinsic properties that make them particularly attractive as additives to polymers and composites as well as for energy storage applications. Full advantage of these multifunctional nanomaterials requires not only a high level of dispersion but also novel processing methods to generate 2D and 3D microstructures within the polymers in which they are dispersed. Professor Drzal's group is investigating chemical, electrical and flow methods to induce desirable structure of nanomaterials by themselves as well as within polymers to optimize their performance in structural and energy generation and storage applications.

Philip Eisenlohr

The mechanical behavior of structural materials is intricately influenced by their chemistry as well as their microstructure. The latter is strongly impacted by processing conditions, making the prediction of the behavior of existing materials and the design of new materials with targeted properties a remarkable challenge. To address this challenge, Philip Eisenlohr is modeling material behavior at multiple length and time scales, with the goal to ultimately formulate a reliable description of material behaviors at the scale of engineering components. Professor Eisenlohr's work will facilitate searching for a material that meets a given property demand. One salient application of his tools is their use as a virtual laboratory for materials testing, which holds the promise of substantial reductions in cost and time spent on real experiments during the design of materials and components.

David Hodge

There is a strong need to develop energy and material alternatives such as through the capture and redirection of energy in the carbon cycle by utilizing the chemical constituents of plant cell walls as a renewable chemical and energy feedstock. However, the higher order structures of plant cell walls prevent utilization of these carbohydrates due to what could be considered the "recalcitrance" of lignocellulose. It is noteworthy that this vast resource of reduced carbon is overwhelming used for its existing structural value (as fiber and as a construction material) or for combustion rather than for the value of its chemical constituents. Work in David Hodge's laboratory addresses the challenges associated with the conversion and fractionation of plant cell wall biopolymers (as well as food crops) to renewable fuels and chemicals by catalytic and biochemical means.

K. Jayaraman

K. Jayaraman's research group is developing processing strategies, flow models and design tools for shaping polymeric materials into products for various industry sectors: automotive, energy and building or construction. This research combines computational modeling, melt processing, and characterization with chemical, imaging, mechanical and rheological methods. The focus is on rheology modification and microstructure development during melt processing and solid-state processing of polymer composites, nanocomposites, foams and thermoplastic elastomers. Professor Jayaraman's research has been applied to develop processing strategies for polymer composites, recycled polymers and polymer nanocomposites to make foam core panels, multilayer blown film, and light-weight panels for use in construction.

Wei Lai

Generating electricity from renewable energy sources is one of the greatest challenges that scientists and engineers will face in the 21st century. The intermittent nature of many renewable energy sources such as solar and wind requires energy storage solutions that can match a variable energy supply with variable demand. Electrochemical energy conversion and storage devices (fuel cells, batteries, and supercapacitors) enable direct, clean, and efficient conversion between electrical and chemical energy. Wei Lai's research is focused on the study of advanced materials and electroanalytical methods for electrochemical energy conversion and storage devices. Professor Lai is uniquely interested in understanding the structure and dynamics of solid-state battery electrode and electrolyte materials. In particular, his research seeks to understand the long-, medium-, and short-range atomic structures of these materials and their effect on the materials' electrical/electrochemical properties and applications.

Andre Lee

Andre Lee's group has been interested in exploring various materials applications using nano-structured chemicals for the past several years. Applications include improving high temperature performance in polymeric materials, improve oxidative stability of metallic materials used in electronic interconnects, retard the materials transport across the hetero-interface when subjected to external thermal and electric loads. More recently, technique capable to separate geometrical isomers of functionally useful nano-structured chemicals was developed. This advancement is expected to extend our investigation to explore chemically selective engineering applications.

Ilsoon Lee

Ilsoon Lee's nano bio engineering laboratory is utilizing nanotechnology and self-assembly as new tools to design new nanostructured materials and systems to solve existing engineering problems in energy, materials, and environment. Professor Lee's research focuses on the design and fabrication of nano / bio particles and films to advance energy, biocatalytic systems, and functional materials. Specific projects include 1) Prevention of Bacterial Biofilm Formation on Surfaces, 2) Solar-Bio-Nano Based Wastewater System for the Production of Energy and Potable Water, 3) Hybrid Nanostructured Metal Foam Material Systems for Blast Impact (and Wrinkle-free films), 4) Fabrication of Functional Nanoparticles and Delivery System, 5) Fast and Efficient Production of Cellulose Nanowhiskers and the Use in the Composite Materials, and 6) Understanding and Modulation of Interfacial Properties within Plant Cell Wall Pores to Facilitate Enzymatic Deconstruction and Conversion to Biofuels.

Carl Lira

Make it, boil it, dissolve it, purify it. The Lira Research group is fascinated by characterizing these relatively common properties for pure components and mixtures, and the way the chemical structure determines these properties. When an alternative fuel is developed and blended with petroleum fuel, what are the cold flow properties? What is the effect on the boiling curve? When new chemicals are made from renewable feedstocks, how will they behave in a reactive distillation column? We are also interested in improving modeling of vapor-liquid-liquid equilibria that occurs frequently for bioderived molecules.

Richard Lunt

The Molecular and Organic Excitonic laboratory led by Richard Lunt focuses on developing inorganic and organic semiconductors for 1) low-cost solar energy production and 2) efficient energy utilization technologies. The MOE lab looks to exploit oriented, crystalline, nanostructured, and excitonic films through organic-inorganic and organic-organic interactions while studying fundamental relationships between structure and photophysical properties of these new semiconductor materials. These studies are leading to highly deployable photovoltaics, light-emitting diodes and luminescent solar concentrators. Professor Lunt and his students have produced a number of key scientific and technological achievements including, most notably, the first demonstration of transparent solar cells and solar concentrators, which are creating a new paradigm for building integrated photovoltaics. Professor Lunt has been contributing to the commercialization of many of these technologies having co-founded the company Ubiquitous Energy Inc. that is developing light-harvesting products and surfaces.

Dennis Miller

Research in Dennis Miller's group focuses on the development of chemical pathways, catalysts, and processes to produce chemicals and biofuels from renewable biomass resources. Research projects involve both the development of new catalysts and reactor designs to carry out conversion of feed stocks to desired products, and the separation and purification of products from the reaction mixtures. Major efforts in current work are in reactive separations, where the chemical reaction and purification take place in a single process unit, and in upgrading low-cost intermediates from biomass such as ethanol and furan-based compounds to higher-profit products. Twenty U.S. patents along with numerous publications have come out of this work, and several technologies have been licensed for commercial development.

Donald Morelli

Donald Morelli works at the interface between experimental solid state physics and materials science to explore and develop new electronic materials for energy conversion applications. A major focus of his current work is new thermoelectric semiconductors, materials capable of converting heat directly to electricity. Potential applications include power generation from primary heat sources such as the sun or from waste heat sources such as vehicle exhaust gas. Work in Professor Morelli 's laboratory is centered on the synthesis of new forms of matter, including both single phase alloys and compounds and composite structures created using nanoscience. Ultimately, the aim is to develop design rules to predict properties of advanced thermoelectric materials, and realize these structures through innovative synthesis and advanced structural as well as chemical characterization. Some recent work has explored the use of natural minerals for thermoelectrics, potentially offering increased performance at a fraction of the cost of traditional materials.

Ramani Narayan

The Biobased Materials Research Group led by Ramani Narayan engineers new biobased and biodegradable-compostable polymer materials and bio processes using agricultural crops and residues (soybean, and corn), lignocellulosic biomass, and algae. These products find commercial application in plastic bags, injection molded articles, thermoformed products, protective and insulation packaging, arts and crafts materials, and biomedical applications. Successful technology commercialization exemplars are: poly(lactic acid) (PLA) technology; the world's foremost 100% biobased and biodegradable-compostable material with a 150,000 ton commercial plant operating in Blair, Nebraska by NatureWorks LLC (www.natureworksllc.com); biopolyester and modified PLA resins for biodegradable-compostable films, molded products, and engineering plastics through Northern Technologies(www.natur-tec.com); biofoam sheet manufacturing for cushion and insulation packaging under the trade name GreenCell by KTM Industries (www.ktmindustries.com); biobased polyols technology for flexible and rigid polyurethanes in partnership with Zeeland biobased products (www.zfsinc.com); and licensing 4 patents on thermoplastic modified starch and its copolymers with biopolyesters to Ingredion Inc.

Jason Nicholas

World energy demand is anticipated to increase 50% in the next 25 years. Solid oxide fuel cells (SOFCs) have the unique ability to reduce the environmental impact of today's hydrocarbon based economy while simultaneously providing the infrastructure for a CO2-neutral economy utilizing biofuels, solar fuels or hydrogen. Unfortunately, the low chemical reaction rates found within SOFC electrodes restrict these devices to high operating temperatures that require expensive materials. Jason Nicholas studies how these operating temperatures can be reduced using nano-composite electrodes and stain-engineered catalysts. Some of his recent accomplishments include the development of the world's most highly cited nano-composite Solid Oxide Fuel Cell electrode model, the identification of novel ways to experimentally control nano-particle catalyst morphologies, and the development of an in situ, electrode-free bilayer curvature relaxation technique for measuring oxygen surface exchange coefficients as a function of simultaneously measured stress state.

Robert Ofoli

Robert Ofoli's research addresses the need for sustainable production of energy and materials. His primary interest is in the synthesis, characterization, assessment and optimization of nanoscale catalysts and complexes that efficiently achieve the required transformations. Professor Ofoli's team focuses on four technological goals: reaction specificity; high reactivity under moderate reaction conditions; catalyst robustness and recyclability; and development of generic protocols to enable easy adaptation to other feedstock and products. Their general approach is to integrate rational catalyst design and synthesis, characterization and assessment, and modeling and simulation to understand structure-function relationships. Professor Ofoli is currently focusing on two areas of significant scientific and societal interest: biomimetic water oxidation to produce hydrogen and organic materials; and transformation of renewable materials to high-density liquid fuels capable of replacing those traditionally obtained from crude oil.

Charles Petty

Turbulent flows occur ubiquitously with numerous examples in engineering, atmospheric science, oceanography, astrophysics, biology, and environmental science. Charles Petty is currently developing improved models for turbulence that will have a direct impact on the current use of advanced computational fluid dynamic methods for process design, process diagnostics, and process safety assessments by engineers and others. The results will support the discovery of new flow phenomena in disciplines that depend on accurate predictions of the mean velocity field and the mean pressure field. The goal is to develop a new class of low-order turbulent closure models that account for the transport of momentum, energy, and chemical constituents within single phase (and multiphase) rotating and non-rotating turbulent flows.

Yue Qi

At the Materials Simulation for Clean Energy (MSCE) Lab, Yue Qi and her group develop multi-scale simulation methods to design materials atom by atom. Her team screens materials chemistry by solving quantum mechanical equations to predict the properties that are difficult to measure experimentally. Professor Qi simulates deformation and reaction processes that involve millions of atoms using molecular dynamics with faster and accurate atomic interactions. Utilizing the high performance computer center (HPCC) at MSU, they are predicting chemical-mechanical degradation mechanisms in Li-ion batteries without fitting parameters. They model how electrons and ions transport in complex materials and interphases in order to design new materials and optimize operating conditions for advanced Li-ion batteries and solid oxide fuel cells. Professor Qi simulates how mechanical properties of light-weight metals change in gas and liquid environments starting from their atomic interactions in order to design new tool coatings and manufacturing processes. All of these materials are critically important for an energy efficient and sustainable transportation industry.

Jeff Sakamoto

Jeffrey Sakamoto's research is interdisciplinary, guided by the fields of energy storage/conversion and biomedicine. He argues that the entire length scale, from atoms to the macro scale and everything in between, must be viewed holistically in the design, synthesis and development of advanced materials and materials technology. Porosity is central to his group's research. In some instances porosity, particularly at the nano scale, enables the solution-based synthesis of complex and often metastable ceramics and hydrogels with unique electrochemical, biological and mechanical properties. In other aspects of Professor Sakamoto's research, ironically, porosity is initially used to synthesize complex materials, in gels and powder form, to enhance subsequent densification. Essentially, he is interested in ceramics and hydrogels with a focus on studying the interplay between length scales and the absence of mass (porosity or vacancies). Professor Sakamoto hopes to use this experience to discover and develop new materials and materials technology for energy and biomedicine.

S. Patrick Walton

One achievable goal of the 21st century is "personalized medicine", the design of diagnostics and therapeutics specifically for a single patient. The Applied Biomolecular Engineering Laboratory (ABEL), led by S. Patrick Walton, is currently working on development of both novel therapeutics and diagnostics, specifically on technologies that rely on nucleic acids (i.e., DNA and RNA). Areas of investigation include: i) designing nucleic acid-based therapeutics based on understanding their mechanism of action and ii) developing diagnostics to measure protein levels in parallel. Recent foci have been a new class of therapeutics, short, interfering RNAs, with the goal of developing guidelines for designing these molecules. Additionally, Professor Walton is developing a technique for parallel measurements of transcription factors, proteins that help the cell respond to stimuli, using a solution-phase magnetic bead-based approach.

Tim Whitehead

Engineering life is a broad-stated goal of the new generation of biological engineers. These engineers seek to design novel functions rather than rely on a catalog of 'parts' culled from nature. For proteins, imparting novel and specific functions is a difficult problem because protein structures are only marginally stable, protein structure-function relationships are not well understood, and many targeted small molecule substrates differ by as little as a single hydroxyl group or a methyl bond.

Tim Whitehead's group is working to solve the problem of engineering proteins. They use and develop computational techniques to design proteins for new functions, have pioneered experimental approaches to comprehensively assess the effect of a protein's sequence on its desired function, and have imparted evolutionary and computational ideas to formulate efficient routes to optimize protein function. Professor Whitehead is now interested in optimizing proteins for diverse applications like vaccine design and creating the next generation of biofuels.

R. Mark Worden

R. Mark Worden's research group integrates engineering and biological principles to study two main research areas. The first area, biomimetic interfaces, involves understanding the mechanisms by which biological systems operate, and then applying those mechanisms in new ways. For example, Professor Worden's lab is using artificial cell membranes to study nanoparticles toxicity. He is also studying protein "nanowires", which are produced by certain bacteria, that are believed to be conductive enough for use in new types of electronics and sensors. The second main research area, microbial catalysis, uses microorganisms to carry out desired chemical reactions. One example is gas fermentations, in which microorganisms convert energy-rich gases, such as hydrogen or methane, into high-value products. In collaboration with the nearby Michigan Biotechnology Institute, new types of microbubble-fed reactors are being developed for gas-based fermentations.

Value-Added Products from Agricultural and Forest Raw Materials

Kris Berglund
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Our group's activities are aimed at the creation of value-added products utilizing raw materials obtained from agricultural and forest raw materials. In particular, we utilize fermentation processes to develop integrated production for foods, beverages, biochemicals, and biofuels.

1. Beverage science and technology
Sponsors: MSU AgBioResearch (Project GREEEN), Michigan Grape and Wine Industry Council
Collaborators: David Miller, Paul Jenkins

The artisan distilling industry in Michigan is poised to undergo significant expansion in the next few years resulting in positive economic impact for the State. Challenges for the entrepreneurs entering this business are access to technological expertise and facilities to develop and market products. An additional complication of the distilled spirits industry lies in the regulations governing it. Unlike beer and wine, there is no minimum amount of spirits that can be produced without Federal and State licenses. Furthermore, it is required to have constructed an operational distillery in order to apply for a Federal license. These regulations place the potential new producer in the position that in order to attract investment it is necessary to produce products and show their market value, but to do so, it is necessary to have the investment in a plant to get a license. We work to break this cycle by assisting new entrepreneurs in development and marketing of their spirits in order to attract the required investment for construction of their own facility.

2. Bio4Energy
Sponsors: Swedish Department of Energy; Swedish National Research Council
Collaborators: Ten professors at the three participating institutions.

Bio4Energy is a strategic research program which was granted 20 million euros for five years by the Swedish government. The ambition is to become an internationally leading research environment – from seed to advanced fuels and chemicals – in the field of sustainable biomass energy usage. It is a joint research project between the universities in northern Sweden: Umeå University, Luleå University of Technology and the Swedish University of Agricultural Sciences. The constellation also includes more than 20 R&D companies and industrial partners. Our group at MSU collaborates with the institutions in Bio4Energy with joint students and post-docs working in the general area of fermentation technology.

Xylose derived from hemicellulose is a low cost source of substrate for butyric acid fermentation given that extraction could be integrated into current industrial pulp and paper processes yielding hemicellulosic sugars for the fermentation while retaining the properties of the cellulose fraction to be used in the subsequent pulp production. One of the main issues concerning such an integration is that hydrolysis of hardwood hemicellulose releases not only xylose but also acetic acid (up to 40 g/L), a microbial inhibitor. To achieve biologically conversion of xylose to butyric acid, the inhibiting acetic acid must either be removed from the extraction broth or

the fermentation strain adapted to tolerate such high levels (Figure 1). This study focuses on the impact of high levels of acetic acid on *C. tyrobutyricum* fermentation growth kinetics and product yields in order to establish a process with extracted xylose as a substrate without requiring the removal of the toxic acetic acid from the broth.

A second important phenomenon under study is strain degeneration, a process where the original solvent-producing strain mutates or is outgrown by a degenerated version incapable of solventogenesis. This phenomenon is often encountered during ABE (**A**cetone, **B**utanol and **E**thanol) fermentations with *C. acetobutylicum*. Here, two viable alternatives to circumvent the problem of strain degeneration of solvent producing strains of ATCC 824 are under study. They consist of (i) focusing on the precursor of solvents, namely organic acids and (ii) applying a technique of systematic pH control that can trigger the degenerated culture into solventogenesis. In organic acid mode, the degenerated culture produced a final acid titer of 34 g/l (acetate and butyrate). With systematic pH control, the degenerated culture yielded a final solvent concentration between 15 and 20 g per liter which is routinely reported for undegenerated strains of ATCC 824. Real-time qPCR was used to quantify the presence of solventogenic DNA before and after applying systematic pH-control.

Recent Publications

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A. Jaros, U. Rova, and K. A. Berglund, "Production of butyric and acetic acids from hemicellulose – the effect of acetic acid on the fermentation production of butyric acid," *Cell. Chem. Tech.* **46**(5-6) 341-347 (2012)

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D. Graiver, R. Dacomba, M. Khawaji, A. Jaros, K. A. Berglund, and R. Narayan, "Steel-Corrosion Inhibitors Derived from Soybean Oil," *J. Am. Oil Chem. Soc.* 2012.

Group Members- Grad. Students: Adam Jaros, Ryan Hendricks, Jake Rochte

Experimental Characterization and Computational Modeling of Heterogeneous Deformation and Damage Nucleation in Metals

Thomas R. Bieler, bieler@egr.msu.edu

Orientation imaging microscopy™ (OIM, aka EBSP mapping) is used to quantitatively examine the relationships between microstructure and localized deformation that governs damage nucleation, recovery, and recrystallization mechanisms. Combined with other experimental and analytical tools, such as 3-D X-ray diffraction, new insights on formability and damage nucleation mechanisms are found. This enables development of optimal material processing strategies to gain more predictable and reliable properties. Three materials are investigated:

Damage Nucleation in Titanium and Titanium Alloys, NSF/DFG Materials World Network Grant and DOE/BES SISGR Grant, with Martin A. Crimp, Carl J. Boehlert, Philip Eisenlohr at MSU, collaboration with Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Figure 1 shows a patch of equiaxed microstructure of a grade 1 pure titanium bens sample surface strained to about 4% strain. The right side shows which slip systems could lead to slip transfer. Slip transfer is most likely when either prism (red) or basal (blue) slip systems are active (high Schmid factors (*m*) indicated in colored numbers), and have a high degree of alignment with slip or twin systems in a neighboring grain, as indicated by bold black numbers. Boundaries with gray slip transfer numbers describe either lower values (below 0.9) or alignment between slip systems involving lesser active slip systems on pyramidal planes (green and gold planes and Schmid factors). There are two instances of twin nucleation at grain boundaries, one with strong evidence for slip transfer (0.93 between grains 1 and 2) and one less likely instance at the bottom center, with a low slip transfer number (0.78) where basal slip is not very well aligned with a twin system (darker gray plane with a lower Schmid factor). There is no evidence for basal slip, though there is evidence for <c+a> slip on the SEM micrograph. In this case, it is more likely that twin nucleation at the triple junction created the driving force for twin nucleation.

Twin nucleation is being investigated in samples deformed in-situ while monitoring grain strain using synchrotron x-ray diffraction in beamline 1ID-E at the Advanced Photon Source (APS). This method uses diffraction based tomography to identify stress states in grains throughout the volume of a tensile sample. Of seven twin nucleation events analyzed to date, there are a variety of stress conditions associated with twin nucleation, making a general rule for twin nucleation difficult to identify. About 1/3 of these observations have neighboring grains with active slip systems that could have triggered the observed twin similar to that observed in Figure 1 between grains 1 and 2.

Crystal plasticity finite element modeling of patches of microstructure using 3-D information obtained from beamline 34-ID-E at the APS has been used to build a

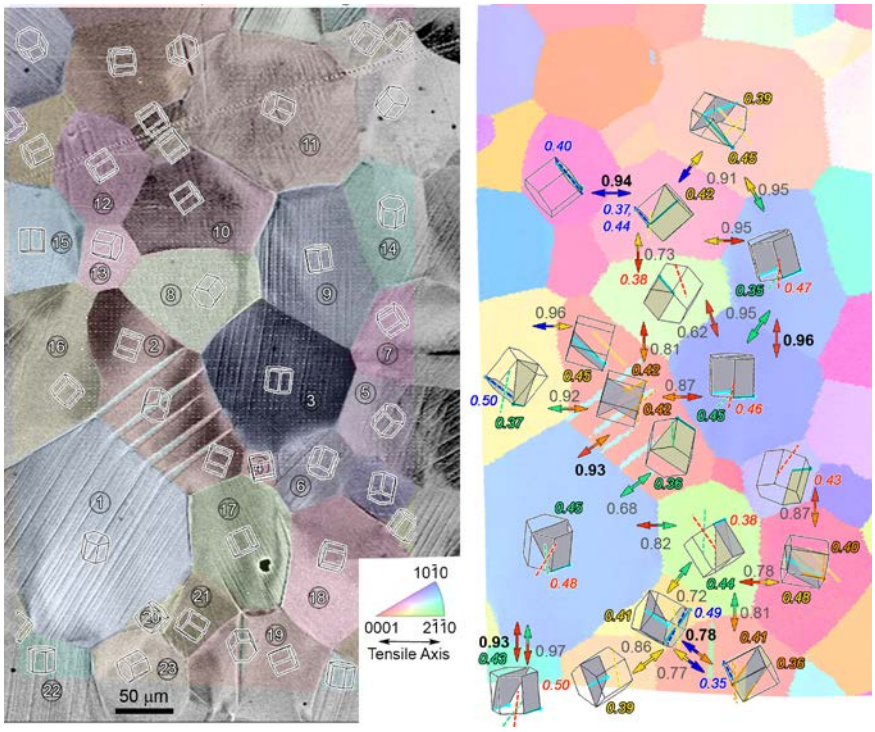

Figure 1 A microstructural patch illustrating heterogeneous deformation and slip activity in commercial purity titanium deformed in tension. Crystal orientations are illustrated, slip system traces and their Schmid factors are indicated in different colors, and slip transfer parameters computed. There is clear evidence for slip transfer in boundaries with high (bold black) values with prism (red) or basal (blue) slip.

model of a microstructure in a Ti-5Al-2.5Sn titanium alloy. Figure 2 shows a grain with clear slip traces on the basal slip system (blue) and some strange surface ledges that could be explained by activated 2nd order prism slip, which is not normally observed in titanium. However, the grain beneath the surface grain (middle prism), is oriented in a way that highly favors activation of normal prism slip, which is well aligned to stimulate 2nd order prism slip in the surface grain (right prism). This suggests that slip transfer stimulated operation of 2nd order prism slip may generate severe surface features that could facilitate damage.

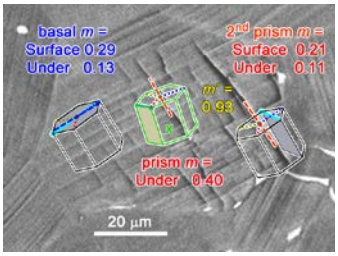

Figure 2. A subsurface grain (middle prism) is well aligned to stimulate 2nd order prism slip in the surface grain, leading to strange surface ledges (damage).

Microstructural Evolution During Thermo-mechanical Cycling in Lead-free Solder Joints, NSF/GOALI with Cisco Systems, Inc, with Farhang Pourboghrat at MSU and Tae-kyu Lee at Cisco.

Figure 3 shows how synchrotron characterization of a wafer level chip scale package at different stages of thermal cycling lead to an alteration of the grain orientations. Each block with a shade of gray indicated that change in effective coefficient of thermal expansion, which demonstrates a change in crystal orientation of solder joints in different locations. The bottom row of joints is illustrated using EBSP c-axis maps. This in-situ observation of changes in grain orientation during thermal cycling is the first of its kind, and clearly demonstrates the evolution of grain orientations in a spatial non-destructive way.

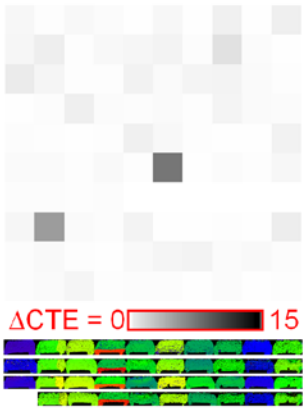

Figure 3 Change in CTE between 320 and 420 thermal cycles of a wafer level chip scale package measured using synchrotron radiation.

Characterization and modeling of deformation and recrystallization in high purity Nb for particle accelerators, DOE/OHEP, with F. Pourboghrat and N.T. Wright at MSU, and C. Compton at FRIB.

High purity Nb is used for particle accelerator cavities, but because of its limited use, the fundamental physics of deformation processing and microstructure evolution are not well understood. We are assessing details of slip deformation mechanisms to develop material models that can be used to optimize forming operations that lead to more consistent performance of cavities. For example, Figure 4 shows that annealing single crystals cut from an ingot changes the way that the crystal reorients during tensile testing; this implies that removal of dislocations changes which slip systems are activated during deformation, and this implies that prediction of deformation depends sensitively on prior heat treatments.

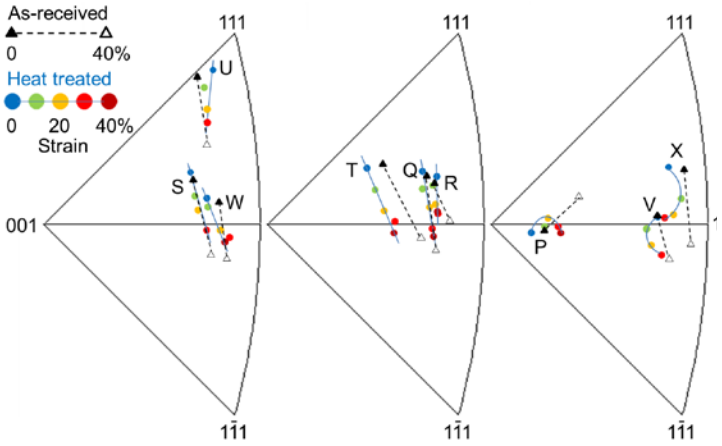

Figure 4 Differences in rotation in pure Nb tensile samples as extracted from an ingot, and after a heat treatment.

Group Members:

Chen Zhang, James Seal, Harsha Phukan, Yang Su, Jason Zhou, Aboozar Mapar, Di Kang, Mingmin Wang, Mengge Zhao, Bret Dunlap

Recent Publications

In Situ Characterization of Twin Nucleation in Pure Ti Using 3D-XRD, T.R. Bieler, L. Wang, A.J. Beaudoin, P. Kenesei, U. Lienert, Metall. Mater. Trans. A, 45A, 109-22, 2014.

Crystal Plasticity Finite Element study of deformation behavior in commonly observed microstructures in lead free solder joints, Payam Darbandi, Tae-kyu Lee, Thomas R. Bieler, Farhang Pourboghrat, Computational Materials Science 85, 236–243, (2014).

Physical and mechanical metallurgy of high purity Nb for accelerator cavities, T.R. Bieler, et al., Physical Review Special Topics - Accelerators and Beams 13, 031002 (2010)

In-Situ Analysis of the Deformation Behavior of Mg-1Mn-1Nd(wt.%)

Carl J. Boehlert and Ajith Chakkedath
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The research group of Associate Professor Carl Boehlert is collaborating with the IMDEA Materials Institute (IMDEA), located in Madrid, Spain, on a National Science Foundation (NSF) Materials World Network Program supported by the NSF Division of Material Research (Grant No. DMR1107117). The following abstract highlights this research.

An extruded Mg-1Mn-1Nd(wt.%) (MN11) alloy was tested in tension in a scanning electron microscope (SEM) at temperatures of 323K (50°C), 423K (150°C), and 523K (250°C) in order to analyze the local deformation mechanisms through *in-situ* observations. Electron backscatter diffraction (EBSD) was performed before and after the deformation. It was found that the tensile strength decreased with increasing temperature, and the relative activity of different twinning and slip systems was quantified. At 323K (50°C), extension twinning, basal, prismatic <a>, and pyramidal <c+a> slip were active. Much less extension twinning was observed at 423K (150°C). At 523K (250°C), twinning was not observed, and basal slip controlled the deformation.

These *in-situ* experiments provide new insight on the deformation mechanisms of Mg-RE alloys. The relative contributions of the different deformation modes as a function of temperature are illustrated in Figure 1. It appeared that the activity of basal and non-basal slip was more balanced at lower temperatures compared with higher temperatures, where basal slip was dominant. The percentage of basal slip increased from 50% to 75% to 87% with increasing temperature from 323K (50°C) to 423K (150°C) to 523K (250°C), respectively. Twinning decreased from 31% to 3% to 0% with increasing temperature from 323K (50°C) to 423K (150°C) to 523K (250°C), respectively. The prismatic slip and pyramidal <c+a> slip system percentages did not change markedly with temperature. Upon grouping the twin and basal slip systems, the percentage of these "soft" modes remains basically the same for all three of the deformation temperatures analyzed. Essentially, the strain accommodated by twins is replaced by basal slip at the higher temperatures. Overall, the results suggest that the activation of basal slip compared to non-basal slip and twinning is easier at higher temperatures compared with lower temperatures and the relative activity of twinning is reduced significantly with increasing temperature.

The following conclusions were drawn from this study:

1. The relative slip activity between the basal and prismatic and pyramidal slip systems was quantified. At 323K (50°C), extension twinning, basal, prismatic <a>, and pyramidal <c+a> slip

were active. At 423K (150°C), much less extension twinning was observed. At 523K (250°C), twinning was not observed, and basal slip controlled the deformation.

2. Overall the prismatic slip and pyramidal <c+a> slip system percentages did not change markedly with temperature and the percentage of these basal slip+twinning modes remained basically the same for all three of the deformation temperatures. Therefore, the strain accommodated by twinning at the lower temperatures was replaced by basal slip at the higher temperatures.
3. The CRSS of basal slip is believed to decrease with increasing temperature for MN11.

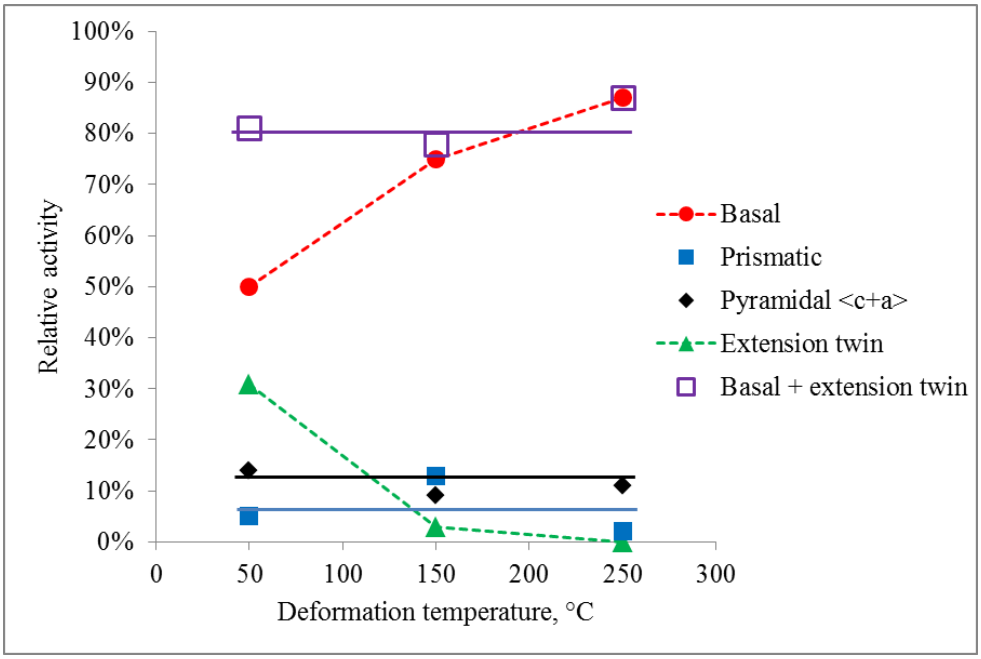

Figure 1. Plot depicting the percentages of each deformation mode with respect to temperature.

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2. D.D. Yin, Q. Wang, and C.J. Boehlert, "Creep and Fracture Behavior of As-Cast Mg-11Y-5Gd-2Zn-0.5Zr(wt.%)", Journal of Materials Science, Vol. 47 (2012) 6263-6275 (DOI: 10.1007/s10853-012-6546-4).
3. Z. Chen, A. Shyam, J. Huang, R.F. Decker, S.E. LeBeau, and C.J. Boehlert, "The Small Fatigue Crack Growth Behavior of an AM60 Magnesium Alloy", Metallurgical Transactions, (2013) (doi: 10.1007/s11661-012-1449-1).
4. H. Li, C.J. Boehlert, T.R. Bieler, and M.A. Crimp, "Analysis of Slip Activity and Heterogeneous Deformation in Tension and Tension-Creep of Ti-5Al-2.5Sn(wt.%) Using *In-Situ* SEM Experiments", Philosophical Magazine, Vol. 92 No. 23 (2012) 2923-2946.
5. C.J. Boehlert, Z. Chen, I. Gutiérrez-Urrutia, J. Llorca, and M.T. Pérez-Prado, "*In-situ* analysis of the tensile and tensile-creep deformation mechanisms in rolled AZ31", Acta Metallurgica, Vol. 60 (2012) 1889-1904. (DOI: 10.1016/j.actamat.2011.10.025).
6. R. Muñoz-Moreno, C.J. Boehlert, M.T. Pérez-Prado, E.M. Ruiz-Navas, and J. Llorca, "*In situ* Observations of the Deformation Behavior and Fracture Mechanisms of Ti-45Al-2Nb-2Mn-0.8vol%TiB2 XD", Metallurgical Transaction, Vol. 43A (2012) 1198-1208. (DOI: 10.1007/s11661-011-1022-3).
7. H. Li, D.E. Mason, T.R. Bieler, C.J. Boehlert, and M.A. Crimp, "Methodology for Estimating the Critical Resolved Shear Stress Ratios of α-Phase Ti Using EBSD Based Trace Analysis", Acta Materialia, Vol. 61 (2013) 7555-7567. http://dx.doi.org/10.1016/j.actamet.2013.08.042

Group Members: Graduate Students: Vahid Khademi, Ajith Chakkedath, Uchechi Okeke, Aida Amroussa, Indraroop Dastida

Electrochemical Energy Laboratory

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Our research addresses engineering and materials issues in fuel cells, particularly mass transport within fuel cell electrodes. We focus on non-precious metal catalysts based on redox enzymes and transition metals, which have lower costs compared to precious metals, but are challenging in terms of overall activity and stability and often are implemented at high loadings that lead to transport limitations. Below are brief descriptions of current projects.

Metal Nitrogen Carbon (MNC) Oxygen Reduction Catalysts for Automotive Fuel Cells

Sponsor: DOE
Collaborators: Northeastern University, Pajarito Powders LLC, Nissan Technical Center NA, et al.

We are developing a new process for inexpensive Metal-Nitrogen-Carbon (MNC) catalysts for oxygen reduction cathodes. High-pressure pyrolysis yields active MNC catalysts from transition metal (iron or cobalt) and nitrogen precursors (pyridine, melamine) combined with high surface area carbon materials in a closed, constant volume reactor. Activity approaches precious-metal platinum in acid, and exceeds platinum in alkaline solutions (Fig. 1).

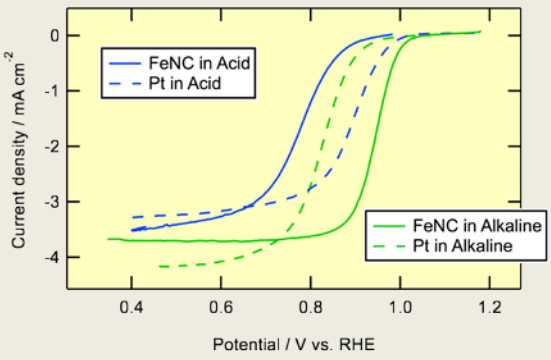

Figure 1. Catalyst activity as measured by rotating disk electrode for both MNC catalyst and carbon-supported platinum. MNC activity exceeds that of Pt in alkaline solution.

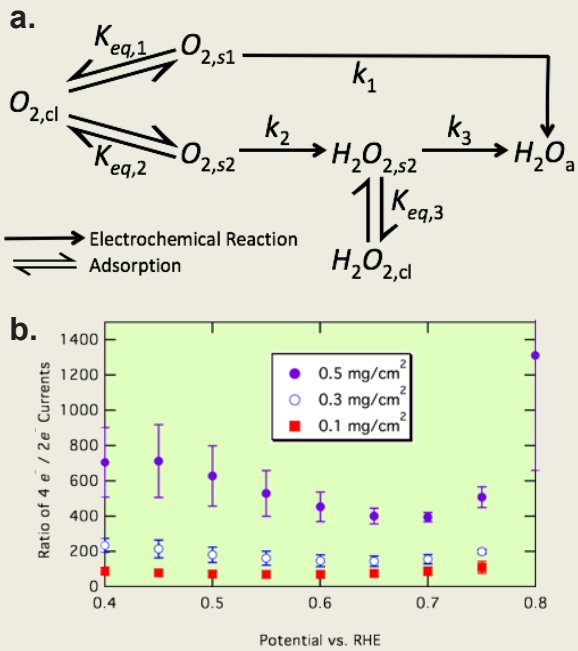

Figure 2. Effect of surface pH on catalyst activity at rotating disk electrodes, 0.8 V vs. RHE, for both neat carbons and prepared catalysts [2]. Positive pH shift indicates high surface pH.

Optimum catalyst composition is determined through electrochemical characterization combined with analysis such as X-ray photoelectron spectroscopy (XPS), and combustion analysis. Thermogravimetric analysis demonstrates that increasing nominal Fe content leads to increased weight loss during pyrolysis, particularly at high temperatures. Activity of catalysts prepared in the absence of iron source, and with iron removed by washing with hot aqua regia, indicate that Fe is an active site component [3].

We also explore hydrogen peroxide generation in the catalyst. Figure 2a shows how oxygen reduction proceeds by two possible branches: direct reduction to water and indirect reduction via hydrogen peroxide. Peroxide

generation has been studied via rotating ring-disk electrode (RRDE) at various metal loadings (Fig. 2b). The catalyst shows high selectivity towards direct oxygen reduction.

Redox polymer mediated bioanodes

We mathematical model the current density obtainable by glucose oxidizing electrodes catalyzed by mediated glucose oxidase. Film thickness, determined by confocal microscopy, atomic force microscopy (AFM), ellipsometry, or profilometry (Fig. 3), impacts the performance of the electrode via mobility of the redox active centers and species transport.

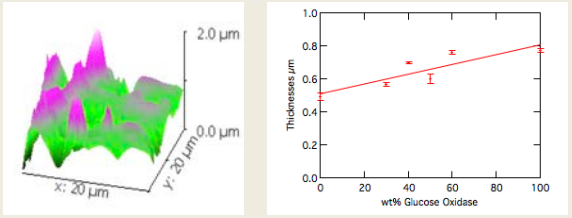

Figure 3. Film thickness studies. (a) Film thickness as measured by AFM. (b) Film thickness correlated to enzyme content.

These studies improve quantitative understanding of mediated enzyme electrode behavior, enabling engineering design and optimization of biosensors, biofuel cells, and bioreactors.

Renewable Dehydrogenase-based Interfaces for Bioelectrocatalysis

Sponsor: NSF
Collaborators: R. Mark Worden, Claire Vieille

Dehydrogenase enzymes catalyze myriad reactions relevant to biosensors, fuel cells, and chemical conversion. However, NADH oxidation occurs at high overpotentials, which lead to inefficiency and increased side reactions.

We have recently discovered that NADH-oxidizing electrocatalysts may be immobilized

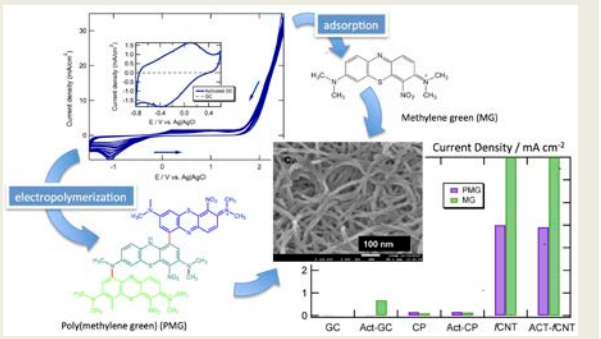

Figure 4. Formation of NADH oxidizing electrodes via electrochemical activation of carbon materials [1]. Compared to electropolymerization, formation is conformal and leads to higher catalyst loading and milder chemical environments.

by electrochemical activation of carbon substrates such as fibers and nanotubes [1]. Using high-applied-potential cyclic voltammetry redox active functional groups are formed that improve adsorption of bioelectrochemically active azine dyes. In comparison to conventional electropolymerization of dyes, this approach leads to higher catalyst loading without exposing the catalyst to extreme potentials due to electropolymerization.

Recent Publications

1. H. Li, R. Li, R. M. Worden and S. Calabrese Barton, "Facilitation of High-Rate NADH Electrocatalysis Using Electrochemically Activated Carbon Materials", *ACS Appl. Mater. Interfaces*, **Accepted**, (2014).
2. N. Leonard, S. Ganesan and S. Calabrese Barton, "Rotating Ring-Disk Study of Metal-Nitrogen-Carbon Catalyst Prepared by High Pressure Pyrolysis", *ECS Trans.*, 58, 1681 (2013). doi:10.1149/05801.1681ecst.
3. S. Ganesan, N. Leonard and S.C. Barton, "Impact of transition metal on nitrogen retention and activity of iron-nitrogen-carbon oxygen reduction catalysts." *Physical Chemistry Chemical Physics : PCCP*, **16**(10), 4576–4585 (2014). DOI:10.1039/c3cp54751e

Graduate Students:

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Nate Leonard
Yira Feliciano Vega
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Postdoctoral Associate:

Selvarani Ganesan

Undergraduate Students:

Nate Sunderlin (MSU '14); Nam Tran (MSU '15); Travis Hebden (MSU '14); Philip Kim (CCNY '15)

Mechanical properties and processing of thermoelectric materials and porous brittle materials

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Mechanical properties often determine whether or not a particular material is viable for a given application. For example, in the harvesting of waste heat from automotive or industrial sources, thermoelectric (TE) materials convert heat directly into useful electricity but the TE materials must withstand stresses generated by the repetitive cold start-up and hot shut-down of engines. For many porous materials, the functionality depends on volume fraction porosities of, say, 0.1 to 0.5, but the structural integrity of the material must be maintained. A key cross-section between the work on porous materials and thermoelectrics is that materials is controlled porosity can enhance the thermal fatigue resistance that is crucial for waste heat harvesting.

Processing/mechanical properties of thermoelectric materials: Three areas of recent effort include (1) nanoparticle and nanoplatelet additions (2) processing to reduce bloating and (3) controlled porosity. In many TE materials post-densification annealing leads to bloating, where "bloating" refers to a solid phase decomposition reaction that leads to the formation of pores during thermal annealing. While bloating-induced porosity degrades mechanical and thermoelectric performance, our group has shown that pulsed electric current sintering (PECS) eliminates bloating, likely due to the reported cleaning of powder surface contamination.

In addition, our group has shown that SiC nano-particle (SiC_{np}) additions to PbTe-based, SnTe-based or skutterudite materials inhibits the grain growth that typically occurs during annealing. (Inhibiting grain growth enhances fracture strength). Also, SiC_{np}) inclusions promote transgranular fracture which in turn can benefit fracture toughness, the resistance to crack propagation.

Incomplete densification may occur in many material systems, including thermoelectrics, so it is important to understand changes in elastic

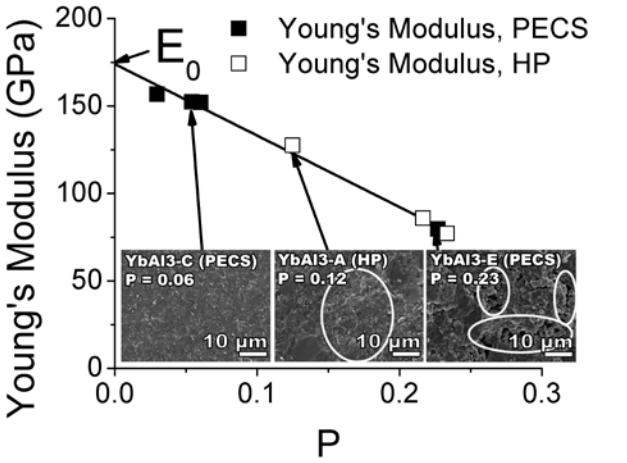

Figure 1. The Young's modulus, E, of $YbAl_3$ specimens as a function of function of the volume fraction porosity, P (Schmidt 2013). The E versus P behavior is independent of the sintering technique, namely pulsed electric current sintering (PECS) or hot pressing (HP).

elastic moduli as a function of porosity (Figure 1) in order to accurately model stress-strain behavior in TE modules and generators. In addition, as part of a DOE-sponsored work with General Motors, our group is exploring the engineering of porosity in pressure-less sintered skutterudite specimens fabricated from melt-spun ribbons. The porosity can potentially enhance the resistance to thermal fatigue damage, in analogy with the excellent resistance to thermal fatigue exhibited by commercial thermal barrier coatings with volume fraction porosities ranging from about 0.1 to 0.3

Mechanical properties of porous brittle materials: Application areas for porous brittle materials include filters, sensors, catalyst supports, biomedical materials and electrodes for solid oxide fuel cells. Fracture strength decreases rapidly as porosity increases. However, in a number of applications, the scatter

in strength values (measured by the Weibull modulus, *m*) is as important to designers as the magnitude of the strength itself. Despite its importance, there are limited studies in the literature of *m* for volume fraction porosities $P > 0.1$ and no systematic studies of *m* as a function of *P* for $P > 0.2$. In our studies, we examined the Weibull modulus for $0.07 < P < 0.62$ for 652 HA specimens along with the limited Weibull data from the literature (Figure 2). In Regions II and III (which span the P range of interest to many applications), $4 < m < 11$, but for P values near the green (unfired) density, m increases. The m versus P behavior agrees with a recent numerical model of m versus P for brittle, porous materials.

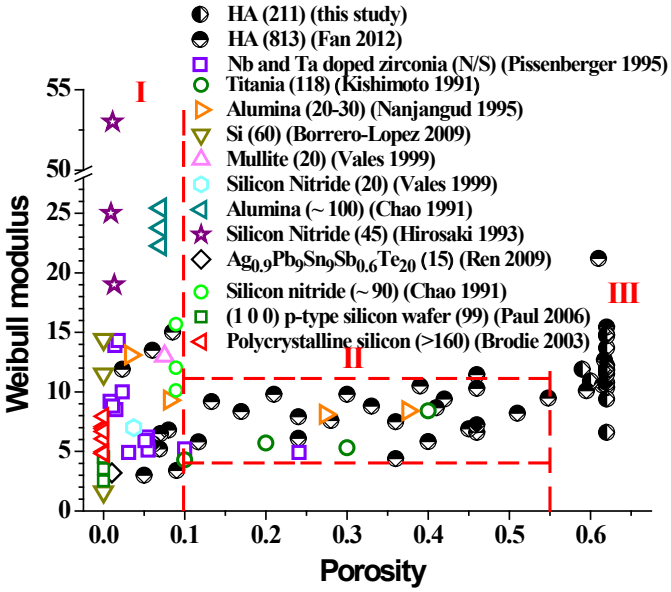

Figure 2. Weibull modulus as a function of porosity showing the combined data set of HA in this study and data from literature for other brittle materials.

Recent Publications

J. E. Ni, E. D. Case, Thermal Fatigue of Cast and Hot Pressed LAST (lead-antimony-silver-tellurium) thermoelectrics, J. Electronic Materials, 42[7]: 1382 – 1388 (2013).

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R. D. Schmidt, E. D. Case, J. E. Ni, R. M. Trejo, E. Lara-Curzio, R. J. Korkosz, M. G. Kanatzidis, High temperature elastic moduli of $SnTe_{1+X}$ - ySiC nanoparticle, J. Mater. Sci. 48 [23] 8244 – 8258 (2013).

X. Fan, E. D. Case, Q. Yang, and J. D. Nicholas, Room Temperature Elasticity of Gadolinia-doped Ceria as a Function of Porosity, Ceramics International, 39: 6877 – 6886 (2013).

J. Ni, E. D. Case, Chun-I Wu, Timothy Hogan, R. Trejo, E. Lara-Curzio, M. G. Kanatzidis, Fracture mode, microstructure, and temperature-dependent elastic moduli for thermoelectric composites of PbTe-PbS with SiC nanoparticle additions, Philos. Mag. 93:35, 4412-4439 (2013).

P. Gao, I. Berkun, R. D. Schmidt, M. Luzenski, P. Bordon Sarac, E. D. Case, T. P. Hogan, Transport and mechanical properties of high ZT $Mg_{2.08}Si_{0.4-x}Sn_{0.6}Sb_x$ thermoelectric materials, accepted, J. Electronic Materials.

Group Members:

Graduate students: Robert D. Schmidt, Aaron Foster

- **Undergraduates:** Miguel Angel Valdes Tabernero, Andreia Ditzel Facci, Alex Zettler, Irene Bernal Perez, Patricia Bordon Sarac

Integrative Systems and Computational Biology Laboratory

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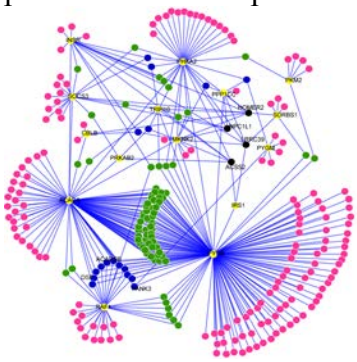
The Integrative Systems and Computational Biology (ISCB) Laboratory is focused on understanding the molecular, signaling and cellular processes that are altered in diseases. The overall objectives of the lab fall into two research directions. The first aim is to identify novel targets involve in diseases, i.e. cancer and Alzheimer's disease. This involves activities ranging from developing computational methods that integrate high throughput technologies to traditional molecular and cell biology techniques in the identification of novel targets. The second aim of the lab is to develop tools and approaches to ameliorate the disease, through targeted delivery or cell-based therapies; or prevent the disease through identifying and characterizing molecular targets of known bioactive components involved in disease prevention. Specific ongoing projects include:

1) Network analysis to identify novel targets for cancer (Sponsor: NIH)

The goal is to elucidate the effect of elevated levels of free fatty acids (FFAs), specifically palmitate, on cellular function, given its association with a number of diseases, such as steatosis, obesity, cancer and Alzheimer's disease. This project addresses the development of a modeling framework that integrates both top-down and bottom-up approaches to generate a phenotype-specific network for cell signaling to help better elucidate how the targets interact to induce a disease phenotype. Below are results using network analysis that identified a novel player in promoting liver metastasis, namely the loss of DSP due palmitate induces epithelial–mesenchymal transition (EMT).



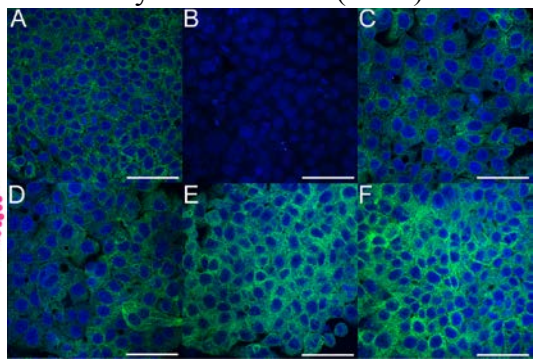


***Figure**. (Right) Immuno-fluorescence images of liver cells stained for DSP (green) and cell nuclei (blue) obtained using confocal microscopy. Scale bars represent 50µm. A) Untreated, control cells grown in regular growth media. B) Cells treated with palmitate for 48 hours show decrease in DSP levels C) Cells treated with palmitate for 48 hours and recovered in normal growth media for 72 hours show partial recovery of DSP expression. Cells treated with palmitate for 48 hours and recovered in growth media with insulin for D) 24 hours and E) 48 hours show partial recovery, whereas for F) 72 hours show complete recovery of DSP expression.*

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1) Yang, X., Wang, X., Wu, M., Dalkic, E., and Chan, C., "Construction of the gene network by synergy analysis of the genes related to palmitate-induced cytotoxicity", Methods in Bioengineering in Systems Analysis of Biological Networks, Chapter 5, p. 75 – 93, eds. Arul Jayaraman & Juergen Hahn, Artech House Publishers, 2009.
2) Wang, X., Nath, A., Yang, X., Portis, A., Walton, S. P., and Chan, C., "Desmoplakin: Synergy analysis reveals a new player in the pathogenesis and progression of fatty liver disease", (2011) Plos One, 6(11): e28138. doi:10.1371/journal.pone.0028138.

2) Biophysical Mechanisms of Palmitate-Induced Signaling and Cytotoxicity (Sponsor: NSF)
Collaborator: Amadeu Sum (CSM), Michael Feig (MSU BMB), Nikolai Priezjev and Neil Wright (MSU Mechanical Engineering)

This project integrates molecular biology, biophysics, and cellular studies with molecular modeling to enhance our understanding of complex biological systems comprising of multiple interacting processes. Specifically we are studying the endoplasmic reticulum transmembrane protein kinase/ endoribonuclease

(IRE1), which is activated in response to the Unfolded Protein Response (UPR). This has broad implications on a number of diseases, since UPR is known to be activated in cancers, viral infection and many other diseases. We are developing a multi-scale model to integrate the various domains of the transmembrane protein to understand how palmitate activates the protein.

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1) Cho, H. J., Mukherjee, S., Palasuberniam, P., Pillow, L., Bilgin, B., Nezich, C. L., Walton, S. P., Feig, M., and Chan, C., "The role of palmitic acid in inhibiting PKR activity", (2011) Biochemistry, 50 (6): 1110–1119.
2) Cho, H.J., and Chan, C., "IRE1 transmembrane domain in SDS", (2012) Biochemical and Biophysical Research Communications 427(4): 764–767.
3) Cho, H. J., Wu, M., Zhang, L., Thompson, R., Nath, A., and Chan, C., "Palmitate-induced dysregulation of ER-related stress responses in HepG2 cells mediated by ATF4 and CREB", (2013) BMC Sys Bio, 7:9.

3) Delivery of siRNAs by polymeric nanoparticles (Sponsor: NIH)
Collaborators: S. Patrick Walton, Mitch Smith (MSU Chemistry)

The overall goal of the proposed research is to design siRNAs with maximal function through manipulation of the siRNA structure and sequence and the design of vehicles with optimal chemical and physical characteristics. Further, the interactions of siRNAs with delivery vehicles built from chemically-diverse oligomeric and polymeric nanoparticles are quantitatively analyzed to determine those structural features that encourage complex formation and release of siRNAs into the cell.

References:

1) Portis, A. M., Carballo, G., Baker, G. L., and Chan, C., and Walton, S. P., "Confocal microscopy for the analysis of siRNA delivery by polymeric nanoparticles", (2010) Microscopy Research and Technique, 73:878–885.
2) Malefyt, A.P., Walton, S.P., and Chan, C. "Analysis of Endocytosis Pathways for Nucleic Acid Therapeutics", (2012) NanoLife, 2(3): 1-9. 10.1142/S179398441241005X
3) Malefyt, A., Wu, M., Vocelle, D., Kappes, S., Lindeman, S., Chan, C., and Walton, S. P., "Improved asymmetry prediction for siRNAs", (2014) FEB Journal, (in press).

4) Role of Alignment on Axonal Growth and Myelination (Sponsor: NIH, NSF)
Collaborators: Jeff Sakamoto, Mark Tuszynski (USCD), S. Patrick Walton, Seungik Baek (MSU ME)

Mechanical cues in the cellular environment play important roles in guiding various cell behaviors, such as cell alignment, migration, and differentiation. We hypothesized that the cell senses the physical environment through a more active mechanism, namely, even without external forces the cell can actively apply traction and sense an increased stiffness in the stretched direction and align in that direction. We found the mesenchymal stem cells aligned in the direction of the statically pre-stretched surface. Next we will evaluate how alignment modulates axonal growth and myelination in context of spinal cord injury.

References:

1) Mehrotra, S., Lynam, D., Maloney, R., Pawelec, K. M., Tuszynski, M., Lee, I., Chan, C., and Sakamoto, J., "Time controlled protein release from layer-by-layer assembled multilayers functionalized agarose hydrogels", (2009) Advanced Functional Materials, 19: 1-12
2) Liu, C., Baek, S., Kim, J., Vasko, E., Chan, C., "Effect of Static Pre-stretch Induced Surface Anisotropy on Orientation of Mesenchymal Stem Cells", (2014) Cellular and Molecular Bioengineering, (in press).

Group Members

Graduate Students: Aritro Nath, Chun Liu, Ryan Thompson, Hussein Hijazi, Daniel Vocelle (co-advised with S. Patrick Walton), Amber Cussen, Amrita Oak

Undergraduate Students: Irene Li, Christina Casalich, Josh Schwallier, Victoria Toomajian, Soraya Molinero (visiting), Jeremy Kray (summer), Purva Shanker (high school)

Advanced Electron Beam Characterization Group

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The overall focus of this group is to develop and apply advanced electron beam characterization techniques. The group works on a range of interdisciplinary projects that deal with diffraction based imaging approaches, using both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). While the core research programs in this group deal with advancing the understanding of deformation and fracture in structural metals, collaborative studies have included magnetic multilayer structures, carbon nanotubes, ceramic joining, oxygen sensors, and cholesterol.

1) Investigation of Damage Nucleation Mechanisms in Polycrystals

Sponsors: NSF, Deutsche Forschungsgemeinschaft, DOE-BES, Sandia National Laboratory

Collaborators: T.R. Bieler, C. Boehlert, P. Eisenlohr (MPIE)

The lifetime and fracture behavior of structural components has traditionally been assessed using continuum fracture mechanics. Implicit to these approaches is an assumption of an initial flaw size, often dictated by the minimum flaw that can be detected non-destructively, that is the starting point for predicting properties such as fracture toughness and fatigue life. Nevertheless, many structural materials do not have well defined flaws in the as-processed state, and there is no clear understanding how flaws nucleate, particularly at grain or phase boundaries. In this study, the nature of how such flaws develop as a consequence of heterogeneous polycrystalline plastic deformation is being examined. This work combines an array of experimental techniques, including atomic force microscopy, nano-indentation, and electron back scattered diffraction in SEM to characterize how various deformation systems interact in polycrystalline arrays. These measurements are being compared directly to simulations of finite element meshes developed to mimic the experimentally characterized polycrystalline regions (Figure 1). In two-phase alloys, damage nucleation is expected to result from deformation system interactions with phase boundaries. Figure 2 illustrates how crystal orientations across such boundaries will influence the local deformation transfer.

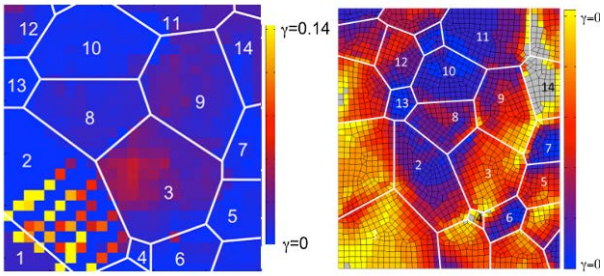

Figure 1. AFM measured deformation system activity (left) and CPFEM simulated activity of the same polycrystalline region.

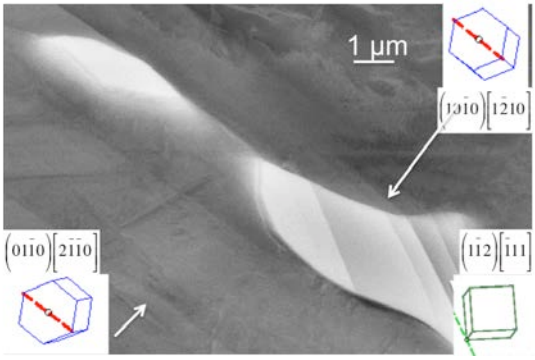

Figure 2. Backscattered electron SEM image showing slip transfer at α/β interfaces in Ti-5Al-2.5Sn

2) Dislocation Imaging in Bulk Crystalline Materials Using SEM
Sponsor: NSF, University of Lorraine

Crystalline defects such as dislocations often play the controlling role in materials behavior, For example, dislocations motion controls the deformation and fracture behavior of structural metals, while dislocations serve as current leakage paths and recombination centers in many electronic materials. Historically, it has been necessary to revert to TEM in order to image and study dislocations. However, this approach is time consuming, is subject to thin foil artifacts, and is destructive in natures. We have developed techniques that allow these defects to be directly imaged in the near surface region of bulk materials using scanning electron microscopy (see Figure 2). Currently, we are extending these approaches to allow mapping of dislocation networks through 3-D volumes of materials.

3) Material Imaging at Space-Time Limits
Sonsor: NSF, MSU Foundation Strategic Partner Gant
Collaborators: C.-Y. Raun, M. Berz, P. Duxbury

Many critical materials processes, including a wide array of chemical reactions and phase transformations, occur not only at the nanoscale, but also at very short time scales. The goal of this research program is to develop a novel high electron flux femtosecond imaging diffraction microscope that allows images and diffraction patterns to collected in the femtosecond time scale with spatial resolutions at the scale of 10s of nanometers. To achieve this, we are developing a unique electron buncher that allows many of the currently limiting space-time limits to be overcome.

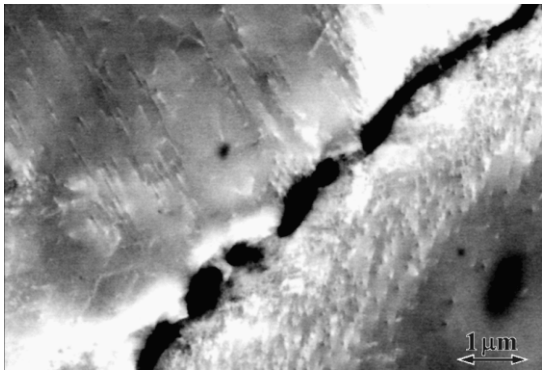

Figure 2. Electron channeling contrast image (ECCI) of dislocations along a crack path in a bulk bend specimen of NiAl.

Recent Publications

H. Li, D.E. Mason, T.R. Bieler, C.J. Boehlert, and **M.A. Crimp**, "Methodology for Estimating the Critical Resolved Shear Stress Ratios of α-Phase Ti Using EBSD Based Trace Analysis", *Acta Mat*., 61 (2013) pp. 7555-7567.

H. Li, D.E. Mason, Y. Yang, T.R. Bieler**,** **M.A. Crimp**, and C.J. Boehlert. "Comparison of the Deformation Behavior of Commercially Pure Titanium and Ti-5Al-2.5Sn(wt%) at 293 and 728K", *Phil. Mag. A,* 93 21 (2013) pp. 2875-2895.

Y.Yang, R. Tomlinson, E. Patterson, and **M.A. Crimp**, "Quantitative Measurement of Plastic Strain Field at a Fatigue Crack Tip", *Proc. Roy. Soc. A*., (2012) DOI: 10.1098/RSPA-2011-0418.

Y. Yang, L. Wang, T. R. Bieler, P. Eisenlohr, **M. A. Crimp**, "Quantitative AFM Characterization and Crystal Plasticity Finite Element Modeling of Heterogeneous Deformation in Commercial Purity Titanium", *Met. and Mat. Trans*., 42 (2011) pp. 636-644.

Group Members
Graduate Students: James Seal V, Yang Su, Brett Dunlap

Biomass Conversion Research Laboratory (BCRL)

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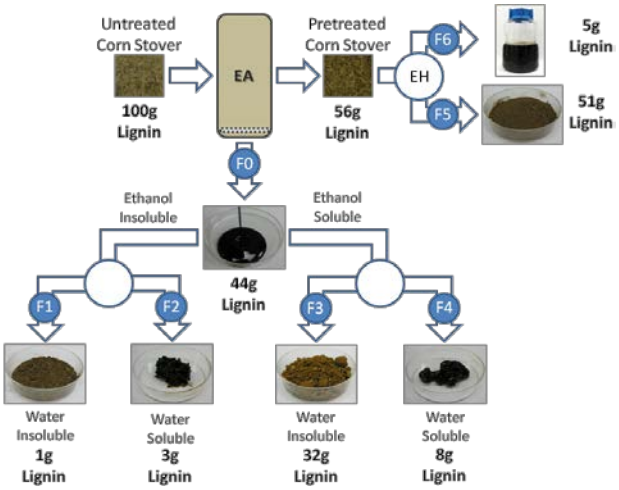
The BCRL develops the conceptual and experimental foundation for large scale, economical, environmentally sustainable systems to produce fuels, animal feeds and chemicals from cellulosic (non-food) plant biomass. Experimentally we focus on pretreatment and enzyme systems to produce low cost sugars and aromatics from biomass. Our conceptual work uses life cycle assessment and techno-economic analysis to design and evaluate integrated systems by which cellulosic biomass is grown, harvested, transported and processed in ways that are economically and environmentally sustainable. Our work is highly collaborative, involving biochemists, microbiologists, plant scientists, economists, ecologists, bio-geochemists and others. Most of our collaborations are funded by the US Dept. of Energy through the Great Lakes Bioenergy Research Center (GLBRC).

Space limitations prevent listing all BCRL projects. Here are some selected ones:

1. Aromatic Compounds from Biomass for Fuels and Materials
Sponsor: DOE-GLBRC
Lead: Dr. Leo da Costa Sousa
Collaborator: Dan Jones (analytical chemistry, Michigan State University)
Plant biomass contains both carbohydrates and aromatics. We are directing the carbohydrate streams toward fermentation for biofuel production. The aromatic streams offer interesting potential for upgrading to fuels, chemicals and materials. One stream extracted by concentrated ammonia from plant biomass contains the complex aromatic compound called lignin at 93% purity and in high yield. Extracting lignin facilitates carbohydrate processing to simple sugars. We are investigating the composition and properties of these unique extracted lignin materials and have implemented multiple collaborations to upgrade these lignin streams to fuels, chemicals and materials such as carbon fibers.

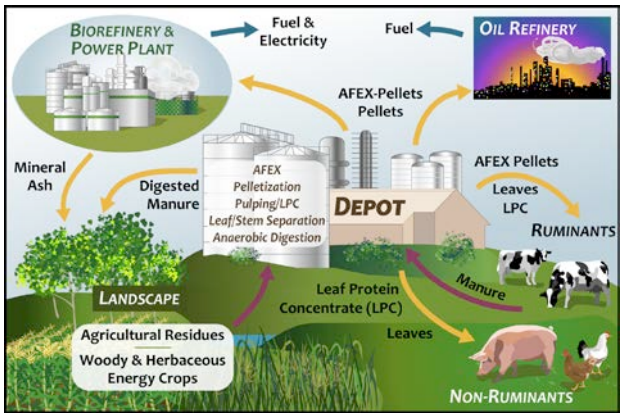


2. Designing Sustainable Bioenergy Systems
Sponsor: DOE-GLBRC
Collaborators: Dr. Tim Meehan (landscape ecology, Univ. of Wisconsin), Dr. Nick Jordan (plant genetics, Univ. of Minnesota)
Industrial society is driven by fossil energy, which is increasingly problematic for both cost and environmental reasons. In this context, new, large scale energy systems will be under intense pressure to be profitable and also to fulfill social/environmental objectives. This is particularly true of bioenergy systems, such as those we are developing. We are attempting to develop and implement a rigorous, but limited set of design criteria by which tentative bioenergy systems can be assessed and implemented. These criteria include soil fertility, biodiversity, greenhouse gases, local employment, impacts on food production, air

and water quality as well as traditional engineering design criteria like capital and operating costs. Our work shows that processing of productive perennial crops and crop residues to biofuel feedstocks and animal feeds within smaller scale processing depots can offer many desirable features for social, environmental and economic sustainability.

3) Food, Feed and Fuel from Biomass
Sponsor: DOE
Collaborators: Dr. Michael Blummel, International Forage Research Institute; MBI, International (derisking), many others

The apparent conflict between using land for food and using it for biofuel production is perceived as a major limitation to large-scale biofuels. Looking more closely, however, we find that human beings do not "grow food". Well over 80% of our arable land is actually used to produce animal feed. Thus the key to minimizing "food vs. fuel" conflicts is coproduce animal feeds along with biofuels, and to do it while meeting multiple sustainability goals. This is actually quite easy to do technically, especially if we focus on local biomass processing at smaller-scale regional depots (below). Our work involves fitting the pieces together and showing by both modeling and experiment how such systems can function.



Selected Recent Publications
-Advanced Regional Biomass Processing Depots: a key to the logistical challenges of the cellulosic biofuel industry. 2011. P. L. Eranki, B. D. Bals and B. E. Dale. *Biofuels. Bioproducts and Biorefining.* 5:621-630
-Probing the Early Events Associated with Liquid Ammonia Pretreatment of Native Crystalline Cellulose. G. Bellesia, S. P.S. Chundawat, P. Langan, B. E. Dale, and S Gnanakaran. *J. Physical Chem. B.* Vol. 115, pp. 9782-9786 (2011).
-Consolidated Bioprocessing (CBP) of AFEX-Pretreated Corn Stover for Ethanol Production Using *Clostridium phytofermentans* M. Jin, C. Gunawan, V. Balan and B. E. Dale. *Biotechnology and Bioengineering*, Vol. 109, No. 8, August (2012) 1929-1936
- Landlabs: An Integrated Approach to Creating Agricultural Enterprises That Meet the Triple Bottom Line. N. Jordan, L. A. Schulte, C. Williams, D. Mulla, D. Pitt, C. Schively Slotterback, R. Jackson, D. Landis, B. Dale, D. Becker, M. Rickenbach, M. Helmers, and B. Bringi. 2013. *Journal of Higher Education Outreach and Engagement*. 2013. Vol. 17, No. 4, Pp. 175-201

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Dr. Rebecca Garlock Ong, Dr. Mingjie Jin
Dr. Shishir Chundawat
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*Undergraduate Students*Brandon Guthrie, Aaron Vigil, Brennan Furman, Lucas Holcomb,Will Dion, Chris Schwartz, John van Schaik, Tanvi Joshi

Graphene Nano-Platelets: A Multifunctional Additive for Polymers, Composites and Energy Applications

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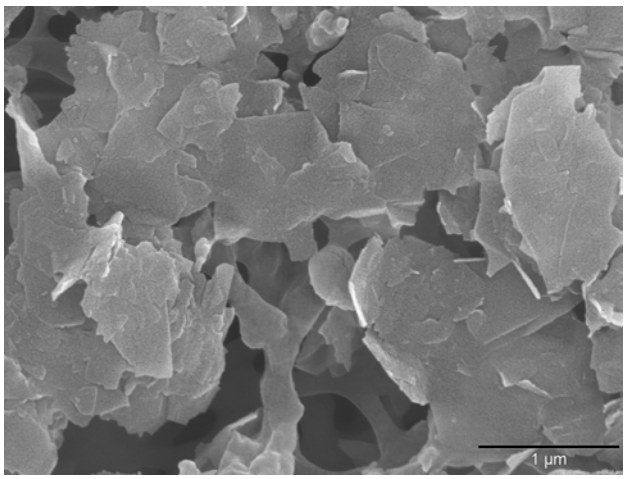
Drzal's research is directed in the areas of polymer composites including; polymer composites reinforced with fibers and nanoparticles (graphene and cellulose); processing of composites; adhesion; biobased composites; and the nanostructuring of these materials in polymers for structural and energy generation and storage applications. He is also

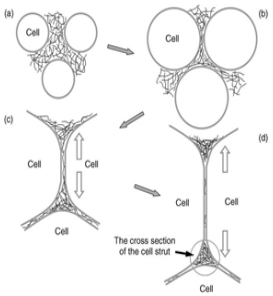


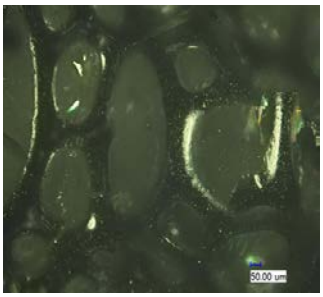
co-founder and Chief Scientist of XG Sciences, Inc., a start-up company to produce graphene nanoplatelets. Specific ongoing projects include:

Multifunctional Graphene Nanocomposite Foams for Space Applications

Sponsor: NASA

The goal of this research focuses on the creation a multifunctional material using a polymer foam as a matrix and utilizing a graphene nanoplatelet (GnP) network as a polymer modifier. Such a nanocomposite would show improved thermal behavior, electrical conductivity and barrier properties while maintaining good mechanical performance. The nanofiller has the potential to





form a percolated network through the ribs and walls of the cells improving the foam resilience as well as the thermal and electrical conductivity. Two polymer matrices are being investigated: rigid polyurethane and flexible polydimethylsiloxane. GnP was chosen as the nanofiller due to its multifunctional properties, which we seek to impart on the light-weight polymer matrices. A graphene nanoplatelet consists of multiple stacks of graphene sheets with an average thickness of 10 nm. Graphene materials are an attractive filler in nanocomposite work due to the fact that single graphene layers have high tensile moduli (> 1 TPa) and electrical (~104 S/m) and thermal (3000 W/m-K) conductivity.

Advanced Toughening of Polymer Composites for Aircraft Applications

Sponsor; GE Aviation

Advanced composite materials for aviation applications require a combination of high mechanical performance, toughness and durability in various thermal and moisture environments. Graphene nanoplatelets (GnP) offer the potential to modify the polymer composite matrix and the fiber-matrix interface but require a fundamental understanding of the effect of GnP on resin properties, dispersion techniques, and their utilization for tailoring of

resin/composite/epoxy matrix properties to enhance interlaminar strength, impact toughness, durability, and containment capability. A linear aliphatic epoxy and a rubber phase separated material are being investigated as matrix tougheners in conjunction with GnP. The addition of the aliphatic copolymer, both di- and tri-functional, increases the notched Izod impact strength substantially without compromising the modulus or Tg of the epoxy. At low concentrations of aliphatic epoxy copolymer (up to about 3%) the notched Izod impact strength can be increased up to 70%, without negatively affecting the strength and stiffness other mechanical properties of the epoxy system.

Multifunctional Materials for Blast and Impact Resistance

Sponsor: US Army, TARDEC

The objectives of the research is to demonstrate a new approach to improving composite fracture and impact toughness by surface modification and coating with functionalized elastomeric coatings of nanoparticles by the incorporation of GnP into structural composite materials. The primary focus is on glass and carbon fiber reinforced vinyl ester composites used as structural elements in Army ground vehicles.

Incorporation of distributed and layered GnP nanoparticles at both interlaminar and intralaminar locations has been studied. CTBN-coated GnP has been shown to increase vinyl ester Izod impact strength ~230% while maintaining stiffness and strength. GnP C-750 coated on reinforcing fibers has increased transverse and interlaminar properties ~40%; Insertion of CTBN-GnP-15 'paper' particles (10-15 mm, dia and 35-40 micron thick) or 'paper' with 80% porosity have shown significant reductions in surface damage, out-of-plane deformation and lamina damage. Integration and optimization of interlaminar and intralaminar is being conducted to quantify the effectiveness of this approach and to serve as basis for predictive model development.

Recent Publications

Wu, H. and Drzal, L. T. "Graphene nanoplatelet paper as a light-weight composite with excellent electrical and thermal conductivity and good gas barrier properties" Carbon 50 (3) 1135-1145 (2012)

Wang, T. and Drzal, L. T., "Cellulose-Nanofiber-Reinforced Poly(lactic acid) Composites Prepared by a Water-Based Approach", ACS Appl. Mater. Interf 4,(10):5079-85 (2012).

Xiang, J. and Drzal, L. T., "Templated Growth of Polyaniline on Exfoliated Graphene Nanoplatelets (GnP) and its Thermoelectric Properties", Polymer, 53, (19) 4202-4210 (2012).

Wu, H., and Drzal, L. T., "Highly Thermally Conductive Graphite Nanoplatelet/Polyetherimide Composites by Precoating: Effect of Percolation and Particle Size", Polymer Composites, 34 (12), 2148-2153 (2013)

Wu, H., and Drzal, L. T., "Graphene Nanoplatelet - Polyetherimide Composites: Revealed Morphology and Relation to Properties" J. Appl. Polymer Sci. 130 (6) 4081-4089 (2013).

Wu, H., Rook, B. and Drzal, L. T., "Dispersion Optimization of Exfoliated Graphite Nanoplatelets in Polyetherimide Nanocomposites: Extrusion vs. Precoating and Solid State Ball Milling" Polymer Composites, 34 (3) 426-432 (2013).

Wu, H., and Drzal, L. T., "Highly Thermally Conductive Graphite Nanoplatelet/Polyetherimide Composites by Precoating", Polymer Composites, 34 (12) 2148-2153 (2013)

Vautard, F., Honaker-Schroeder, T., Drzal, L. T. and Sui, L., "High Density Polyethylene-Exfoliated Graphene Nanoplatelet Nanocomposites For Automotive Fuel Line And Fuel Tanks Applications" Polymer Bulletin 70, 939-951 (2013).

Xiang, J. and Drzal, L. T., "Improving Thermoelectric Properties Of Graphene/Polyaniline Paper By Folding", Chemical Physics Letters, 593C 109-114, (2014),

Do, I. and Drzal, L. T., "Room temperature ionic liquids: size control of metal nanoparticles on carbon", Carbon, http://dx.doi.org/10.1016/j.carbon.2014.02.067 (28 Feb 2014).

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Computational Materials Mechanics; Meso-scale mechanics of anisotropic materials

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Most technically relevant materials for structural applications are of polycrystalline nature, that is, they are made up of a vast number of crystallites whose sizes can range from below a micrometer up to several millimeters. Due to their regular atomic arrangement, single crystals possess anisotropic mechanical properties. In consequence, a polycrystalline material with non-random orientation distribution of those crystallites (so called crystallographic texture) partly inherits these anisotropic properties.

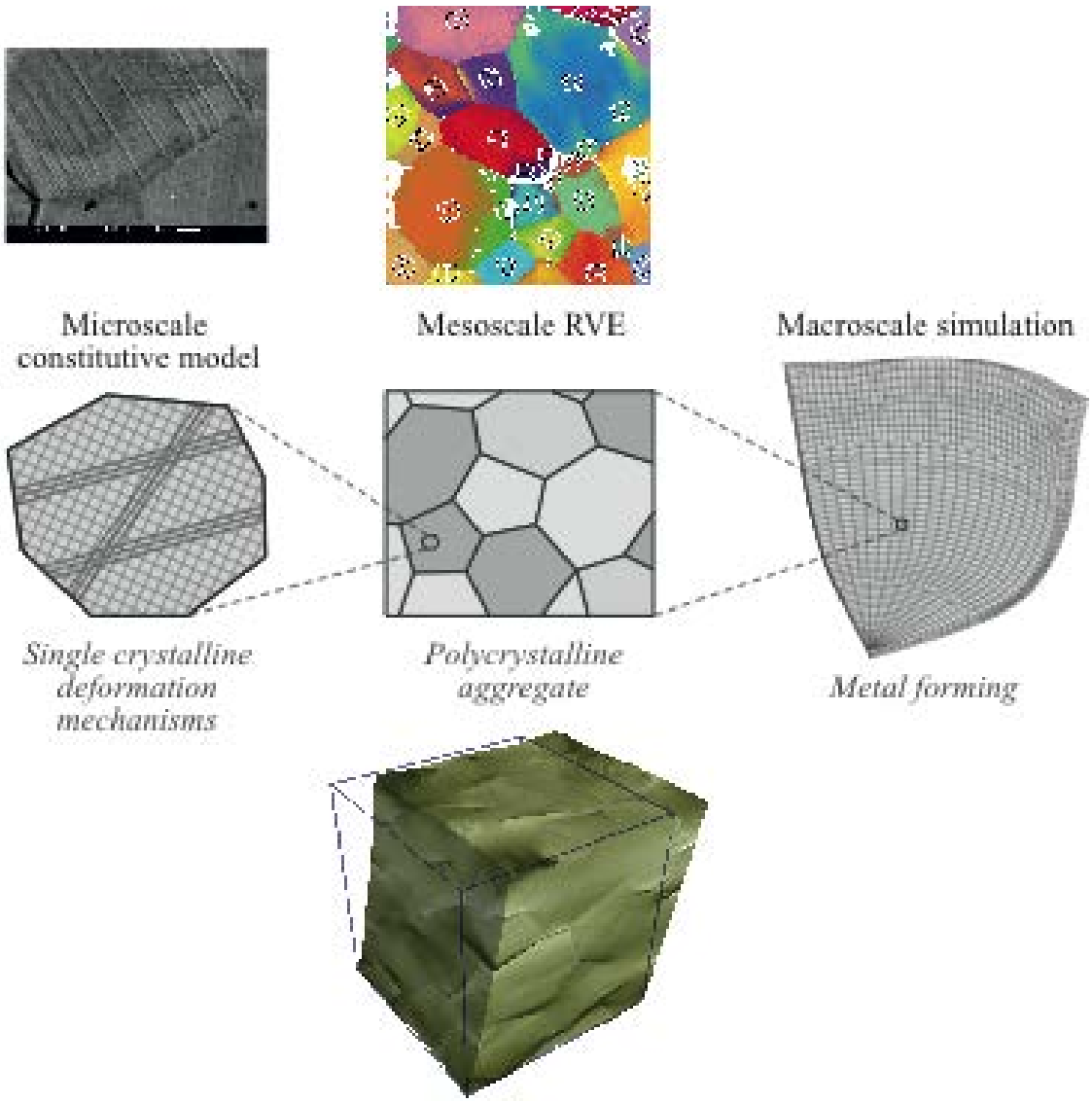
Plastic deformation of polycrystals is the result of a complex interplay of deformation mechanisms in individual grains and grain interactions. The mechanisms mediating plastic deformation, e.g. dislocation glide, mechanical twinning, or displacive phase transformations, occur on the atomic scale. However, the macroscopic response of polycrystalline materials is heavily influenced by a hierarchy of structural details, including, for example, precipitate structure, dislocation arrangement, grain boundaries, or crystallite orientation distribution. To arrive at computationally efficient material models various coarse-graining steps are necessary to incorporate the small-scale behavior in effective continuum descriptions.

During the recent past significant progress has been seen in both the physical understanding and the continuum mechanical simulation of polycrystals. The research in this field is characterized by a close connection between fundamental metallurgical insights and technological applications. The field of crystal mechanics is highly interdisciplinary bringing together approaches from the metal physics of plastic deformation, phase transformation, and interface science; mathematics of non-linear partial differential equations; numerical mathematics; continuum mechanics; and forming and process technology.

Simulation holds the promise to largely replace expensive and time-consuming experiments in the design of the material microstructure, of components, and of the tools used in their manufacturing. However, accurate and validated material models of polycrystal mechanics, which take the microstructure evolution into account, are indispensable for the achievement of such potential cost-savings and reduction in development times.

The research of Dr Eisenlohr revolves around the development and enhancement of novel theoretical approaches for the field of mechanics of crystalline matter with the aim to promote its use for industrial applications such as encountered in the fields of aerospace, automotive, and medical engineering.

In his current research, Dr Eisenlohr is interested, for example, in the role played by crystallite boundaries in the context of large and/or spatially heterogeneous deformation (see top-left in below figure). One important question tied to these studies is how to quantitatively describe their resistance to and structural evolution in the course of plastic deformation. Another very relevant question to be addressed is the propensity for damage nucleation for which a very detailed understanding as well as theoretical modeling of the heterogeneity in polycrystal plasticity is essential.



Regarding the advancement of simulation tools, a prominent aspect in the work of Dr Eisenlohr's research group is the development of a versatile framework to describe crystal plasticity (see http://damask.mpie.de). To date, this framework has already been interfaced to two commercially available finite element solvers (Abaqus and MSC.Marc). Quite recently, an alternative method to solve the mechanical boundary value problem was implemented and complements above framework. This method is valid for periodic domains—since based on spectral collocation—and solves stress equilibrium more precisely than is possible by the finite element method yet much more efficiently due to the use of fast Fourier transforms in its algorithm to solve the associated partial differential equations. An example of the heterogeneous strain evolving in a representative volume element (RVE) that is resolved by 256 x 256 x 256 grid points is depicted at the bottom of above figure.

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There is a strong need to develop energy and material alternatives such as through the capture and redirection of energy in the carbon cycle by utilizing the chemical constituents of plant cell walls as a renewable chemical and energy feedstock. However, the higher order structures of plant cell walls prevent utilization of these carbohydrates due to what could be considered the "recalcitrance" of lignocellulose. It is noteworthy that this vast resource of reduced carbon is overwhelming used for its existing structural value (as fiber and as a construction material) or for combustion rather than for the value of its chemical constituents. Work in the Hodge Laboratory addresses the challenges associated with the conversion and fractionation of plant cell wall biopolymers (as well as food crops) to renewable fuels and chemicals by catalytic and biochemical means. Examples of ongoing research projects are presented below:

Catalytic oxidation of lignin to improve hydrolysis of woody biomass

In nature, microbes successfully degrade plant cell walls using a variety of oxidative approaches. These strategies include the release of reactive oxygen species produced by redox-active metals and metalloenzymes. As co-PI on a project that has been funded by the DOE GLBRC since 2010, we are investigating applying abiotic catalytic oxidative treatments that mimic certain features of these successful biological approaches. Specifically, homogeneous catalysis is applied during alkaline-oxidative pretreatments to improve the delignification and enzymatic hydrolysis of woody biomass as well as generate lignin-derived aromatic monomers such as vanillin and acetosyringone that may offer the potential for recovery as co-products. Ongoing work is focused on understanding the mechanisms by which enzymatic hydrolysis is improved and developing more effective and economic catalytic systems. Select highlights from this work are presented in **Figure 1**.

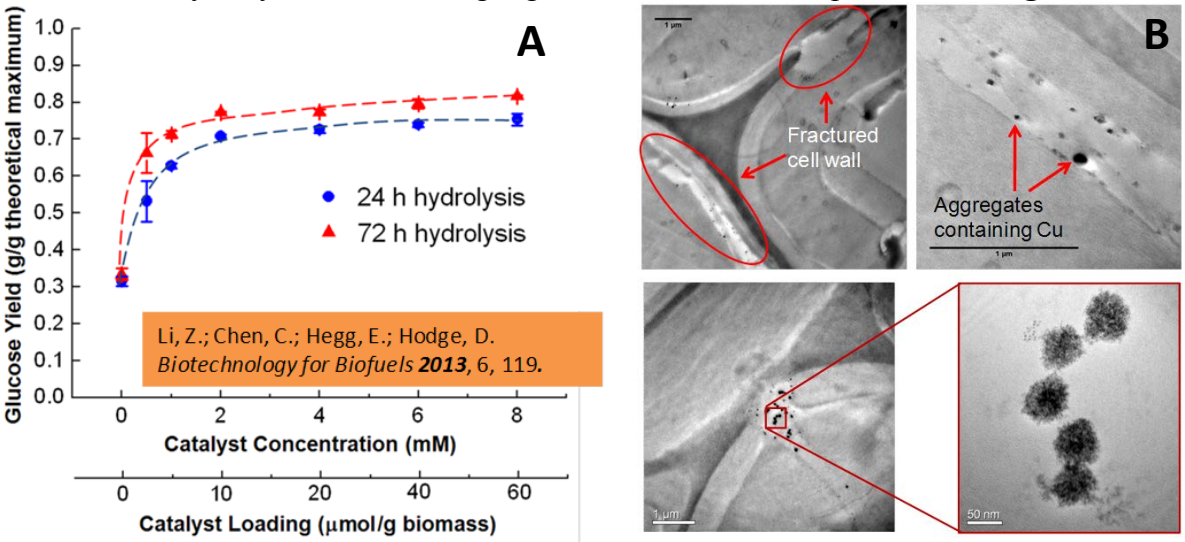

Figure 1: Demonstration of **(A)** improved enzymatic hydrolysis yields using catalyzed oxidative delignification and **(B)** plant cell wall disruption and localization catalyst-containing nanoclusters within the cell wall as validated by EDS.

Understanding the plant cell wall porosity and polysaccharide accessibility

In work funded by NSF CBET beginning 2014 we are investigating the role that the non-covalent forces exerted by plant cell wall polymers within nanoscale cell wall pores have on a number of important phenomena influencing plant cell wall deconstruction and how these properties evolve

during pretreatment and hydrolysis that lead to outcomes of improved polysaccharide conversion. Specifically this involves the role of surface properties in influencing: **(1)** water infiltration into the cell wall and cell wall swelling, **(2)** cellulolytic enzyme accessibility to binding sites within the cell wall, and **(3)** enzyme binding to chemically and physically modified surfaces within the cell wall. For this, we propose to investigate a new paradigm for understanding plant cell wall recalcitrance, specifically that the limitations of cell wall porosity and inaccessible surface area to enzymes, can be best investigated in the context of understanding the plant cell wall matrix as a water-swellable hydrogel and understanding the porosity in the context of hydrogel swelling due to the opposing forces of water swelling versus the resistance of the plant cell wall matrix to swelling imparted by lignification. The outline for this project is presented in **Figure 2**.

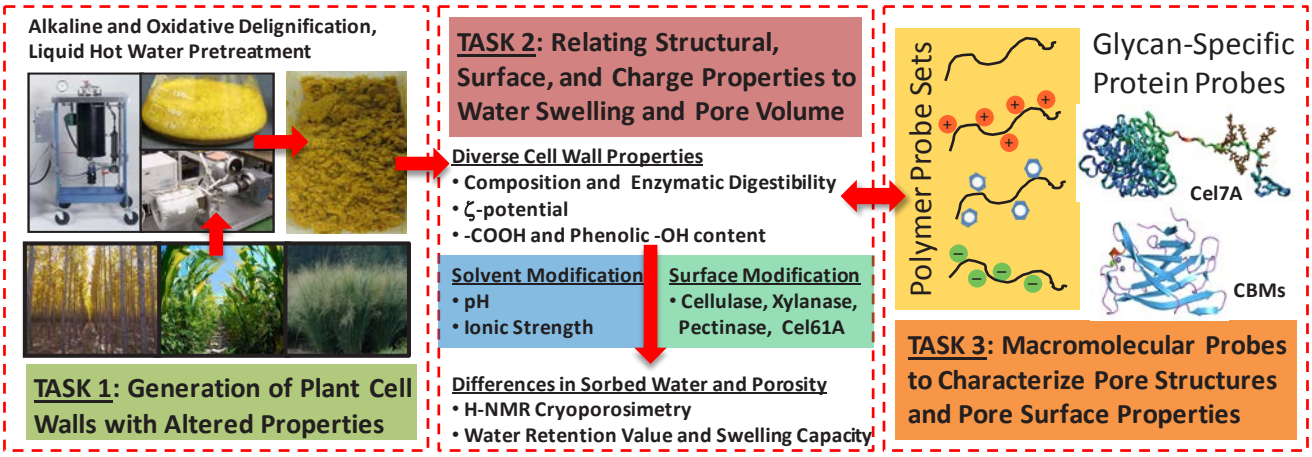

Figure 2: Outline of overall project scope and work flow.

Relating plant cell wall biopolymer properties to phase partitioning behavior

In work funded by the Northeast Sungrant Initiative we are interested in understanding how the properties of cell wall biopolymers solubilized during alkaline pretreatments or chemical pulping processes impact their processing behavior that can be exploited separation processes. Specifically, we are applying alkaline delignification technologies for biofuels and biomaterials applications and linking lignin structural properties to its solubility and phase partitioning behavior in a novel pH-based fractionation process involving sequential CO_2 acidification and separation. Using a number of analytical approaches for lignin characterization, we were able to obtain clear evidence that several structural features of the lignin polymer could be strongly linked to solubility (**Figure 3**).

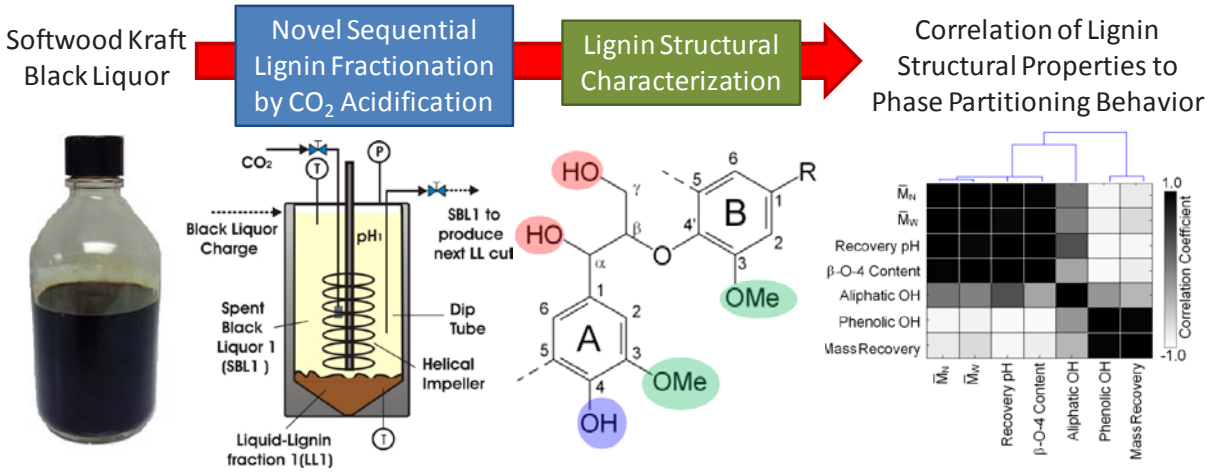

Figure 3: Solubility-based fractionation of alkali-solubilized lignin. *Green Chem.*, 2013, 15, 2904-2912.

Polymer Composites Processing and Rheology

K. Jayaraman
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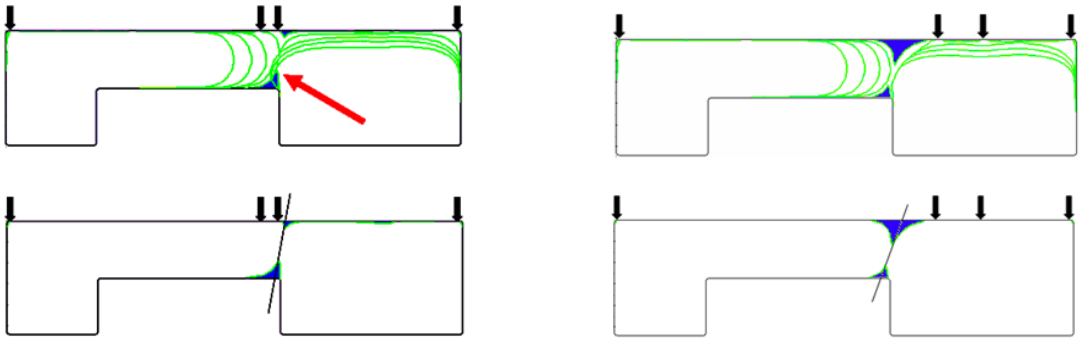
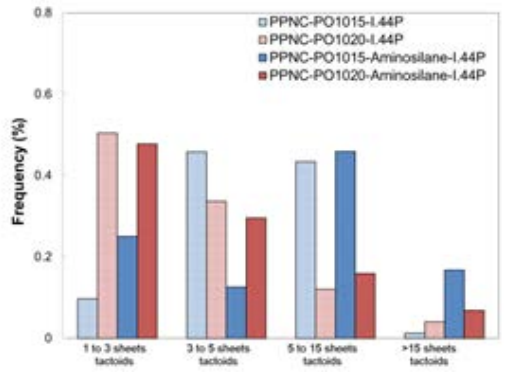
The Polymer Composites Processing and Rheology Research Group at Michigan State University investigates rheology modification and microstructure development during melt processing and solid-state processing of polymer composites, nanocomposites, foams and thermoplastic elastomers. This research has been applied to develop processing strategies for polymer composites, recycled polymers and polymer nanocomposites to make foam core panels, multilayer blown film, and light-weight panels for use in construction.

Modeling Expanding Polyurethane Foam Flow in Vented Mold Cavities
Sponsor: Johnson Controls Inc., Industry Collaborators: J.T. McEvoy, E.F. Fabrizio and D.J. Belding

Flexible polyurethane foam is used widely for cushioning seats in cars, planes and furniture. The reacting mixture is poured at one or more locations at the bottom of the mold; this expands and rises to fill the mold, leaving air pockets or unfilled regions in some cases. Both 2-dimensional and 3-dimensional flow simulations are being run using FLUENT software —the latter set in the High Performance Computing Center (HPCC) at MSU. This is a collaborative project between JCI and MSU aimed at developing accurate predictions of (a) the flow after multiple flow fronts of expanding foam meet around an insert, say and in the presence of different venting patterns – see figures below; and of (b) the effect of serial pours of reacting mixture after a

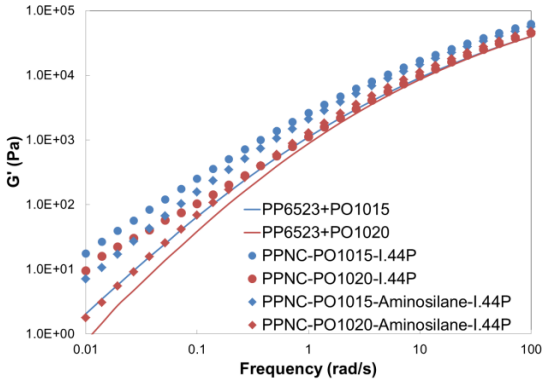


finite time interval on the distribution of temperature in the mold and the meeting of the expansion flow fronts. The figure on the left presents computed flow patterns near the merging foam expansion fronts with one of the best venting patterns resulting in minimal air entrapment; while the figure on the right presents corresponding results for a vent configuration that leads to significant air entrapment (blue region in figure).



Polyolefin-Clay Nanocomposites with Coupling Agents
Sponsors: State of Michigan- MEDC, MIIE, and Petoskey Plastics, MI; Industry Collaborators: Tie Lan, Nanocor; Bryan Kazmer, ViChem; Dav Blankenhagen, Petoskey Plastics

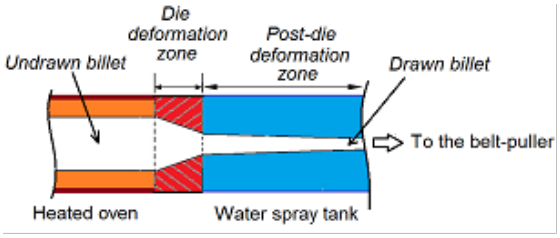
Results obtained in Jayaraman's laboratory from this research show that the addition of organoclay with functionalized polymer or copolymer and other coupling agents to linear polyolefins can produce striking changes in the melt rheology of the bulk polyolefin that are beneficial for processing operations such as foaming and film blowing. Although obtaining good dispersion of organoclay in polyolefins is usually the aim of varying formulations and coupling agents,



the objective of this work was to characterize different formulations not only for the degree of dispersion but also for dynamic shear moduli and extensional viscosity of different formulations in an attempt to understand the contributions from polymer particle contributions and from hindered relaxation of chains that are entangled with surface attached chains. Functionalized polymer chains can be attached to the organoclay both reversibly by hydrogen bonding and irreversibly by covalent bonding. The figures below present results for four different nanocomposite formulations comprised of long functionalized chains and shorter functionalized chains, organoclay without any silane, and organoclay trated with an aminosilane.

Lightened and Highly Oriented Particulate-Filled Polyolefins by Solid Phase Die-Drawing

Sponsors: Dow Chemical Co., Eovations LLC; Collaborators: Kevin L. Nichols, T. R. Bieler



High levels of molecular orientation can be produced in semi-crystalline polymers by solid phase processes such as roll-drawing and die-drawing at elevated temperatures below the melting temperature. Die-drawing of particulate filled polyolefins at elevated temperatures was developed recently to produce expanded and oriented particulate composites that are lighter and stronger after processing. The objective of this research was to investigate the evolution of crystalline orientation or texture in the isotactic polypropylene matrix of talc filled polypropylene at increasing draw ratios or increasing axial strains along the drawn billet and to compare with the evolution of texture in unfilled isotactic polypropylene (i-PP) homopolymer at similar draw ratios. In die-drawn neat i-PP, the (110)[001] texture is prominent – esp. at draw ratios >2. In die-drawn composites, the (010)[001] texture component is more prominent at the highest draw ratios. The growing void volume fraction with draw ratio causes the greater prominence of (010)[001].

Recent Publications

- Ren, W., Jayaraman, K. and Chaudhary, A.K., " Varying Effects of Extrusion on Structure and Rheology of Polypropylene-Layered Silicate Nanocomposites," 85th Annual meeting of the Society of Rheology, Montreal, Canada, Oct 15, 2013
- Jayaraman, K., Hershey, C.J., McEvoy, J.T., "Modeling Polyurethane Foam Flow in a Mold with Constricted Vents," Proc. 71st ANTEC, Society of Plastics Engineers (2013)
- Jayaraman,K., Chaudhary, A.K., "Melt Rheology of Polypropylene-Clay Nanocomposites with Varying Polymer-Filler Interactions," International Congress on Rheology, Lisbon, Portugal, Aug 9, 2012
- Chaudhary, A.K.; Jayaraman, K., "Extrusion of Linear Polypropylene-Clay Nanocomposite Foams," *Polym. Eng. Sci.* 51 (9), 1749-1756 (2011)
- Jayaraman, K., Pathak, T.J., Chaudhary, A.K., "Novel Nanocomposites and Nanocomposite Foams and Methods and Products Related to Same," US Patent Application 12/780,461 Published Dec 9 (2010)
- Rane, R.H., Jayaraman, K., Bieler, T.R., Nichols, K.L., Mazor, M.H., "Evolution of Crystalline Orientation during Solid Phase Die-Drawing of PP-Talc Composites," Proc. 30th International Polymer Processing Society Meeting, Akron, OH, (2014)

Group Members

Current PhD Students: Weijie Ren, Xinting Lin, Christopher J. Hershey

Advanced Materials for Electrochemical Energy Lab (AMEEL)

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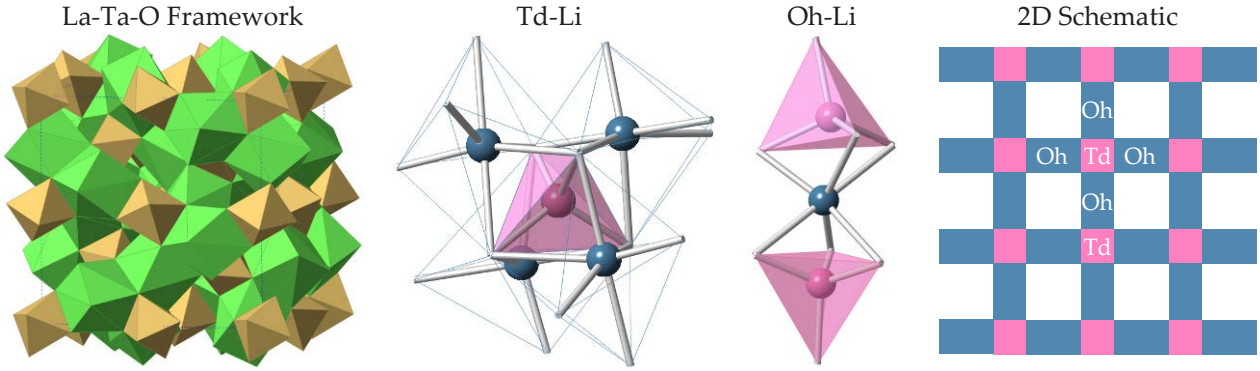
Research at AMEEL is focused on the study of advanced materials and electroanalytical methods for electrochemical energy conversion and storage devices such as fuel cells, batteries, and supercapacitors, etc. Recently our interests are focused on the Solid-state Ionic Conductors (SICs) and Solid-state Mixed Ionic and Electronic Conductors (SMIECs) as battery electrolytes and electrodes.

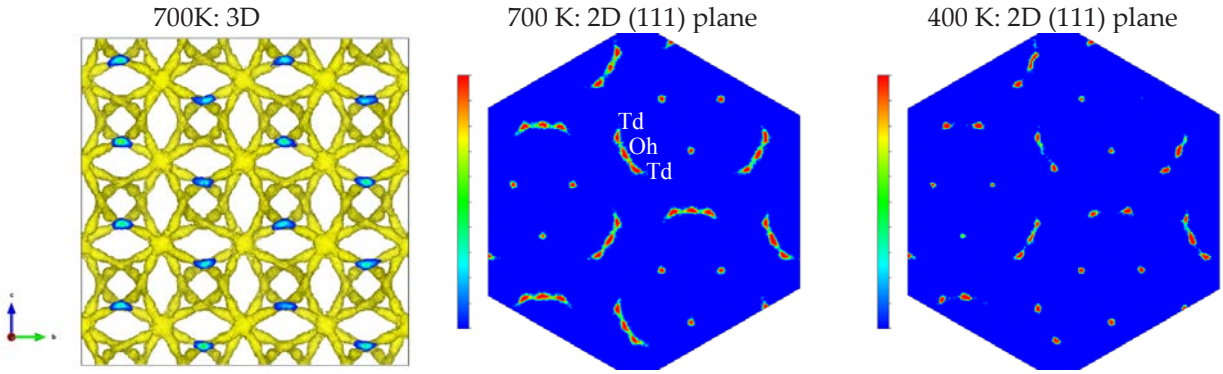
Both SICs and SMIECs are highly disordered crystalline materials which are partially crystalline and partially amorphous while being partially solid and partially liquid at the same time. The complexity of these materials calls for techniques known to both crystallographers and non-crystallographers. We are applying a suite of average and local structure and dynamics probes. It includes scattering-based probes such as regular neutron diffraction with Rietveld refinement and neutron total-scattering with pair distribution function analysis. It also includes atomistic simulation-based probes such as lattice statics and molecular dynamics. The structural and dynamical features of these materials determine their electrochemical properties and applications.

Ongoing projects include:

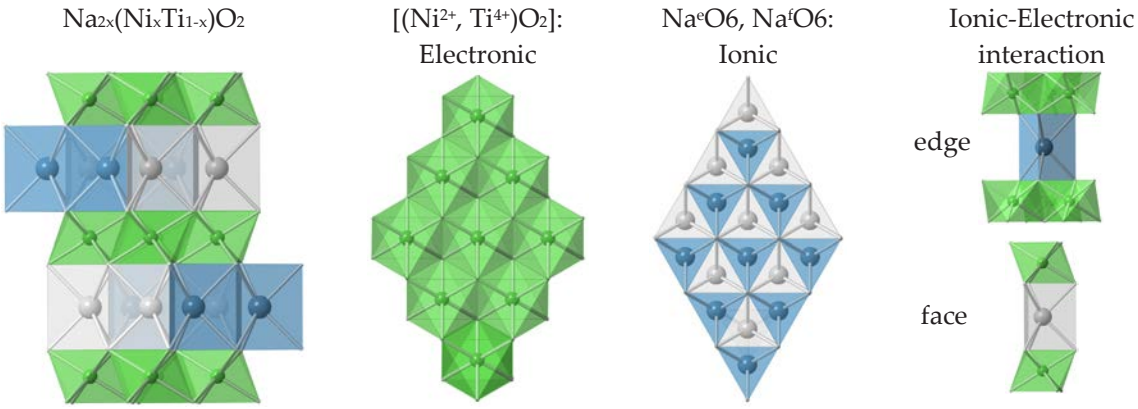
1) Structure and Dynamics of Lithium-stuffed Garnet Oxides



State-of-the-art Li-ion batteries utilize organic solvent based liquid electrolytes that usually have limited electrochemical stability and are also volatile and flammable. Lithium-stuffed garnet oxides are a new class of lithium ionic conductors that have attracted considerable attention for the past ten years. The framework of the materials is composed of LaO8 dodecahedra and TaO6 octahedra. There are two types of cages, tetrahedral (Td) and octahedral (Oh), to host lithium ions. Each Td cage is surrounded by 4 Oh cages and each Oh cage is surrounded by 2 Td cages. Both the Td and Oh cages are only partially occupied. We are investigating a prototypic series of lithium-stuffed garnet oxides $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (x=0-2). The scientific goal is to understand structure and dynamics of lithium disorder in these complex materials. An example of lithium probability density functions or density maps in 3D and 2D plane cuts are given below. Funding: National Science Foundation.



2) "Bi-functional" Electrode Materials for Na-ion Batteries



While Li-ion batteries have dominated the portable electronics market and started their penetration into the transportation and stationary markets, there is growing concern over the lithium abundance and geographical constraints of lithium minerals. Sodium element is more than 1000 times more abundant than lithium in earth's crust and sea and sodium resources are considered practically unlimited. We are studying a class of sodium mixed oxides, $Na_{2x}(Ni_xTi_{1-x})O_2$, that have both high redox-potential transition metals, e.g. Ni, and low redox-potential transition metals, e.g. Ti. This suggests that these materials can be either utilized as a cathode or an anode, i.e. "bi-functional". We have demonstrated the "bi-functionality" of these materials and are currently investigating their structures and electrochemical properties. These materials have layered structures with layered transition metal layers supporting electronic transport and layered sodium prisms (with two different sites) supporting ionic transport.

Recent Publications

Y. Wang, A. Huq, and W. Lai, "Insight into lithium distribution in lithium-stuffed garnet oxides through neutron diffraction and atomistic simulation: Li7-xLa3Zr2-xTaxO12 (x=0-2) series", *Solid State Ionics*, 255, 39 (2014)

R. Shanmugam and W. Lai, "Na2/3Ni1/3Ti2/3O2: "Bi-functional" electrode materials for Na-ion Batteries", *ECS Electrochem. Lett.*

Group Members

Graduate students: Yuxing Wang, Rengarajan Shanmugam, Matt Klenk
Undergraduate Students: Michael Cross

Uses of Nano-structured Chemicals in Materials Science

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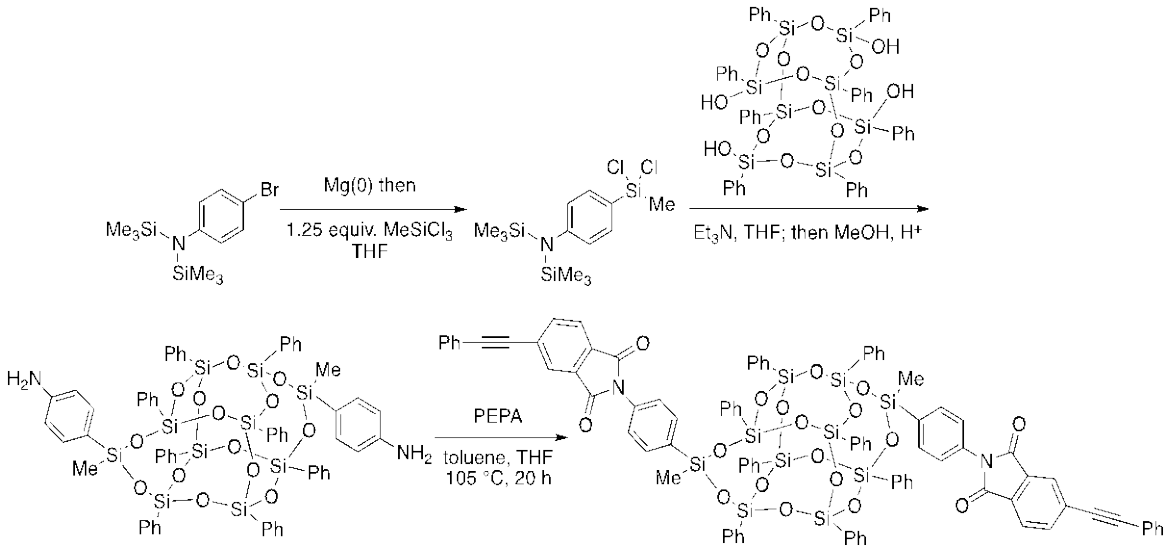
Andre Lee's group has been interested in exploring various materials applications using nano-structured chemicals for the past several years. Applications include improving the high temperature performance of polymeric materials, enhance the oxidative stability of metallic materials in electronic packaging, and retard transport of materials across the hetero-interface when subjected to external thermal and electrical loads. Specifically two examples below highlight the activity in this past year.

Applications in Polymeric Materials:

Began in mid 2009, an effort to develop solvent-free, processible oligoimides for carbon-fiber reinforced composite was initiated. The candidate nano-structured oligoimide was based on a double-decker shaped incompletely condensed SQ architecture. The route used to obtain difunctional phenylethynylphthalimide SQ, bis-PEPI DDSQ, is shown in Scheme 1. This oligoimides exhibited little or no crystallinity, a flow temperature at around 100 ^{o}C and a low wetting angle to carbon fibers. In addition, the presence of the SQ cage does not retard the reaction kinetics as well as the curing of ethynyl groups to form fully cured thermosetting networks. These findings were deemed to be critical for the development of a new class of high temperature thermosetting oligoimides.

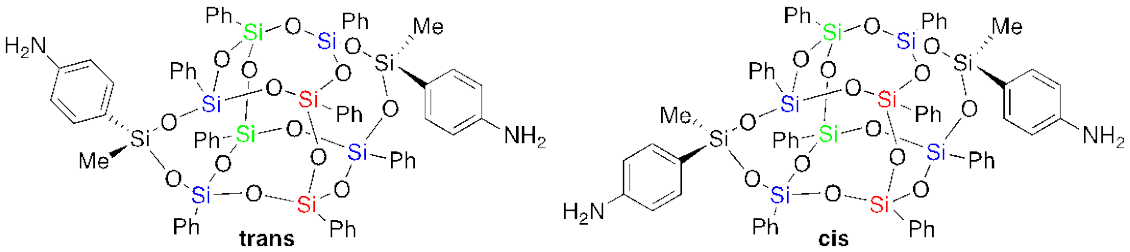
Scheme 1



The scheme as shown above naturally lead to a final product can contains *trans* and *cis* isomer of the intermediate bis-amionpheny DDSQ or the final bis-PEPI DDSQ. An effort to separate the two isomers was initiated to gain better understanding on the property of these isomers and well as its mixture.

Taking advantage of the solubility difference of the two isomers of bis-aminophenyl DDSQ, ultra high purity of *trans* and *cis* isomers of bis-(*meta*)aminophenyl DDSQ and bis-(*para*)aminophenyl DDSQ were obtained and verified using using ^{29}Si,^{1}H NMR with 2-D analysis through ^{3}J-coupled Si-H bonding. In addition, by adjusting the ratio of THF/hexanes used, it was possible to obtain products with specified *trans/cis* ratio.

Figure 1



Using a mixture of *meta* and *para* aminophenyl dichlorosilane as the starting capping agents, product containing six different isomers can be obtained. Initial experiment using 50:50 mixture of *meta* and *para* aminophenyl dichlorosilane, the resultant bis-PEPI DDSQ product exhibited a viscosity that enables the process to form carbon-fiber pre-preg at temperature as low as 150^{o}C. Moreover, the viscosity can be adjusted by controlling the ratio of the six isomers present. This product is a significant advancement in high temperature oligoimide resins. When a large-scale production is developed, it is expected to dramatically improve the performance of light-weight composites with significant reduction in the fabrication cost. Currently US Air Force Research Laboratory is sponsoring the development of the large-scale production and mechanical performance database.

Service Reliability of Cu wire bonding Packages:

Wire bonding is a key packaging technology to make the electrical interconnections between chips and substrates. The necessity to improve density of electrical inter connects, IC density, and cost reduction warrant replacing Au with Cu in the wire bonding packages. Although fabrication processes of the fine-pitch Cu wire bonding packages has been steadily improving, the intrinsic oxidation sensitivity of Cu as compared to Au remains a significant reliability concern when Cu is bonded to environmentally active Al pads. The potential sources of reliability concern are attributed to the observed galvanic corrosion between various Cu-Al IMCs and resulting oxides. In addition, formation of less-stable, self-passivating oxides can cause interfacial cracking during the high humidity stressing that further accelerates the rate of corrosion damage. These proposed damage pathways were retarded in a recent study using Pd-coated Cu wire, where reliability was improved via controlling the diffusion and the IMC formation processes on the Cu-Al interface. Although this qualitative investigation provided a general guideline to be used for reliability improvement, electrochemical details of various entities present at Cu-Al interface are not yet fully understood. Thus accurate lifetime predication of Cu-wire bonding packages remains elusive. Moreover fundamental knowledge on the electrochemical details of Cu-Al interface will enable a systematic development of a more economical Cu wire coating or alloying solution than a solution that needs expensive Pd.

The scientific challenge of this study is to understand the stability of various oxide layers on IMCs at the Cu-X/Al interface that can provide passivation in the wire bonding package environment in molding compounds containing various corrosive chemical entities, as well as the ability of controlling the formation of these reactive interfacial IMCs in the presence of other metallic coatings or alloying. These fundamental generalizations will lead to solutions for optimized service performance and long-term service reliability of Cu-wire bonding in electronic packages. This is expected to create a fundamental pathway leading to a more economical and highly-reliable design methodology and materials selection for future electronic packages.

Group Member:

Research in the area of electronic interconnects is conducted in collaboration with Prof. KN Subramanian
Visiting Scientist: Xu Zhang (Beijing University of technology)
Graduate Students: Yang Lu; David Volgelsang; Yuelin Wu

Nano Bio Engineering Laboratory (NBEL)

Ilsoon Lee
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http://www.egr.msu.edu/~leeil/

The NBEL is utilizing nanotechnology and self-assembly as new tools to design new nanostructured materials and systems to solve existing engineering problems in energy, materials, and environment. The research focuses on the design and fabrication of nano / bio particles and films to advance energy, biocatalytic systems, and functional materials. Specific selective projects include:

1.) Prevention of Bacterial Biofilm Formation on Surfaces
Sponsor: The MSU Foundation (SPG) / Collaborator: Dr. Chris Waters

Bacterial biofilms result in billions of dollars of economic loss due to contamination and corrosion of industrial equipment, biofouling of ships hulls, loss of agriculture products, and medical expenses. Furthermore, bacterial biofilm formation is responsible for millions of infections and hundreds of thousands of fatalities annually in the United States. As bacteria in biofilms are resistance to treatment with traditional antibiotics, it is critical to develop new methods to prevent and remove bacterial biofilms.

Figure 1: Bacterial biofilm examples: Body surface (teeth), ship skull, natural.

2.) Solar-Bio-Nano Based Wastewater System for the Production of Energy and Potable Water
Sponsor: DOD SERDP / Collaborators: Drs. Liao (Biosystems Engineering), Engeda (ME)

The solar-bio-nano project for wastewater system will generate energy and produce drinking water, thus providing a potential blueprint for the future of municipal/ agricultural wastewater treatment systems. The integrated system will comprise three major components. First, the solar unit will use new materials and employ a novel configuration making it up to 80 percent lighter than traditional solar units. Second, biological conversion processes will break down wastewater and food scraps to produce methane that can be used as fuel. Finally, a nano-filtration system will then take the discharge from the biological processes to provide drinking water.

3.) Hybrid Nanostructured Metal Foam Material Systems for Blast Impact (and Wrinkle-free films)
Sponsor: NSF / Collaborators: Dr. Burgueno

The goal is to develop a novel concept for the protection of materials and structures under blast and impact loads by developing new nanostructured functionally-graded cellular materials that will modify the transmission of stress waves in a controlled or tailored manner to improve performance and safety. A high-performance cellular structure is used as the framework for controlled deposition of structural and functional nano-scale reinforcement. A bio-inspired approach, namely ionic molecular self-assembly will be used to develop complex multi-scale multilayer reinforcement architecture with molecular-level control of its composition and microstructure. The work will lead to innovative hybrid functionally-graded materials structured from the nano-scale upward by means of a bio-inspired manufacturing approach.

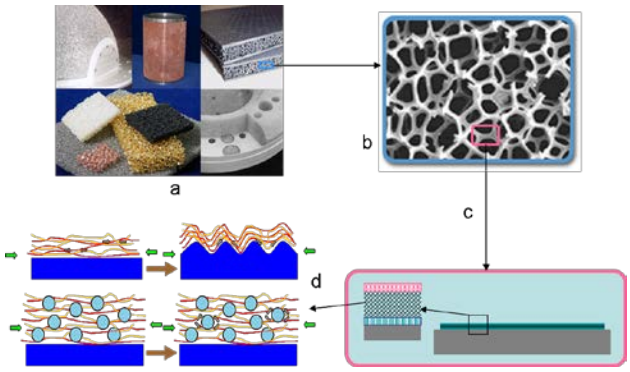

Figure 2: Hybrid nanostructured surface reinforcement coating of metal foam materials. a) Various metal foam products. b) Micrograph of a foam structure. c) LBL nano-assembly process to form hybrid nanostructured surface reinforcement. D) A scheme of nanoparticle incorporated nanostructured reinforcement to enhance stress-wave mitigation of impact and blast.

Selective Publications/Patents:

[h-index **20**, citations **1308** from ISI web of science / h-index **23**, citation **1697** from google scholar]

- **Lee, I**. "Molecular Self-Assembly: Smart Design of Surface and Interface via Secondary Molecular Interactions," *Langmuir* **29** 2476-2489, (2013). html (**Issue Cover**: Vol.29, No. 8, 2/26/2013), html
- Wang, W.; Ji, S.; **Lee, I**. "Fast and efficient nanoshear hybrid alkaline pretreatment of corn stover for biofuel and materials production," *Biomass and Bioenergy* **51**, 35–42, (2013). html (featured in **Renewable Energy Global Innovation** **html**)
- Lu, J.; Weerasiri1, R.R.; Liu, Y.; Wang, W; Ji, S.; **Lee, I.** "Enzyme Production by the Mixed Fungal Culture with Nanoshear Pretreated Biomass and Lignocellulose Hydrolysis," *Biotechnology and Bioengineering* **110**, 2123-2130, (2013).
- Ji, S.; Lu, J.; Liu, Z.; Srivastava, D.; Song, A.; Liu, Y.; **Lee, I**. "Dynamic encapsulation of hydrophilic nisin in hydrophobic poly (lactic acid) particles with controlled morphology by a single emulsion process," *Journal of Colloid and Interface Science* **423,** 85-93, (2014).
- Gokhale, A. A.; Lu, J.; **Lee, I**. "Immobilization of cellulase on magnetoresponsive graphene nano-supports," *Journal of Molecular Catalysis B: Enzymatic* **90**, 76-86, (2013).
- Kohli, N.; Srivastava, D.; Richardson, R.J.; Sun, J.; **Lee, I**.; Worden, R.M."Nanostructured biosensor containing neuropathy target esterase activity," **US Patent # 8,623,196,** Issued on Jan. 7, (2014).
- **Lee, I.;** Hendricks, T. R. "Wrinkle-free nanomechanical film," **US Patent # 8,460,785** Issued on Jun. 11, (2013).
- Worden, R.M.; Ofoli, R.Y.; Hassler, B.L.; Kohli, N.; **Lee, I.** "Customizable and renewable nanostructured interface for bioelectronic applications," **US Patent # 8,435,773**, Issued on May 7, (2013).

Group Members

Post-Docs - Shaowen Ji

Graduate Students - Ankush Gokhale, Oishi Sanyal, Xiaopeng Bi, Jing Yu, Anna Song

Undergraduate Students - Andrew Izbick, Ryan Yau, Anna Sommerfeld, Jason Thompson, Alex Hanft, Yi Ji

Thermodynamic Properties for Reactive Separations, Bio-derived Chemicals and Fuels

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The Lira research group focuses on property measurement and prediction for reactive separations and bio-derived chemicals and fuels. Measurement techniques include VLE, LLE, SLE. For VLE we use both P-x-y and T-x-y techniques. For predictive techniques, we use coarse-grain simulation models that bridge the gap between detailed simulations and empirical macroscopic group contributions. We collaborate closely with the Miller research group.

Phase Equilibria Measurements
Recent Sponsors: DOE, DLA, misc industry.
Collaborators: Dennis Miller

The Lira Thermodynamics Research Facility measures and correlates vapor-liquid equilibria (VLE), liquid-liquid equilibria (LLE), solid-liquid equilibria. For VLE, the lab has a Fisher T-xy recirculating apparatus and a custom P-xy apparatus, and a miniature ebuilliometer. We also have capabilities for density and viscosity measurements.

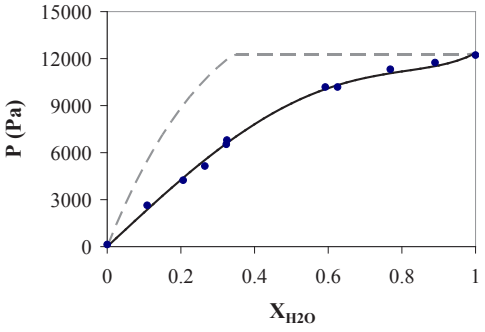

Figure 2. P-x measurements for the monoethyl succinate + water system at 323.15 K. (●) experimental data, (— —) UNIFAC prediction (incorrect LLE), (—) Regressed NRTL - HOC

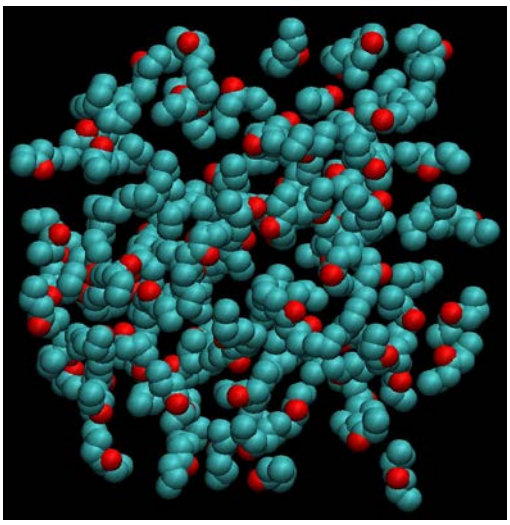

Figure 1. An assembly of 4-heptanone. from a simulation at intermediate density.

Our phase equilibria measurements support the MSU reactive distillation facility and were vital in development of our process development for diethyl succinate by reactive distillation. We have filed a patent on a process to react the sodium succinate salt directly from the fermentation product to diethyl succinate intermediates, bypassing isolation of succinic acid.

An example of P-x measurements are shown in Figure 2, which illustrates the importance of experimental measurements in addition to predictions.

Alternative Fuel Properties
Sponsor: DOE, DLA, Ford Motor Company
Collaborators: Dennis Miller, Kris Berglund, Ramani Narayan. Mechanical Engineering Faculty: Schock, Jaberi, T. Lee.

This is a comprehensive project spanning the synthesis of alternative fuels, blending and characterizing properties, simulating spray and evaporation properties, combustion characteristics and engine tests. The Lira lab is involved in the characterization and prediction of properties. We provide the group with property values from literature, property estimates, and property measurements.

Cold flow properties are critical for practical applications, and a known problem for molecules such as long chain saturated methyl esters in biodiesel. We are actively measuring cloud points in diesel fuels with bioderived additives.

We also actively use simulation to predict vapor pressures and densities. We are building a coarse grained method based on the StePPE method. Figure 4 compares experimental and predicted primary alcohol vapor pressures from methanol to 1-eicosanol within 6.8% with a global parameter set. Densities (not shown) are within 0.8%.

Recent Publications

Hong, X.; McGiveron, O.; Kolah, A.K.; Orjuela, A.; Peereboom, L.; Lira, C.T.; Miller, D.J. "Reaction Kinetics of glycerol acetal formation via transacetalization with 1,1-diethoxyethane," Chemical Engineering Journal, 222, 374-381 (2013). doi: 10.1016/j.cej.2013.02.023

Introductory Chemical Engineering Thermodynamics, 2nd ed., J.R. Elliott, C. T. Lira, Prentice-Hall. 876 pages. ISBN 978-0-13-606854-9, International Edition ISBN 978-0-13-275624-2, Documented at chethermo.net. The text includes an assortment of authored computer programs distributed via the Internet. (2012).

Hong, X.; McGiveron, O.; Lira, C.T.; Orjuela, A.; Peereboom, L.; Miller, D.J "A reactive distillation process to produce 5-hydroxy-2-methyl-1,3-dioxane from mixed glycerol acetal isomers," Org. Proc. Res. Dev., 16, 1141-5, (2012).

Yang, X.; Lira, C.T. "Modeling of adsorption on porous activated carbons using SLD-ESD model with a pore size distribution" Chem. Eng. J. 195-6, 314-322, (2012). doi: 10.1016/j.cej.2012.04.070

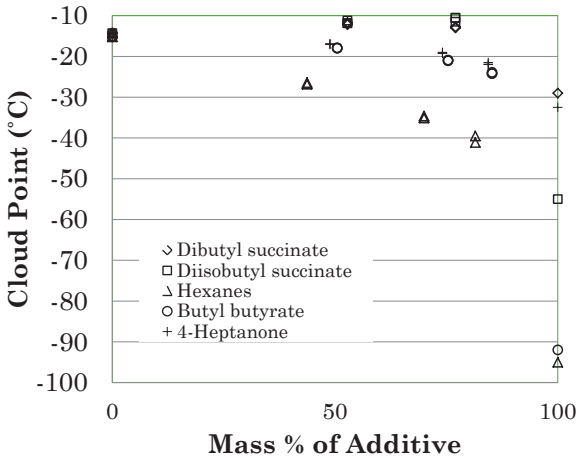

Figure 3. Cloud point behavior of a selected diesel fuel with addition of several potential bio-derived additives.

Hassan, A.M; Vu, D.T.; Bernard-Brunel, D.; Elliott,

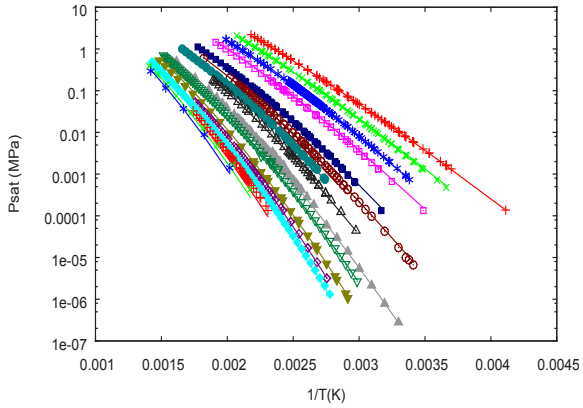

Figure 4. Prediction of primary alcohol vapor pressures from methanol through 1-eicosanol.

J.R.; Miller, D.J; Lira, C.T, "Application of SPEAD to bioderived esters and acetals" Ind. Eng. Chem. Res. 51(8), 3209-3214, (2012). doi: 10.1021/ie2009058

Group Members

Apsi K. Kolah, Ph.D., Research Professor
Lars Peereboom, Ph.D., Research Assoc.
Anne Lown, Ph.D. Student
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Molecular and Organic Excitonic Electronics Laboratory

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The Molecular and Organic Excitonic Electronics lab focuses on inorganic and organic excitonic materials for 1) low-cost solar energy production and 2) efficient energy utilization. We look to exploit oriented, crystalline, nanostructured, and excitonic films through organic-inorganic and organic-organic interactions while studying fundamental relationships between structure and photophysical properties. Ultimately we aim to apply this understanding to enhance device efficiencies, lifetime, and create new functionality

1) Routes to Lower Cost Solar Cells Through Nanostructured and Excitonic Materials

The Earth is continuously bathing in over one-hundred-million-billion watts of sunlight – several thousand times more than mankind's energy demands. While a multifaceted approach is required to transition away from fossil fuels, solar energy will surely be key to a sustainable future. The engineering of PV structures at the nanoscale has attracted tremendous research interest as it may enable substantial reductions in PV installation costs and facilitate wider market penetration. With the emergence of nanostructured photovoltaics, the question has arisen of where the practical and fundamental limits reside in these new systems and whether there are ways to exploit their unique properties. A number of architectures have been proposed for reducing losses in solar cells in order to overcome the SQ single junction limit that are enabled by the nature of nanostructured materials including multiple-exciton generation, exciton fission, and tandem stacking. The practical efficiency limits (a scaling of the thermodynamic limit) are shown in Fig. 1 for several of these systems. Ultimately we aim to further evaluate and exploit these phenomena in thin-film architectures to realize ubiquitous solar energy.

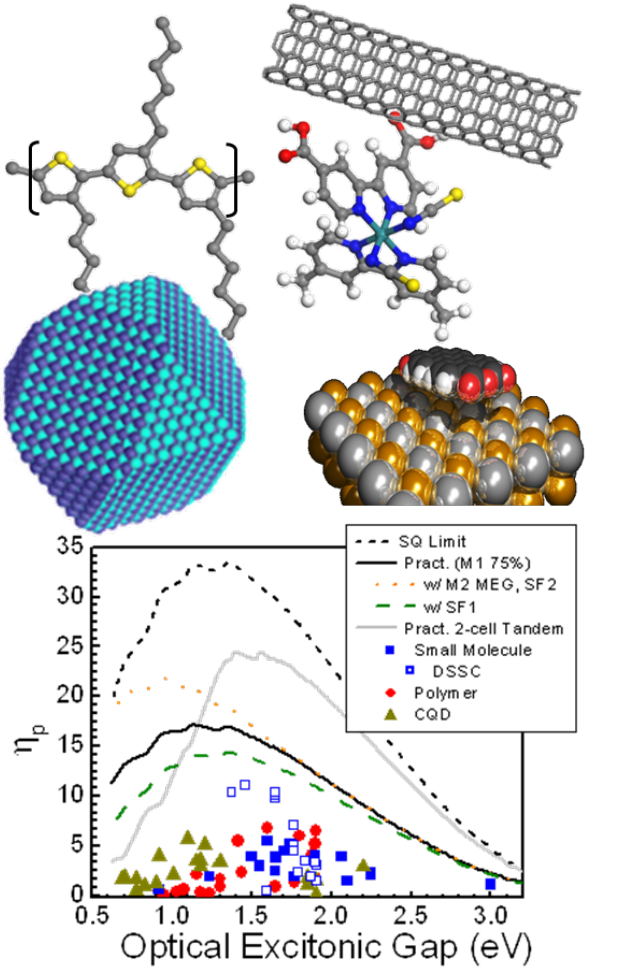

Fig. 1 - (Top) Diagram of nanostructured organic and molecular semiconductors. Theoretical and realistically achievable efficiency limits for nanostructured materials as a function of bandgap with various configurations of single-junction, multijunctions, multi-exciton generation, and exciton fission.

2) Excitonics for Building Integrated Transparent PVs and Solar Concentrators:

We have been developing an additive, transparent, molecular photovoltaic that can retain a high degree of visible-transparency, while absorbing ultra-violet and near-infrared light for power generation. These cells can allow for optimization of overall transparency, efficiency, and lighting aesthetic and lead to a highly deployable solar window that is

Fig. 2 - (Left) Infrared-harvesting transparent flexible solar cell module. (Right) Highlight of our work on one of the covers of *Adv. Energy Mat.* showing a photograph of the pioneering transparent luminescent solar concentrator (LSC) system with comparison to a typical colored LSCs.

retrofittable in window panes in homes, skyscrapers, airports, greenhouses, malls, and automobiles, and enhance the functionality of already utilized transparent surfaces. This is accomplished by exploiting the excitonic character of molecular and organic semiconductors that leads to "oscillator bunching" exhibiting uniquely distinct absorption spectra from the band-absorption of traditional inorganic semiconductors.

3) Next-Generation Organic Light Emitting Diodes for Lighting

An important route to the reduction of green gasses lies in energy utilization. In particular, lighting accounts for about 17% of the total energy consumption in buildings. State of the art white organic light emitting diodes (WOLEDs) are currently poised to make reductions in this consumption rate for lighting as power efficiencies greater than that of fluorescent lighting have been demonstrated. However, WOLEDs are currently limited by external quantum efficiencies (EQE) of ~20% due to waveguided modes and are reliant on precious metal, Pt and Ir, containing phosphorescent dopants To circumvent these shortcomings we are designing the next-generation devices based on phosphorescent nanostructured and abundant molecular materials.

Recent Publications

Y. Zhao, R. R. Lunt. "Transparent Luminescent Solar Concentrators for Large-Area Solar Windows" *Adv. Energy Mat.* 3, 1143-1148, 2013 (*featured on Back Cover*)

R. R. Lunt, R. J. Holmes "Small-Molecule and Vapor-Deposited Organic Photovoltaics". In Handbook of Organic Solar Cells: Materials, Design, and Production. Edited by B. R. Rand and H. Richter. (*In Print)*. 2013.

M. Young, C. J. Traverse, R. Pandey, M. C. Barr, R. R. Lunt. "Angle Dependence of Transparent Photovoltaics in Conventional and Inverted Configurations." *Appl. Phys. Lett*., 103, 133304, 2013.

S. Wagner, R. R. Lunt, P. Zhang. "Anisotropic crystalline organic step-flow growth on deactivated Si surfaces" *Phys. Rev. Lett*., 110, 086107, 2013.

R. R. Lunt. "Theoretical Limits for Visibly Transparent Photovoltaics." *Appl. Phys. Lett.,* 101, 043902, 2012. *(featured in Conservation Magazine)*

R. R. Lunt, T. P. Osedach, P. R. Brown, J. Rowehl, and V. Bulović. "Practical Roadmap and Limits to Nanostructured Photovoltaics" *Adv. Mat.*, 23, 5172, 2011.

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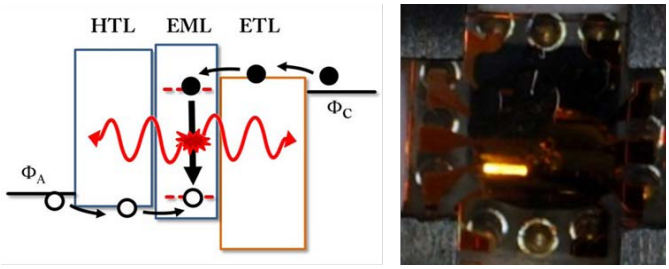

Fig. 3 - (Left) Schematic energy level diagram and (right) operation of a phosphorescent light emitting diode.

Fuels and Chemicals from Renewable Feedstocks

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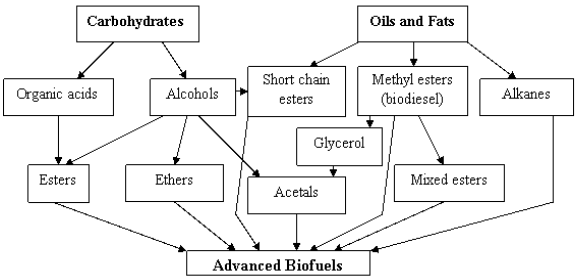
The replacement of fossil resources for our energy and material needs looms as one of the grand challenges of the 21st century. Of the possible alternatives, biomass is renewable, abundant, and well-suited to processing. In the laboratories of the Miller group, cutting edge technology in heterogeneous catalysis and advanced processing is implemented to effectively convert of biomass and biomass-derived intermediates to chemical products and fuels that compete with petroleum-based products in the current socio-economic environment.

Catalysis for renewable feedstocks: Over the past 20 years, the Miller group has examined a number of chemical systems directed at energy and materials production from renewable feedstocks. These have included the catalytic upgrading of biomass platform intermediates, mainly produced in fermentation processes, with the goal of building technical capabilities for the emerging biorefinery. In most cases, the overarching goal of the catalytic chemistry is deoxygenation of the biomass intermediate to a product that replaces a petroleum-derived counterpart. Classes of platform intermediates include carboxylic acids, sugar alcohols, linear alcohols, furanic compounds, and other derivatives; because these platform intermediates are typically of low volatility and are less thermally stable than their petroleum analogs, we have developed expertise in carrying out catalysis at mild temperatures under elevated hydrogen pressures in aqueous solution.

Many discoveries in the Miller lab have led to patents and other intellectual property that has been licensed to companies for commercial development. The ability to carry out closely monitored chemical reactions, detailed analysis of products, and carefully design and preparation of active catalysts has led to extensive interaction with industrial, national laboratory, and other academic partners. The rigorous modeling of multiphase reaction environments such as trickle bed reactors adds additional capabilities in catalyst and process development. Twenty patents have resulted from work done in labs of the Miller group and their collaborators.

Biofuels: The Miller group has partnered with the MSU engine group in mechanical engineering to produce and test advanced biofuels for internal combustion engines. Moving past today's first generation ethanol and biodiesel, emphasis is placed on developing advanced biofuels with enhanced engine performance, high energy density, and storage and flow properties that facilitate their use as direct replacements for petroleum-derived fuels.



Pyrolysis and bio-oil upgrading: There is growing interest in the direct thermochemical conversion of biomass combined with secondary upgrading of the liquid products formed. Pyrolysis has several advantages over other conversion pathways in that it is rapid, converts the entire biomass material, and produces a higher fuel yield. Upgrading of the liquid "bio-oil" product formed during pyrolysis to hydrocarbon-like fuels remains a major barrier to implementation.

Reactive separations: The Miller group uses reactive separations as a platform technology for process intensification in renewable chemicals and fuels production. The group operates the MSU Reactive Distillation Facility, a full pilot-scale system consisting of two ten-meter reactive distillation columns located at MBI on the MSU campus. The columns are housed within a three-story vented enclosure in accordance with safety and health standards; one column is glass for atmospheric pressure and vacuum operation; the second is stainless steel for elevated pressure studies.

Reactive distillation is well-suited for reaction systems that are limited by chemical equilibrium, as the removal of one product by distillation allows the reaction to be driven to completion within the column. Current work emphasizes enhanced process intensification in reactive separation processes, including experimental and modeling studies of side reactors and energy integration. Two major commercial applications are esterification and acetalization; a number of proof-of-concept projects have been carried out with corporations as well as with national laboratories and State agencies.

Recent Publications

Murkute, A.; Jackson, J.E.; and Miller, D.J., "A Supported $MnCeO_x$ Catalyst for Ketonization of Carboxylic Acids," *J. Catal*. **278**, 189-199 (2011).

Xi, Y.; Jackson, J.E.; Miller, D.J.; "Characterizing Lactic Acid Hydrogenolysis Rates in Laboratory Trickle Bed Reactors," *Ind & Eng. Chem. Research*, **50**(9), 5440-5447 (2011).

Hong, Xi; McGiveron, O.; Orjuela, A.; Lira, C.T.; Peereboom, L.; Miller, D.J. "A Reactive Distillation Process to Produce 2-Methyl-5-hydroxy-1,3-dioxane from Mixed Glycerol Acetal Isomers," *Organic Process Research & Development* **16**(5), 1141-1145 (2012).

Orjuela, A.; Orjuela, A.; Lira, C.T.; Miller, D.J. "A novel process for recovery of fermentation-derived succinic acid: Conceptual design and preliminary economics," *Bioresource Technology* **139**, 235-241 (2013).

Pappu, V.K.S.; Kanyi, V.; Muller, E.; Peereboom, L.; Lira, C.T.; Miller, D.J. "Butyric acid esterification over solid acid catalysts: The effect of alcohol carbon chain length and a kinetic model for the Amberlyst 70 catalyzed esterification with 2-ethylhexanol," *Bioresource Technology,* **130**, 793-797 (2013).

Santhanakrishnan, A.; Shannon, A.; Peereboom, L; Lira, C.T.; Miller, D.J. "Kinetics of mixed alcohol esterification of butyric acid," *Ind. & Eng. Chem. Res.*, **52**, 1845-1853 (2013).

Group Members

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Arati Santhanakrishnan	Graduate Student
Tyler Jordison	Graduate Student
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New Materials for Energy Applications

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Research in the Morelli group is aimed at designing, synthesizing, and characterizing new inorganic materials with applications in energy conversion. Currently, two main thrusts or our research are 1) investigation of new thermoelectric materials for conversion of heat to electricity; and 2) development of new materials for cryogenic cooling of Peltier devices for space-based applications.

The **Center for Revolutionary Materials for Solid State Energy Conversion, a US Department of Energy-funded research Center led by MSU,** focuses on solid state conversion of thermal energy to useful electrical power, both to increase the efficiency of traditional industrial energy processes and to tap new unused sources of energy such as solar thermal. Additionally materials with enhanced thermoelectric properties will find application in high efficiency, environmentally benign climate control systems. We are undertaking a broad-based effort in semiconductor energy conversion materials utilizing and combining experimental, theoretical, and computational efforts. A major focus of our effort will be in the synthesis of new forms of matter, including both single phase alloys and compounds and composite structures created using nanoscience.

Ultimately, by working together in this Center we aim to develop design rules to predict properties of advanced thermoelectric materials, and realize these structures through innovative synthesis and advanced structural as well as chemical characterization.

Some examples of current work in our group include:

- *Understanding the relationship between structure and bonding and the thermal conductivity of solids.* Good thermoelectric materials have very low thermal conductivity, and if we can understand how to control this parameter, new materials can be designed with improved properties. In collaboration with colleagues in our Center, we have employed state of the art computational approaches to study the lattice dynamics of a class of promising semiconductors (**Figure 1**). We find that certain types of structural arrangements of atoms give rise to strongly anharmonic lattice vibrations, a key ingredient in determining a material's heat conduction characteristics. We have synthesized these predicted structures in the laboratory and verified the predictions of these computational models.

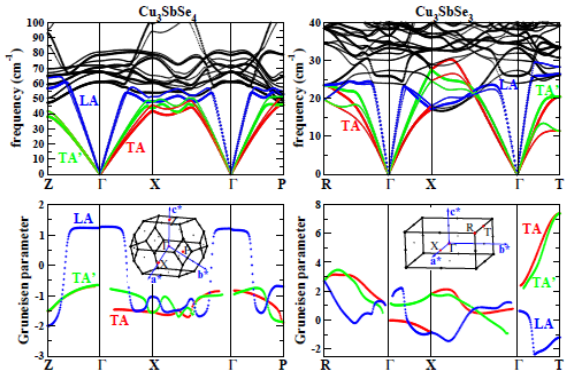

Figure 1 Calculation of the lattice dynamics of Cu_3SbSe_4 and Cu_3SbSe_3. The large Grüneisen parameters shown in the bottom panel for Cu3SbSe3 indicates that this compound will exhibit very low thermal conductivity.

- *Thermoelectric materials synthesized from earth-abundant sources.* We have shown that the mineral tetrahedrite (**Figure 2**) can be used directly as a thermoelectric material with very little compositional modification. Tetrahedrite, of chemical formula $Cu_{12}Sb_4S_{13}$,

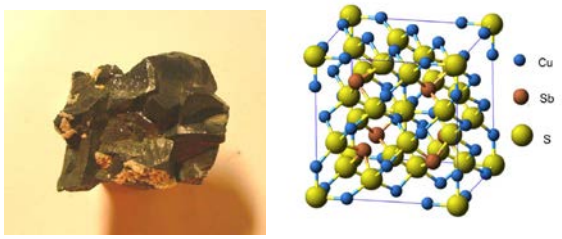

Figure 2 A natural mineral tetrahedrite polycrystal (left). This compound is the most widespread sulfosalt on earth; it is also a semiconductor whose properties can be tailored to produce high thermoelectric figure of merit. The crystal st4ructure of this compound is shown on the right.

is the most common sulfosalt mineral on Earth, and its use as a source thermoelectric material could pave the way to large scale and low cost application of thermoelectricity for energy conversion. We have found that the mineral itself can be used directly in a powder processing methodology to synthesize materials with large thermoelectric figure of merit in a temperature range suitable for the conversion of waste heat from a variety of sources, including vehicle exhaust gas and power plant discharge sources.

- *Thermoelectrics for cooling of infrared sensors*. Our group has also been investigating new materials for low temperature Peltier devices. These devices can be used to cool infrared sensors on satellites to the cryogenic temperatures necessary for them to operate. We are exploring thermoelectric effects below room temperature in alloys comprised of elements containing f-shell electrons. Two new compounds of particular interest are $YbAl_2$ and $YbCu_2Si_2$. We have found that by chemical substitution the magnitude of the Seebeck coefficient can be increased, and the temperature at which it is maximized can be controlled. This provides a means of improving and optimizing the thermoelectric properties in the cryogenic temperature range.

Recent Publications

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Xu Lu and Donald T. Morelli, "Rapid Synthesis of high performance thermoelectric materials directly from natural mineral tetrahedrite," *MRS Communications*, **3**, 129 (2013)

Xu Lu and Donald T. Morelli, "Mineral tetrahedrite as a direct source of thermoelectric materials," *Physical Chemistry Chemical Physics*, **15**, 5762 (2013)

G.J. Lehr, D.T. Morelli, H. Jin, and J.P. Heremans, "Enhanced thermoelectric power factor in $Yb_{1-x}Sc_xAl_2$ alloys using chemical pressure tuning of the Yb valence," *Journal of Applied Physics* **144**, 223712 (2013)

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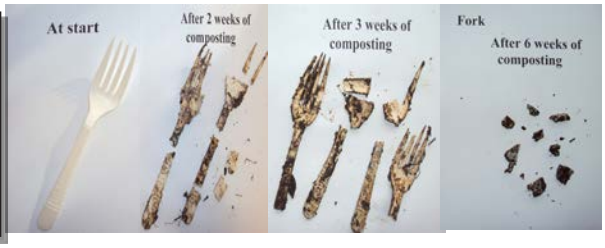
Biobased Materials (Narayan) Research Group design and engineer new biobased and biodegradable-compostable polymer materials and bio processes using agricultural crops and residues (soybean, and corn), lignocellulosic biomass, and algae. These biobased products find commercial application in films for plastic bags, injection molded articles, thermoformed products, foamed sheets for protective and insulation packaging, arts and crafts and toy materials, and biomedical applications. The group's biobased materials technology platform is covered by **29 patents; 150 peer reviewed publications, and eight technologies** have been licensed or resulted in a spin-out company. **15 Ph.D** and **18 M.S**. degree students have graduated from the group. Currently there are 8 graduate students, 5 undergraduate students, two senior research staff, one postdoctoral and several visiting research fellows in the group.

Funded by a Phase I & II NSF STTR project with KTM Industries (www.ktmindustries.com) a local Michigan small business, we designed and engineered a portfolio of biodegradable starch based biofoam materials for the protective packaging and insulation market. These materials have (a) the performance of current petro/fossil based polyethylene and polystyrene foam materials (b) 100% biobased carbon content, and (c) can be safely, completely, and efficiently biodegraded in soil or composting operations at the end-of-life. KTM has sales of $2 million +, and employing 15 people

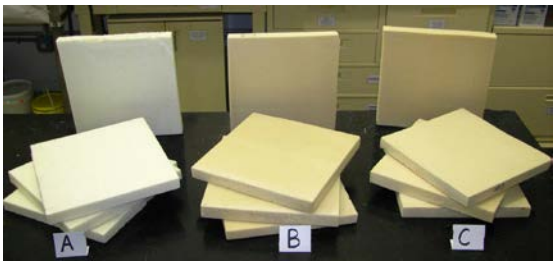
Our technology on biobased and biodegradable-compostable polymers using biopolyesters and poly(lactic acid) (PLA) has been commercialized through Northern Technologies International (www.ntic.com), a $150 million+ publicly traded (NASDAQ symbol: NTIC) micro-cap company formed a strategic partnership with BioPlastic Polymers to commercialize the bioplastics technology world-wide under the brand name Natur-Tec – www.natur-tec.com [U.S. Patents 5,906,783; 5,969,089; 7, 361, 727] Biobased and Biodegradable Materials, Rationale, Drivers, & Technology Exemplars, ACS (An American Chemical Society Publication) Symposium Ser 939, Ch 18, pg 282, 2006; Biodegradable and compostable alternatives to conventional plastics, Phil. Trans. R. Soc. B 364, 2127-2139, 2009. We published two papers based on silicone polymers (Hydrolysis and Condensation of Hydrophilic Alkoxysilanes under Acidic Conditions. SILICON, 4(2): p. 109-119, 2012; Hydroxyl Terminated Hydrophilic Silanes. SILICON, 4(3): p. 167-174, 201) and focusing on biobased and compostable PLA polymers. Our work on the crystallization behavior and kinetics of PLA polymers, and the rheological modification of PLA is part of a NSF-STTR Phase II project with Northern Technologies. Another major focus is on engineering a process for the thermal recycling of PLA to lactide monomer.



In cooperation with NTIC, we are working on a Department of Defense (DOD) Phase II SBIR project on developing non-plastic biobased and biodegradable coatings for non-plastic bags for the Navy. These bags are designed to have high strength, lightweight, water resistant, and can be readily treated with other organic wastes in the on board waste processing equipment. When discharged into the ocean they are readily marine biodegradable as defined by ASTM D7081 specification standards. The coatings technology involves grafting reactive silanes onto the double bonds of the soybean oil (plant oils) and subjecting it to moisture cure. The technology has been scaled to run at an industrial converter and prototype bags have been made [Moisture curable oil and fat compositions and processes for preparing the same U.S. Patent 8,110,036, 2012]

The major R&D and technology commercialization effort underway is building an industrial soybean based

biorefinery producing value added industrial products in Michigan in cooperation with Zeeland Farm Services **(**www.zfsinc.com**).** ZFS is Michigan's largest soybean processor servicing about 2500 Michigan farmers and processing 26,000 bushels of soybean (1.56 million pounds) per day - representing 99% of the soybeans grown in the State. Currently they produce two products namely soybean meal used as animal feed, and oil which is used in food applications. Diversifying the product base with higher value industrial products provides more economic stability and job creation to the Michigan economy. We developed an ozonolysis technology platform to convert the fatty acid methyl esters derived from soybean oil to C-9 diesters and C-9, C-7 monoesters which have industrial applications (see earlier reports). The plant oils are being converted into biobased polyols which is used in making flexible polyurethanes for automotive and industrial applications.



The soymeal residue remaining after removing the oil by solvent extraction is rich in proteins and carbohydrates. We are developing technology to make rigid polyurethane foams. The attached figure shows samples: A is reference formulation with no soy polyol; B contains 25% and C contains 50% of soy polyol. Another synthetic strategy being developed is to convert the soy meal to polyurethane building blocks by eliminating or reducing the use of the toxic isocyanate reagent. The hulls are being investigated for creating higher value biobased composites using styrene-butadiene rubber and PLA as the matrix polymer.

The group is also working on developing Interpenetrating Polymer Networks (IPNs) derived from silylated soybean oil and polydimethylsiloxanes; see. J. Applied. Polym. Sci., 2013.

Senior Staff Researchers: Dr. Daniel Graiver (Adjunct Prof, MSU), Ken Farminer (formerly with Dow Corning)

Postdoctoral & Visiting Research Fellows: Dr. Mohan Patil (UICT, India); Dr. Elodie Hablot (Univ. of Strasbourg, France); Dr. Yuya Tachibana (AIST, Japan); Professor Philippe Dubois (Univ of Mons, Belgium); Professor Y. Z. Wang (Sichuan University, China), Dr. Jean Marie (Ben) Raquez (Univ of Mons, Belgium),

Graduate students: graduated 16 Ph.D and 23 Master's students – Currently 8 graduate students; Siva Chalasani, Chetan Tambe; Hugh McDonald ; Atishi Bali; Sudhanwa Dewesthale, Yanje Zhao, Jeff Schneider, Samenah Rahimi + 5 undergraduate students

Solid State Ionic Transport for Energy Conversion, Energy Storage and Catalysis

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The Nicholas Research Group is dedicated to understanding and utilizing the interplay between stress, microstructure, and materials properties to improve the performance of chemical-to-electrical energy conversion and storage devices (fuel cells, chemical separators, pseudo-capacitors, batteries, etc.) and environmentally-aware devices (electro-chromic coatings, chemical sensors, and chemical actuators). Presently we are focused on a) mechano-chemical coupling in electro-chemically active materials, and b) Solid Oxide Fuel Cell (SOFC) nano-composite electrode performance modeling and micro-structural optimization.

Mechano-chemical coupling in electro-chemically active materials: The Nicholas group has developed a new, electrode-free curvature relaxation (κR) technique to measure the oxygen surface exchange coefficients ($\tilde{k}$'s) of mechano-chemical active materials (i.e. materials where composition changes induce lattice strain). This completely new technique allows $\tilde{k}$ to be measured *in situ*, under actual catalytic converter/SOFC/oxygen sensor operating conditions, without the need for stress-state/film nonstoichiometry altering electrodes [1]. Further, this technique is applicable to both thin film [1] and thick film [2] coatings, and can be used to understand ionic transport and defect equilibria in solid oxide fuel cell electrodes, water-filtration catalysts, solar-energy conversion catalysts, water-splitting catalysts, thermo-electric materials, fuel conversion catalysts, dielectrics, batteries, corrosion-protection coatings, transparent conducting oxide coatings, etc. As shown in Figure 1, by monitoring the curvature response of a mechano-chemically active film | inert substrate bilayer reacting to a sudden oxygen partial pressure change, we have, for the first time, measured $La_{0.6}Sr_{0.4}CoO_{3-x}$ (LSF) thin film oxygen surface exchange coefficients under precisely measured stress states (ranging from 50-100 MPa between 525 and 475°C). Further, these relatively low-stress thin-film $\tilde{k}$'s are the first to be consistent with low-temperature extrapolations of bulk sample measurements; suggesting that either film stress or electrode effects are responsible for the five order of magnitude difference in $\tilde{k}$ observed in Figure 1.

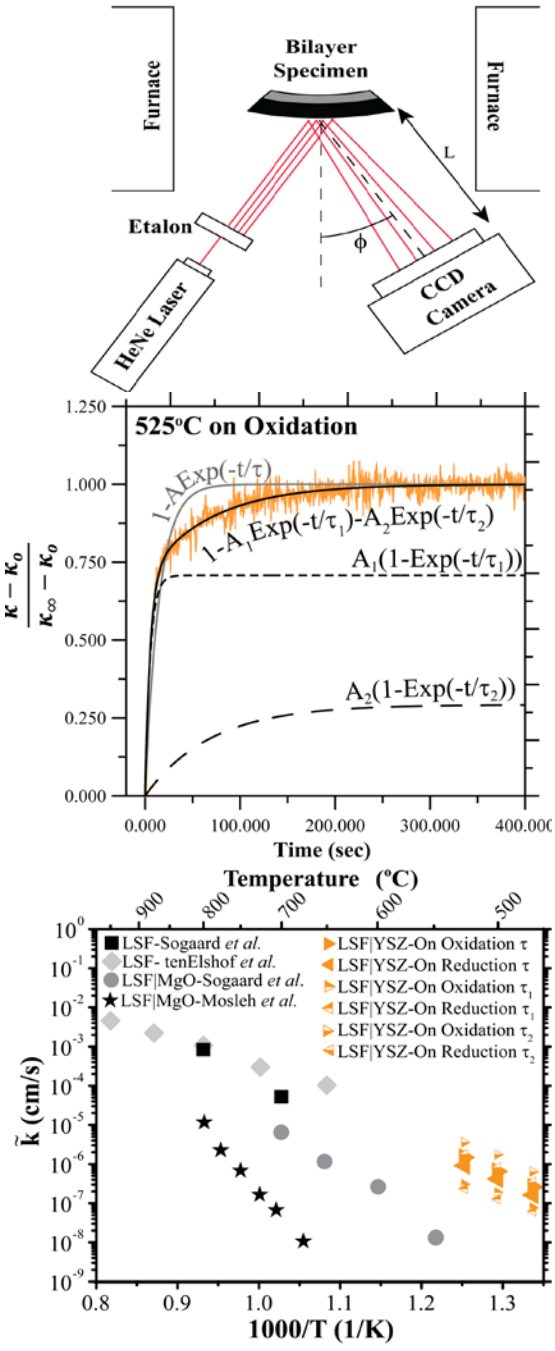

Figure 1. *Schematic of the κR setup (top), fitted κR data (middle), and a comparison of κR-measured $\tilde{k}$'s (orange triangles) to bulk (■◆) and thin film (●★) literature $\tilde{k}$'s.*

Nano-composite SOFC Electrode Micro-structural Optimization and Performance Modeling: Nano-composite SOFC electrodes such as those shown in Figure 2 result in high performance (i.e. low polarization resistance, R_P) because their infiltrated mixed ionic electronic conducting (MIEC) nano-catalyst particles provide multiple sites for oxygen incorporation, and their porous, micron-sized ionic conducting scaffold particles provide high mobility oxygen pathways to the SOFC electrolyte. The Nicholas Group has become the recognized world leader in the production, modeling, and design of SOFC electrodes by developing the world's most highly cited nano-composite SOFC cathode model [3-5] and posting an online SIMPLE model calculator at https://www.egr.msu.edu/nicholasgroup/simple.php to provide real-time nano-composite cathode (NCC) performance predictions. We have also been the first in to discover how to tailor the size of the MIEC infiltrate particle size from 20 to 60 nm [6]. This has allowed us to achieve a R_P of 0.1 Ωcm^2 at the record low SOFC operating temperature of 540°C [6, 7].

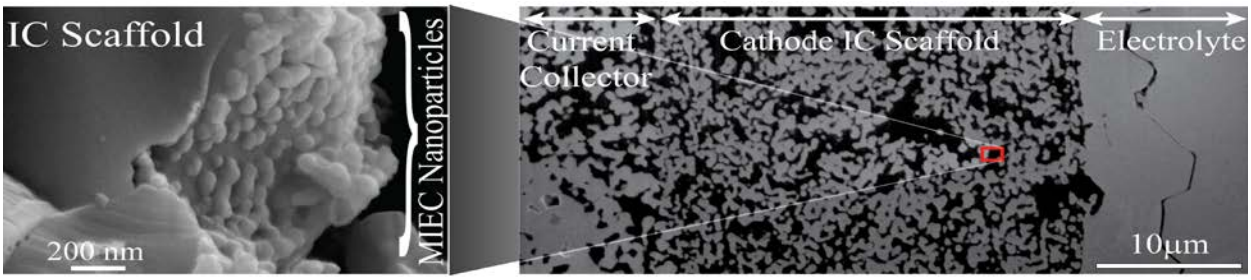

Figure 2. *Scanning electron microscope (SEM) fracture surface image of an infiltrated* $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}\ (LSCF) - Ce_{0.9}Gd_{0.1}O_{1.95}(GDC)$ *NCC from Nicholas et al.[4] (left), and a 2D focused ion beam-scanning electron microscope (FIB-SEM) serial section showing the microstructure of the* $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ *current collector, the GDC scaffold, and the GDC electrolyte (right).*

Group Members

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PhD Students: Qing Yang, Theodore Burye, Tridip Das, Vasiliy Sharikov-Bass
Undergraduate Researcher: Hongjie Tang

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3 Shah, M., Nicholas, J.D. and Barnett, S.A. Prediction of Infiltrated Solid Oxide Fuel Cell Cathode Polarization Resistance using Simple Models. ***Electrochemistry Communications***, 2009, 11(1), 2-5.

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7 Burye, T.E. and Nicholas, J.D. Tailoring the Size of Cobaltite Solid Oxide Fuel Cell Cathode Infiltrate Particles II: The Effect of Precursor Gel Decomposition Catalysts. ***Journal of Power Sources***, 2014, In Preparation.

Nanoscale approach to production of fuels and materials

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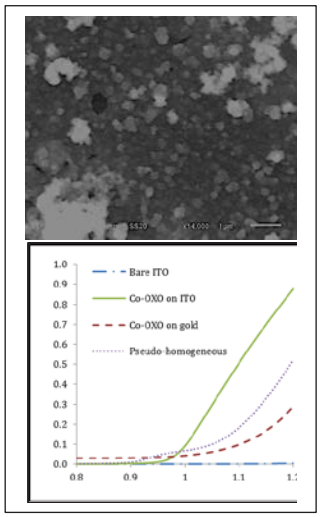
Introduction: There is a critical need to switch to renewable materials as the primary feedstock for the production of fuels and chemicals.[1,2] This need remains, in spite of new US sources of crude oil made possible by recent discoveries and significant improvements in oil and natural gas extraction techniques. Fulfilling this need requires biorefineries with the capabilities to handle a variety of raw materials. Our lab focuses on nanoscale and biomimetic approaches to develop sustainable routes to the production of fuels and chemicals. Our research strives to achieve four technological goals: reaction specificity to enable each transformation to be tailored not only to the raw biomaterial of interest, but also to the target intermediate or final product; heterogeneous catalysis to ensure precise control of reactions under mild conditions; robustness and catalyst recyclability to enable transformations based on green chemistry; and generic protocols that promote adaptation to other target feedstock and products. Two on-going projects that support this philosophy are briefly described below.

Project 1. Synthesis and assessment of biomimetic catalysts for water oxidation to produce hydrogen
Sponsor: US Army ERDC, Champaign, IL
We have synthesized a structural mimic of the natural oxygen-evolving center to obtain a water oxidation catalyst (WOC) for hydrogen production. The cobalt(III) OXO cubane WOC was synthesized *ex-situ*, and its structure and composition characterized by Fourier transform-infrared spectroscopy (FTIR), surface FTIR, scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDS). We immobilized the catalyst on indium tin oxide (ITO) by electrochemical deposition to promote recycling, and the complex was characterized by FTIR and SEM to ensure successful attachment to the substrate. We used cyclic voltammetry (CV) to assess the functionality, stability, and recyclability of the anchored catalyst in an electrolyte solution of 0.1M PBS at pH = 7.0. For comparison, we also assessed the functionality of the same catalyst immobilized on a gold electrode, the catalyst in a pseudo-homogeneous system, and a bare ITO electrode in solution with no catalysts.

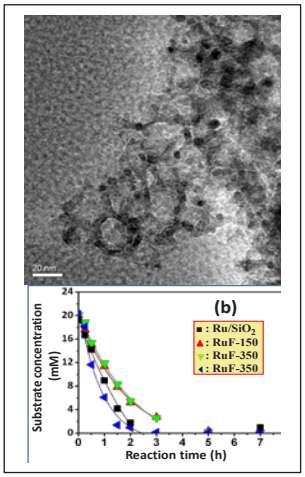


The results provide clear evidence that the catalyst can be successfully immobilized on ITO, and that it functions in the same manner as it does in solution.[3] The study also showed that, in terms of populating a conductive surface with a catalyst, the current density profile for the deposition of a catalyst synthesized *ex situ* is the same as that of a classical heterogeneous catalyst during *in situ* synthesis. This study has demonstrated that *ex situ* synthesis and electrochemical deposition can be an effective route to functional heterogeneous Co-based catalysts. We believe the separation of catalyst synthesis and immobilization into separate independently controllable functions has the potential to enable a more systematic approach to optimization of the resulting complex. The Co-OXO catalyst used in this study is only one of a large number of cubane-like WOCs that can be anchored to various conductive surfaces by electrochemical deposition. Thus, this work provides one effective pathway for recycling this group of water oxidation catalysts

Project 2: Effects of surface activation strategies on ruthenium nanocatalysts supported on mesoporous silica
Financial support: MEDC.
Supported metallic nanoparticles with well-defined size and shape have excellent potential for use as heterogeneous catalysts that enable sustainable energy production from renewable materials.[4-9] However, conventional methods for preparing supported catalysts often lead to ill-defined

morphologies and uneven distribution of active sites. By contrast, colloidal-based schemes, where nanoparticle synthesis and deposition on support are separated into two sequential events, enable independent control of the morphology and composition of active sites and their deposition on supports, thus allowing more rational assessment of mechanistic aspects at the molecular level.[10-13]

We assessed the effects of three surface activation protocols on the structural and catalytic properties of monodisperse Ru nanoparticles supported on mesoporous silica (MSU-F): gentle thermal oxidation at 150°C, thermal reduction at 350°C, and calcination at 650°C under flowing argon. After each of the activation procedures, the MSU-F support retained its mesoporous structure with no damage to the framework. The supported Ru nanoparticles were also dispersed individually on the support without agglomeration. In addition, the colloidal particles maintained a uniform morphology similar to that of the unsupported Ru nanoparticles prior to treatment. The activity of the supported catalysts was evaluated by the hydrogenation of pyruvic acid to lactic acid in a Parr multi-batch reactor (Model 5000, Parr Instrument Co., Moline, IL) equipped with a coupled magnetic stirring unit. For comparison, the reaction was also run on a commercial Ru/SiO_2 catalyst.



The results showed that thermal oxidation at 150°C does not completely decompose and remove the PVP stabilizer from nanoparticle surfaces; thermal reduction at 350°C was better but left residues on particle surfaces; argon-protected calcination was an excellent surface activation method and resulted in complete removal of the stabilizing agent, a high degree of particle crystallinity, and the best metal dispersion among the three catalysts. All the Ru catalysts prepared for this study had higher reactivities for the aqueous phase hydrogenation of pyruvic acid than a commercial Ru/SiO_2 catalyst. In particular, the reaction rates and TOF obtained with the catalyst activated at 650°C were both more than twice those of the commercial catalyst. The supported Ru nanoparticles activated at 650°C also retained their uniform morphology and metal dispersion during the reaction, demonstrating the potential for catalyst recovery and reuse.

Related Publications

R. Lin, R.G. Freemantle, N.M. Kelly, T.R. Fielitz, S.O. Obare and R.Y. Ofoli. *In-situ* immobilization of palladium nanoparticles in microfluidic reactors and assessment of catalytic reactivity. *Nanotechnology* 21(32): 30265 (2010)

R. Lin, X. Ma, T.R. Fielitz, S.O. Obare and R.Y. Ofoli. Facile hydrogenation of carbon-carbon double bonds using catalytic noble nanoparticles immobilized in microfluidic reactors. *Catalysis Communications* 18: 168-175 (2012).

Xianfeng Ma, Rui Lin, Christopher Beuerle, James E. Jackson, Sherine O. Obare and Robert Y. Ofoli. Effects of surface activation on the structural and catalytic properties of ruthenium nanoparticles supported on mesoporous silica. *Nanotechnology* 25 (4) 045701 (2014).

Hao Yuan, De'Andra L. Newton, Luke A. Seymour, Anja Metz, Donald Cropek, Alvin Holder and Robert Y. Ofoli. Characterization and functional assessment of a cobalt(III)-oxo cubane cluster water oxidation catalyst immobilized on ITO. *Cat. Comm.*, *In review*.

Graduate Students: Rui Lin, Xianfeng Ma, Hao Yuan

Undergraduate Students: John Luzenski, Isaac Wolf.

Collaborators: Gary Blanchard, James Jackson, Dennis Miller, Sherine Obare (W. Michigan Univ.), Alvin Holder (Old Dominion Univ.), Don Cropek (CERL, Urbana-Champaign)

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Multiphase Transport Phenomena Research

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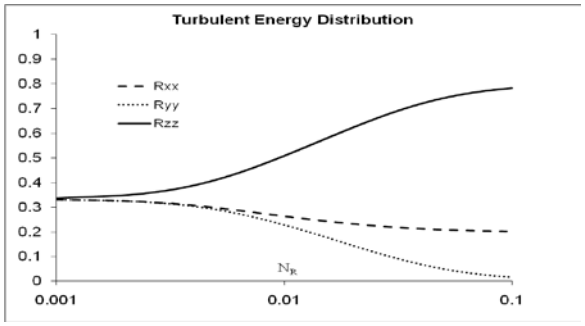
Flows of multiphase fluids are important and occur throughout the chemical, food, mining, petrochemical, pharmaceutical, pulp and paper, and transportation industries. These flows are often unstable and involve large-scale secondary motions that can significantly influence multiphase mixing and separation, interfacial mass and heat transfer, and multiphase reactions.

Professor Petty and his colleagues are interested in research related to the further development and experimental validation of next generation multiphase transport phenomena models and to the further development of novel computational methods for rapid analysis and design of processes with an emphasis on safety. This technical brief summarizes a few ongoing projects.

1.) Universal Realizable Anisotropic Prestress (URAPS) Closure for the Normalized Reynolds Stress

Sponsor: NSF/IUCRC (2004-2011); NSF (pending)
Collaborator: André Bénard (Mechanical Engineering, MSU)

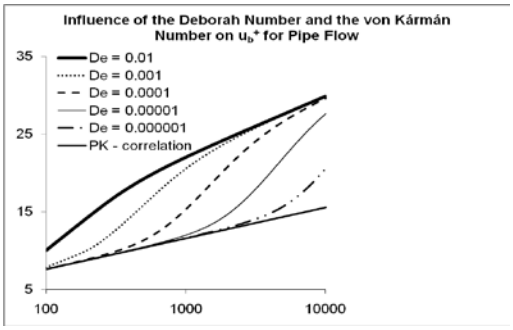
The solution of the Reynolds-Averaged Navier-Stokes (RANS) equation is the only viable means for simulating high Reynolds number flows typically encountered in engineering practice. The use of such an approach is impeded by the lack of practical and accurate turbulence closure models. While numerous closure strategies are presented in the literature, MSU research is based on developing an explicit, realizable, algebraic closure for the Reynolds stress. As illustrated by the figure below, the URAPS theory predicts the observed distribution of turbulent kinetic energy among the three components of the velocity in simple mean shear flows. The new turbulent closure model is presently being used to analyze atmospheric scintillations induced by local gradients in the Coriolis acceleration. The relationship between this phenomenon and bird migration may provide an explanation of a longstanding question in biology: How do birds navigate over global scales?



2.) Turbulent Drag Reduction by High Molecular Weight Polymers

Sponsor: NSF/IUCRC (2004-2011); industry (pending)
Collaborator: André Bénard (Mechanical Engineering, MSU)

The mean velocity and pressure fields for turbulent flows of constant property viscoelastic fluids are governed by the continuity equation and the Reynolds averaged Cauchy (RAC-) equation. The RAC-equation is an exact, unclosed equation for the mean velocity. Closure requires a model for the mean Cauchy stress and for the Reynolds stress. In this research, a recently developed closure for the normalized Reynolds (NR-) stress for turbulent flows of viscous fluids is extended to turbulent flows of viscoelastic fluids. As illustrated in the figure below, the new theory predicts the influence of polymer additives on the NR-stress in fully-developed channel flows.



3.) Cross Flow Filtration Hydrocyclone for Liquid/Liquid Separation

Sponsor: NSF/IUCRC (2004-2011); NSF PIRE (current); DOE and industry (pending)
Collaborators: George Chase (Chemical Engineering, UAkron), Ram Mohan (Mechanical Engineering, UTulsa), André Bénard (Mechanical Engineering, MSU) and Volodymyr Tarabara (Environmental Engineering, MSU)

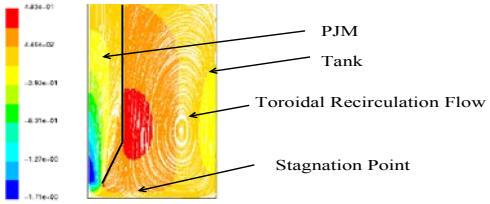
A cross flow filtration hydrocyclone (CFFH) combines the desirable attributes of a vortex separator and a filter. By selecting a hydrophilic filter medium, a CFFH clarifier has the potential to produce a filtrate phase with a low concentration of a dispersed organic phase in a single stage. The CFFH concept may provide a practical means to mitigate the following three problems associated with current hydrocyclone clarifiers: 1) the loss of separation performance due to core flow reversal; 2) the loss of separation performance due to entrained particles in the sidewall boundary layer; and, 3) the loss of separation performance due to turndown. The third feature may be the most significant inasmuch as the CFFH environment provides a self-regulating means to reduce the local filtrate flux across the sidewall filter. The CFFH concept for produced water can be extended to crude oil dehydration, to liquid/liquid separation of concentrated phases encountered in liquid/liquid extraction

applications, and to downhole and subsea separation of oil and water. The objective of current research is to develop a prototype oil/water separator for field testing.

4.) Multiphase Modeling

Sponsor: NSF/IUCRC (2004-2011); NSF (pending)
Collaborators: André Bénard (Mechanical Engineering, MSU)

Particle-laden flows are widely encountered in the oil and gas industry. An accurate description of particle transport in turbulent flows is of great importance for predicting fouling of various equipment as well as erosion of pipe walls. As illustrated by the jet-pulsed mixer shown below, deposition of particles on the walls is influenced significantly by streamlines curvature of the flow field.

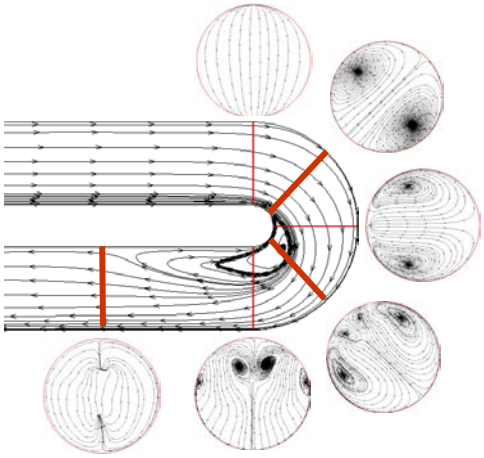


Path lines colored by axial velocity (m/s) at 5 seconds into Cycle 4 (suction phase). Note the toroidal secondary flows within the PJM as well as in the tank.

For dilute suspensions, particle deposition onto a surface can be estimated by using a Lagrangian tracking method. The relative motion between a dispersed particle and the continuous phase can be computed by a time integration of an appropriate force balance on the particle. A discrete particle force balance accounts for turbulent fluctuations by including an anisotropic *fluctuating* force in the particle equation-of-motion. A critical step in this approach is the prediction of the turbulent intensities (i.e., normal components of the Reynolds stress) by using an anisotropic closure for the Reynolds stress, such as the URAPS closure mentioned above. For flows in curved pipes, the RANS-equation together with a second-order closed transport equation for the Reynolds stress (i.e., RSM-closure) for a single phase fluid provides a means to predict the anisotropic structure of turbulence in complex geometries.

For concentrated (and dilute) suspensions, a mixture model based on the theory of interpenetrating continua can be used to predict the deposition rate of particles onto a surface. This Eulerian-Eulerian approach can be simplified significantly by using an algebraic slip model between phases to predict phase segregation, phase mixing, and phase deposition rates onto solid surfaces. Current research is focused on the development of guidelines on the use of Lagrangian/Eulerian and Eulerian/Eulerian transport models for estimating particle deposition in a turbulent flow field with curved streamlines (esp., curved pipes and/or curved ducts). An RSM-closure and an algebraic anisotropic prestress (URAPS) closure for the normalized Reynolds stress will be used to calculate the anisotropic distribution of turbulent kinetic energy.

The following figure, which was developed by Pusheng Zhang (ME student, PhD MSU 2012), illustrates the flow patterns through an 180^{o} bend with cutouts that show various recirculation patterns at different cross-sections. The turbulence model and the wall functions strongly influence the qualitative accuracy of the simulation.



Selected Publications

"The URAPS closure for the normalized Reynolds stress", Karuna S. Koppula, Satish Muthu, André Bénard, and Charles A. Petty, Physica Scripta, Topical Issue: Turbulence Mixing and Beyond, **Phys. Scr.** T155 (2013) 014052.

"Turbulent Energy Redistribution in Spanwise Rotating Channel Flows", K. S. Koppula, A. Bénard, and C. A. Petty, **Ind. Eng. Chem. Res.**, **50** (15), 8905-8916, 2011.

"The URAPS Closure for the Normalized Reynolds Stress", C. A. Petty, K.S. Koppula, S. Muthu, A. Bénard, **Proceedings of the Third International Conference on Turbulent Mixing and Beyond,** The Abdus Salam international Centre for Theoretical Physics, Trieste, Italy, 21-28 August 2011.

"Interpenetrating Continua and Multiphase Turbulence", C.A. Petty, S. Muthu, K.S. Koppula, and A. Bénard, **Proceedings of 8th International Conference on CFD in Oil & Gas, Metaluurgical and Process industries,** SINTEF/NTNU, Trondheim, Norway, 21-23 July 2011.

"Realizable Algebraic Reynolds Stress Closure", K. S. Koppula, A. Bénard, and C. A. Petty, **Chem. Eng. Sci.**, 64, 4611-4624, 2009.

ChE/MSU Student Collaborators, 2001-2013

Andrew Bowden (undergraduate,2013-2014, Professorial Assistant); YoChan Kim (PhD, 2006); Hemant Kini (MS, 2003); Karuna S. Koppula (PhD, ChE, 2009); Satish Muthu (MS, ChE & Math, 2009/2010); Chinh T. Nguyen (MS, ChE, 2001).

Members of NSF I/UCRC, 2004-2011

Ansys, Bechtel, BP, CD-adapco, Chevron, ConocoPhillips, M-I Swaco, Petrobras, Pfizer, National Science Foundation, Department of Interior (MMS), Michigan State University, The University of Tulsa, Central Florida University, The University of Akron.

Materials Simulation for Clean Energy Lab

Yue Qi

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Qi's lab at MSU is focused on **Materials Simulation for Clean Energy (MSCE).** We are interested in materials that deliver clean energy, such as Li-ion batteries, fuel cells and light-weight materials. Utilizing the high performance computer center (HPCC) at MSU and both commercial and homemade software, we are specialized at designing materials from their atomic structures. We screen materials chemistry with First-Principles methods, which solve the fundamental quantum mechanical equations of matter to calculate accurately the properties that are difficult to measure experimentally. We simulate materials behavior that involves millions of atoms using molecular dynamics with faster and accurate atomic interactions (force field). We have successfully integrated nano-scale insights learned from atomic simulations into meso- and micro- structures, governed by continuum theories, to design materials that are important for energy efficient and sustainable transportation industry. Central to these applications is a combination of "top-down" and "bottom-up" multi-scale modeling strategy with an associated experimental/ modeling research program. Therefore, most of our projects have strong collaboration with experimental groups and industry.

Group Members: Christine James, Kwang Jin Kim, Tridip Das, and Dr. Sung-Yup Kim

Currently, the on-going projects include:

1) **Electron and ion transport in complex materials and interphases**

Defect mediated diffusion greatly affects the power performance of battery and fuel cell devices. Using density functional theory (DFT) informed thermodynamics, we can identify the dominant diffusion carriers and their diffusion pathways as a function of voltage, pressure, temperature, and strain. Thus, new materials with dopants can be tested, and operating conditions can be optimized. Currently, we are designing high energy density cathode materials and artificial solid electrolytes interphase (SEI) preventing capacity loss for **Li-ion batteries**. We also design catalyst at desired strain for low temperature **solid oxide fuel cells**.

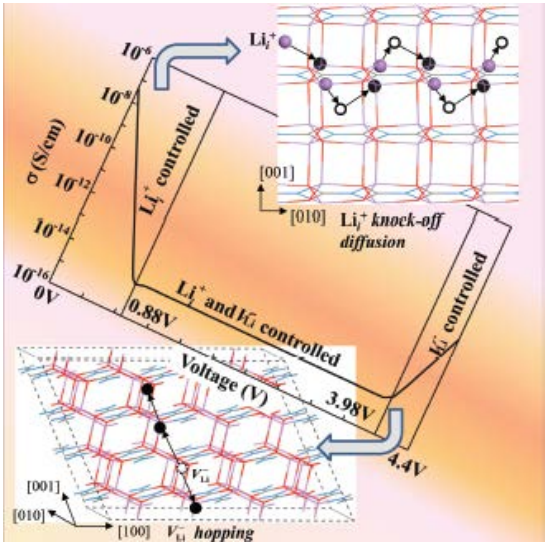

Fig 1: Direct calculation of diffusion carriers and ionic conductivity in Li_2CO_3 as a function of voltage, ***J. Phys. Chem. C****, 2013, 8579, cover article.*

2) Predicting chemical-mechanical degradation in Li-ion batteries

In order to computationally screen and design future battery materials for improved durability, we need to be able to predict failure starting from materials' properties and structures without using non-physical fitting parameters.

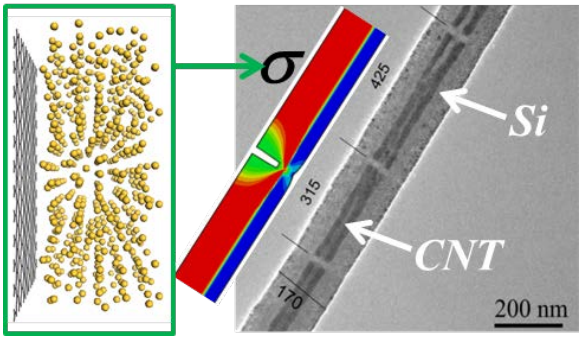

Fig 2, Design of always conducting Si-CNT nanostructure. The weak Si/CNT interface contributes to cracks in Si (as seen in the computed stress field model and by situ-TEM). **ACS Nano** 7, 2717 (2013)

We have used DFT to predict elastic and fracture properties of electrode materials and their interfaces integrated into meso-structures to predict the lithiation-induced stress and failure of composite electrodes. Many of our predictions have been confirmed by *in-situ* experiments. Currently, we are integrating structural evolution and chemical degradations into a battery predictive life model. We are using these methods to develop high capacity and long-lasting nano-structured electrodes.

3) The impact of environment on forming and machining light-weight materials

The environment (air, water, solution, electrolyte) can have a profound impact on deformation processes for light-weight metals (Al, Mg, Ta, Li …) that have a high affinity to oxygen. Similar impacts of the environment are seen for electrode materials. One can further imagine that as the characteristic size of these materials shrinks, surface reactions will contribute more and more, likely changing substantially the mechanical properties of the nano-device. By developing a reactive molecular dynamics method, we demonstrated how oxidation changes the deformation and failure mechanism in a nano-scale device, for example in an Al nano-wire. The nano-scale mechanisms also have a profound impact in large scale manufacturing processing, such as the tribology and surface quality of Al sheets for car panels made with hot forming processes.

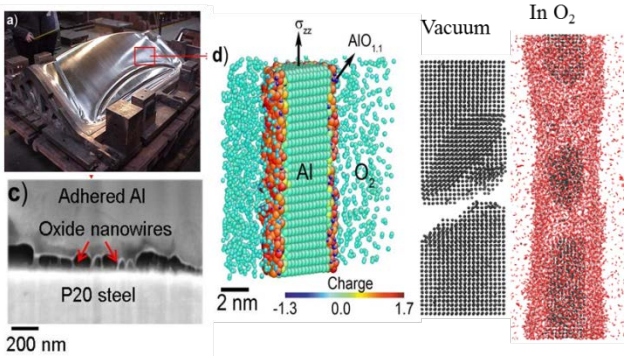

Fig 3, During hot-forming of Al-Mg alloy to make the lift gate of a car, nanowires were formed at adhered interfaces. Reactive molecular dynamics shows that Al nanowire deformation is drastically different in vacuum and O_2. ***Nature Communication*** *(2014).*

We are further addressing environmental effects for a variety of problems. For example: how Mg fractures differently in air and vacuum; why nano-crystalline Al_2O_3 appears to be superplastic when oxygen diffuses into the grain boundaries; under what conditions do diamond-like carbon films become almost frictionless in a H_2 or H_2O environment; and how to ensure an always-passivated surface?

Complex materials for energy and biomedicine

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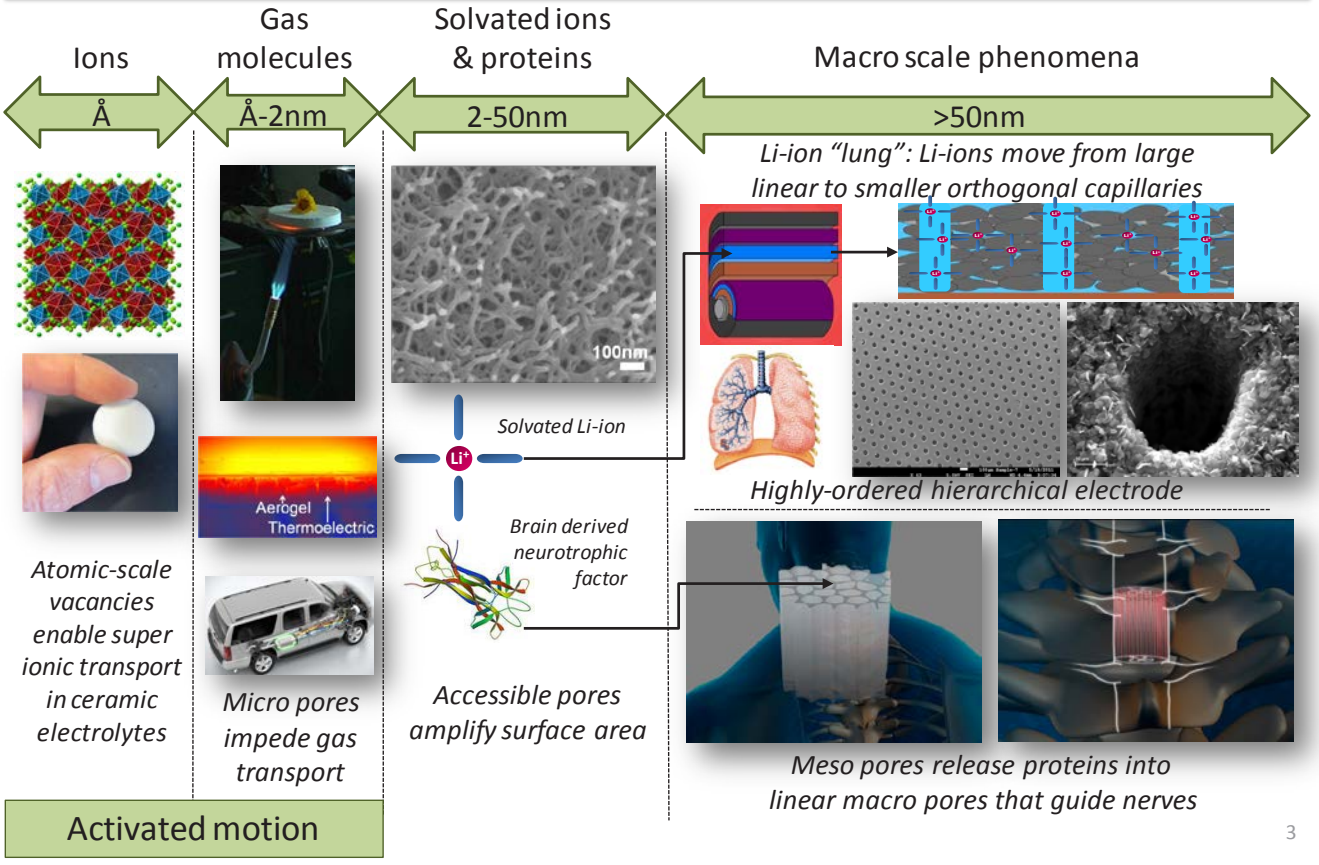
Sakamoto group: Engineering nothing



As a materials scientist and chemical engineer with an interest in synthesis, processing, and functionalization of ceramics and hydrogels, my research is interdisciplinary guided by the fields of energy storage/conversion and biomedicine. I argue that the entire length scale, from atoms to the macro scale and everything in between, must be viewed holistically in the design, synthesis and development of advanced materials and materials technology. Porosity is central to my group's research. In some instances porosity, particularly at the nano scale, enables the solution-based synthesis of complex and often metastable ceramics and hydrogels with unique electrochemical, biological and mechanical properties. In other aspects of my group's research, ironically, porosity is initially used to synthesize complex materials, in gels and powder form, to enhance subsequent densification. Essentially, I have established a career in ceramics and hydrogels focused on studying the interplay between length scales and the absence of mass (porosity). I hope to use this experience to discover and develop new materials and materials technology for energy and biomedicine.

Research Challenges:

1) Minimizing the dependence on fossil fuels and reducing CO_2 emissions are compelling arguments to electrify vehicles (EV). If EVs can improve energy efficiency in the short term and the technology for non-fossil-fuel-based/renewable electrical power generation can be realized in the long term, the benefits to our country's current and future sustainability are clear. However, transitioning to EVs is hindered by the cost and energy density of state of the art batteries. There is a clear need for advanced energy storage/conversion technology to enable vehicle electrification.

2) Approximately 1.2 million Americans have sustained some form of spinal cord injury (SCI), with an estimated annual economic impact of $20 billion. SCI tragically disables its victims and extracts a psychological toll on patients and caregivers. Rehabilitation optimizes use of remaining systems, but there is great need for newer therapies to promote recovery.

Above are the two research challenges that inspire and guide my group's research. As you peruse this website, you will read about my plans to address these topics. Tackling the vehicle electrification challenges involves a two-pronged approach; electrochemistry and thermoelectricity. Establishing a viable therapy for spinal cord injuries involves materials and materials processing to fabricate scaffolds that promote and guide nerve growth.

Group Members

Dr. Y. Park (Postdoctoral fellow from ETRI, South Korea)

Ph. D. Candidates

Dan Lynam, Travis Thompson, Dena Shahriari, Isabel David, Yunsung Kim, Asma Sharafi, Regina Garcia, and Shaubhik Bhattacharjee

Undergraduate Researchers

Tom Heuser, Kayla Felger, and Rachel Schuldt

Abstract

As a materials scientist with an interest in the synthesis, processing, and functionalization of ceramics, my research is interdisciplinary guided by the fields of energy storage/conversion and biomedicine. I argue that the entire length scale, from atoms to the macro scale and everything in between, must be viewed holistically in the design functionalization of advanced materials and materials technology.

Applied Biomolecular Engineering Laboratory (ABEL)

S. Patrick Walton
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http://www.egr.msu.edu/abel/

The ABEL is focused on the analysis and application of nucleic acid-based technologies. Our goals are the understanding of critical biophysical and biochemical parameters involved in these processes and, in turn, the tuning of these parameters to achieve an improved technology. The current foci of the lab fall into two categories: i) novel therapeutics designed through mechanistic analysis of RNA interference (RNAi) (Figures 1-3) and ii) advanced parallel analytical platforms for cellular molecules (Figure 4).

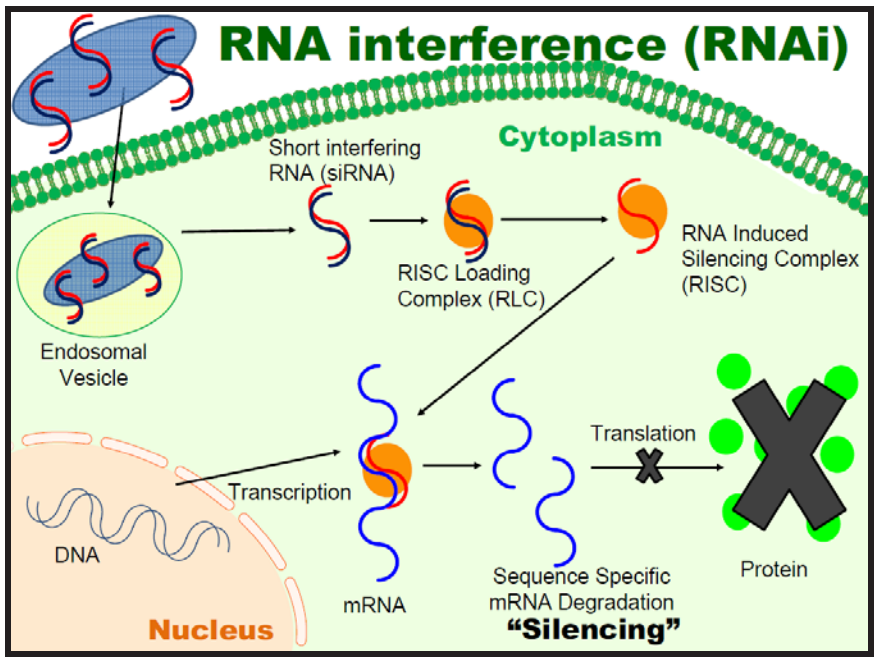

Figure 1: RNA interference. RNA interference is initiated upon successful delivery of an siRNA into cells. Upon release from the delivery vehicle and entry to the cytoplasm, siRNAs are bound by a complex of proteins, Dicer, TRBP, and Ago2, known collectively as the RISC loading complex (RLC). The active RNA Induced Silencing Complex (RISC) then utilizes one strand of the siRNA, the guide strand, to bind the target mRNA by complementarity, leading to sequence specific degradation of the mRNA and a subsequent reduction in protein expression.

Our goal in studying RNAi is to understand the factors that influence the activity of the active molecules in the pathway, short, interfering RNAs (siRNAs). We have shown that two factors, terminal nucleotide classification and terminal hybridization stability (ΔΔG), are predictive of active siRNAs (Figure 2). We are currently studying the interactions of siRNAs with RNAi pathway proteins to determine how these factors result in differential siRNA activities.

Unfortunately, designing a highly-active siRNA does not alone guarantee its function. Prior to initiating silencing, siRNAs must first enter the targeted cells by a

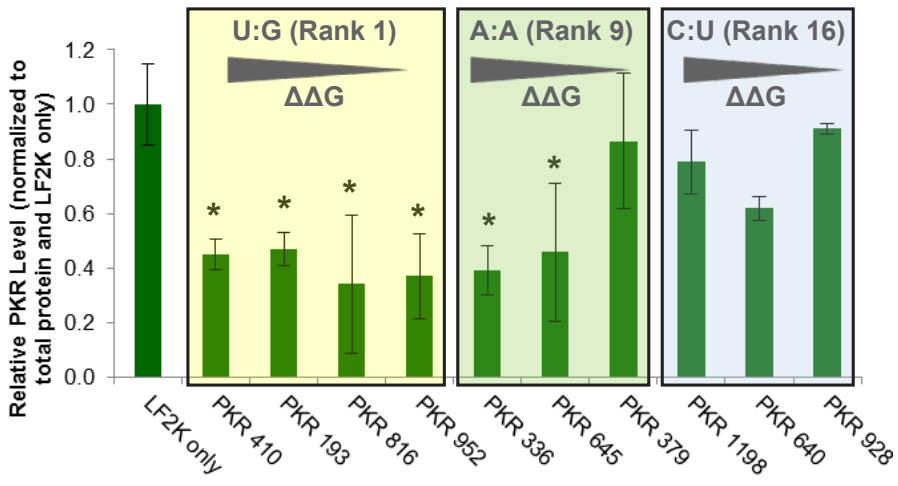

Figure 2: Silencing of PKR by selected siRNAs. HepG2 cells were reverse-transfected with 100 nM of siRNA for 48 h using Lipofectamine 2000 (LF2K). Results are normalized to both total protein level and PKR level of LF2K-only treated control cells (black). siRNAs were grouped by terminal nucleotide classification rank, U:G (yellow), A:A (green), and C:U (blue). Error bars = +/- 1 standard deviation, n = 3. Stars indicate a significant difference ($p < 0.05$) when compared to LF2K only treatment.

mechanism that allows them to be active. The uptake pathways that result in maximal siRNA function are poorly understood. We are currently investigating the properties of siRNA delivery vehicles, in particular silica nanoparticles (NPs), that result in highly efficient delivery and subsequent silencing (Figure 3).

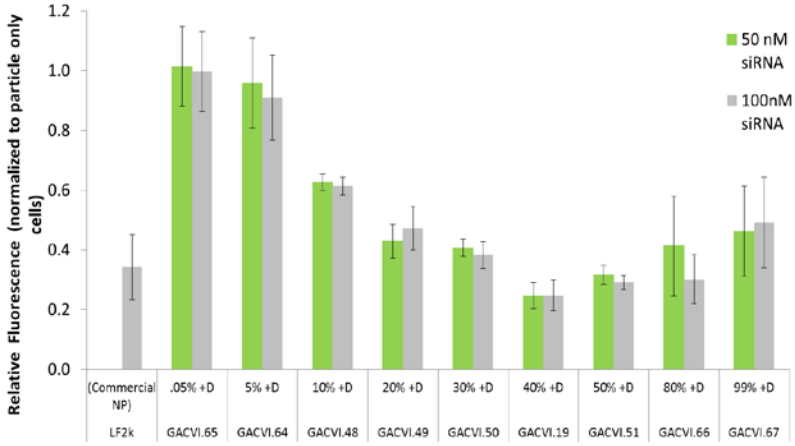

Figure 3: Effect of NP amine content on siRNA activity. While delivery with silica NPs results in silencing by siRNAs (% values indicate increasing amine added to the NP synthesis), none of the NPs effectively delivered plasmid (data not shown). This strongly suggests that different design rules must be applied for siRNA and plasmid delivery vehicles.

Our group also focuses on building new parallel diagnostic tools for analysis of cellular molecules other than nucleic acids. Currently, we are focusing on the analysis of transcription factor (TF) levels. Inappropriate or unregulated expression of TFs has been implicated in many diseases, including cancer, AIDS, and diabetes. Current methods for measurement of TF expression are inadequate for simultaneous measurement of all relevant proteins. We have demonstrated analysis of TFs in parallel (GR, CREB, STAT3, NF-κB, and TBP; Figure 4) by our technique for kinetic responses to multiple stimuli including cytokine (TNF-α) stimulation.

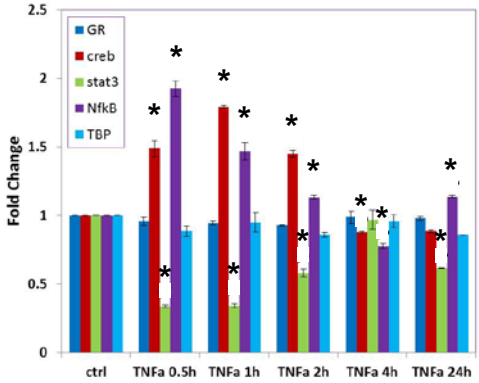

Figure 4: Parallel quantification of TF levels in HepG2 nuclear extracts after TNF-α stimulation. Signals were normalized with respect to an internal standard and then the ratio with respect to control was calculated. (n = 3, * indicates $p < 0.05$).

Acknowledgments:
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Recent Publications:

Malefyt, A.P., Wu, M., Vocelle, D., Kappes, S., Lindeman, S., Chan, C., and **Walton, S.P.** 2014. Improved asymmetry prediction for siRNAs. *FEBS J*. 281(1): 320-330.

Angart, P., Vocelle, D., Chan, C., and Walton, S.P. 2013. Design of siRNA Therapeutics from the Molecular Scale. *Pharmaceuticals*. 6(4): 440-468.

Bilgin, B., Liu, L., Chan, C., and Walton, S.P. 2013. Quantitative, solution-phase profiling of multiple transcription factors in parallel. *Analytical and Bioanalytical Chemistry*. 405(8): 2461-2468.

Cho, H., Wu, M., Bilgin, B., **Walton, S.P.**, Chan, C. 2012. Latest developments in experimental and computational approaches to characterize protein-lipid interactions. *Proteomics*. 12(22): 3273-85.

Group Members

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Rebecca Carlson
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Design and engineering of protein function

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Engineering life is a broad-stated goal of the new generation of biochemical engineers and synthetic biologists. To better accomplish this goal, these engineers pursue the ability to design novel functions rather than rely on a catalog of 'parts' culled from nature**.** Yet proteins, the workhorses of the biological cell and one of the main categories of biological parts, resist simplistic reprogramming. Proteins are wondrously complex biomolecules comprised of thousands of atoms, which fold into tertiary structures necessary for function by balancing competing inter- and intra-molecular forces. Imparting novel and specific functions into proteins is a difficult problem because protein structures are only marginally stable, protein structure-function relationships are not well understood, and many targeted small molecule substrates differ by as little as a single hydroxyl group or a methyl bond. The net result is that efforts to engineer or design new/improved proteins are either empirical in nature or suffer from low success rates, frustrating efforts to rationally and reliably redesign components for cellular life.

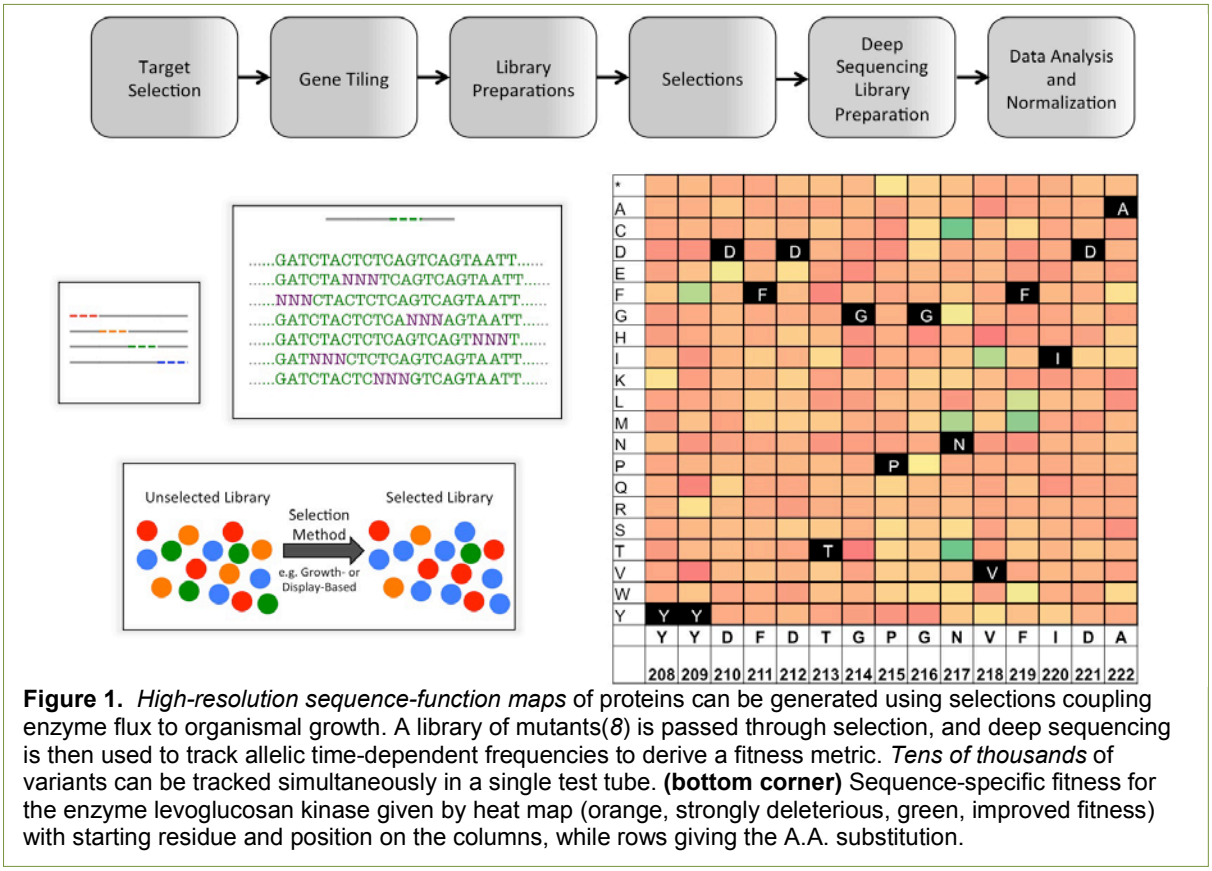

Figure 1. *High-resolution sequence-function maps* of proteins can be generated using selections coupling enzyme flux to organismal growth. A library of mutants(*8*) is passed through selection, and deep sequencing is then used to track allelic time-dependent frequencies to derive a fitness metric. *Tens of thousands* of variants can be tracked simultaneously in a single test tube. **(bottom corner)** Sequence-specific fitness for the enzyme levoglucosan kinase given by heat map (orange, strongly deleterious, green, improved fitness) with starting residue and position on the columns, while rows giving the A.A. substitution.

Our research group overcomes these problems by developing general, powerful technologies to construct proteins on demand. We utilize and improve computational design software to impart nascent function in proteins. To better understand sequence determinants of function, we are pioneering a high-resolution sequence-function mapping method for large proteins and to cover all sorts of protein classes like enzymes and membrane proteins (see **Figure 1**). We have used these methods to design and optimize protein inhibitors that detect and broadly neutralize the influenza virus [1-2]. We are now interested in optimizing proteins for diverse applications like *cancer therapy*, *vaccine design,* and *deconstruction and conversion*

of biomass to next generation fuels and chemicals. Example projects are shown below. Our young lab is supported by multiple competitively awarded grants, including an NSF CAREER Award.

Creating the Next Generation of Biofuels (Funding: NSF)

The conversion of plant biomass to transportation fuels and commodity chemicals can supplant existing routes from petroleum, yet significant inefficiencies occur in the production of the biomass, the deconstruction of biomass to sugars, and the conversion of these sugars to fuels and chemicals. We have initiated several projects where our expertise can help resolve some of these inefficiencies.

Metabolic Engineering. A common biomass conversion strategy involves deconstructing biomass to sugars, which are then fermented to value-added chemicals by microbes implanted with new or restructured metabolic pathways. Most of these routes are naturally occurring and often suffer from poor carbon economy, redox imbalances, and reliance on complicated cofactors. By contrast, we use computation to formulate thermodynamically optimal, high-yield metabolic pathways, which we then construct in living organisms. For example, we are computationally redesigning rate-determining enzymes in the biosynthesis of isoprene and acrylic acid. We are using high resolution sequence-function mapping to optimize a microbial pathway to catabolize woody biomass pyrolysis oil. This is important because this opens a new path to convert renewable biomass. Such top-down engineering of microbial primary metabolism is possible only because of our methods.

Enzyme Engineering. The abundant biomass polymer cellulose is very recalcitrant to deconstruction to its component sugar glucose, and the high cost of this process step is the single largest barrier to economical biofuel production. Cellulases are enzymes that deconstruct cellulose to fermentable sugars. We are improving cellulases by preventing cellulase inactivation by residual lignin in biomass extracts, allowing recycle streams for this homogeneous catalyst.

Improving Antibodies for Cancer Therapy and Vaccines (Funding: NSF, NIH)

Monoclonal antibodies (mAb) are a special class of proteins for use in cancer therapy, inflammation, and other therapeutic areas. For example, the mAb Herceptin targets HER2+ breast cancers, extending life for many patients. We are pioneering several new methods in order to make monoclonal antibodies and antibody mimetics cheap, safe, and specific for their intended target.

Epitope Mapping. We have developed an approach to quickly map the location of where an antibody binds to its target antigen. This method can be used to improve the affinity, specificity, and function of the antibody.

Sequencing Full Antibody Repertoires. When you take the flu vaccine every fall, your immune system rapidly creates an antibody repertoire to the antigenic determinants encoded in the shot. To enable smarter vaccine preparation and identification of unique, effective antibodies, my group is developing techniques to fully sequence a human's antibody portfolio at different time points.

Selected Recent Publications

[1] Whitehead T.A., et al. (2011), "Computational design of proteins targeting the conserved stem region of influenza hemagglutinin", ***Science*** 332(6031):816.
[2] Whitehead T.A. et al. (2012), "Optimization of affinity, specificity, and function of designed influenza inhibitors using deep sequencing", ***Nature Biotechnology*** 30(6):543.

Group Members

Post-Docs: Jim Stapleton
Graduate Students: Emily Detwiler, Carolyn Haarmeyer, Justin Klesmith, Caitlin Kowalsky

Biomimetic and Biocatalytic Solutions to Engineering Challenges

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Dr. Worden's research group uses an interdisciplinary approach that integrates engineering and biological principles. Research is focused in two areas: biomimetic interfaces and microbial catalysis.

Bilayer lipid membranes (BLM) and other biological molecules can be combined with synthetic nanomaterials to create hybrid nanostructured biomimetic interfaces. These biologically inspired interfaces exhibit structural and functional properties well suited for fundamental studies of biological phenomena, as well as development of novel products and processes. In collaboration with Gemma Reguera, Dr. Worden's lab is using biomimetic nanostructures to study the mechanisms of uranium remediation by metal-reducing bacteria including *Geobacter* species, which reductively precipitate water-soluble uranium salts. We are assembling key molecular components of the uranium reductase system in a molecular architecture that mimics *Geobacter's* cell envelope. *Geobacter*'s periplasmic *c*-cytochrome (PpcA) was immobilized onto a self-assembled monolayer of alkanethiols on gold and characterized electrochemically by cyclic voltammetry. As shown in Fig. 1, the rate constant for U(VI) reduction is significantly higher than for Fe(III) reduction, providing insight into how U(VI) may be reduced and precipitated by *Geobacter*. We are now adding additional components of *Geobacter's* electron transfer machinery (e.g., OmcB) to the biomimetic interface to mimic multistep electron transfer among cytochromes and to achieve reductive precipitation of U(VI).

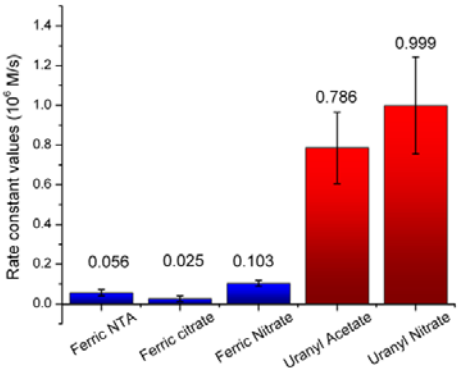

Fig. 1. Rate constants for metal ion reduction by *G. sulfurreducens* PpcA.

Engineered nanomaterials (ENM) can induce toxicity through a variety of mechanisms, several of which involve molecular interactions with cell membranes. Understanding the fundamental mechanisms by which ENM interact with biomembranes may help assess the health risk of ENM exposure and develop new nano-enabled biomedical applications. We have been measuring molecular interactions between ENM and model synthetic BLM that mimic biomembranes. An ENM's ability to reduce resistance of a tethered BLM (tBLM) is being measured using electrochemical impedance spectroscopy. Statistical analysis and hierarchical clustering have shown the method can distinguish between polystyrene nanoparticles (PNP) that are identical except for their surface functional groups (amidine vs. carboxyl) and their size (20 vs 100 nm) (Fig. 2). A planar BLM (pBLM) technique is also being used to explore the molecular mechanisms of ENM interactions with biomembranes and the effects of reactive oxygen species (ROS) and reactive nitrogen species (NOS), such as peroxynitrite, on pBLM integrity (Fig. 3).

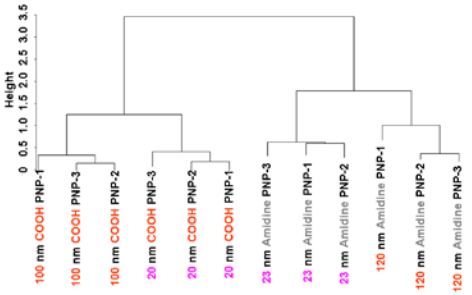

Fig. 2. Dendrogram showing ability of tBLM method to distinguish nanomaterials by their size and surface functional groups.

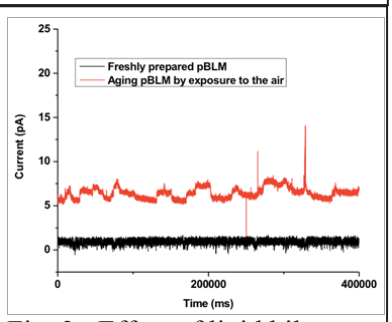

Fig. 3. Effect of lipid bilayer charge on permeability ratio.

In collaboration with Jack Harkema and Norbert Kaminski in the MSU Center for Integrative Toxicology, the potency of polyethylene glycol-coated amorphous silica nanoparticles (SNP) for promoting allergic airway disease was investigated. Co-exposure to SNP during

ovalbumin sensitization caused a dose-dependent increase in allergic airway disease, as evidenced by increasing production of cytokines (e.g., Fig. 4).

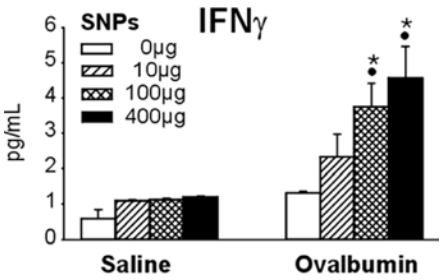

Fig. 4. Bronchoalveolar lavage IFNγ cytokine expression profile for various silica nanoparticles (SNP) exposure levels measured by enzyme-linked immunosorbent assay

Biocatalysis by living cells can be harnessed to produce desired compounds or degrade unwanted chemicals in polluted environments. The Worden lab has developed a novel bioreactor system to produce the biofuel isobutanol (IBT) from H_2, CO_2, and O_2 gases using a *Ralstonia eutropha* strain that was genetically modified in the lab of Anthony Sinskey at MIT. *R. eutropha*'s ability to produce energy-rich products from gaseous feedstocks is being harnessed to produce biofuels while reducing greenhouse gas (CO_2) emission. The use of solar-derived H_2 as an energy source for biofuel production would eliminate the need for expensive biomass hydrolysis. We have developed a novel hollow-fiber bioreactor that delivers H_2 and O_2 to the cells while preventing formation of potentially explosive gas mixtures. The system operates under a control network consisting of an Opto 22-based controller, gas sensors, solenoid valves, mass flow controllers and safety alarms to facilitate safe automated processes. A mathematical model of the reactor has been developed to simulate its performance and enable future scale-up (Fig. 5).

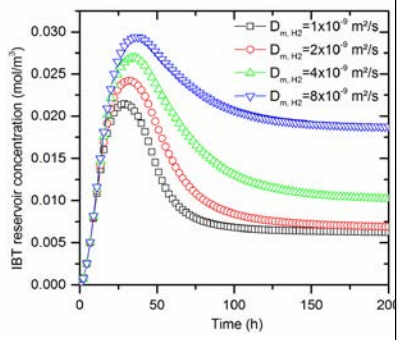

Fig. 5. Effect of H_2 diffusion coefficient in hollow-fiber wall on predicted IBT concentration.

In collaboration with researchers at the Michigan Biotechnology Institute, microbubble (µbubble) sparged bioreactors are being developed to optimize and scale-up gas-intensive fermentations (Fig. 6). The µbubbles' small size (on the order of 50 µm) allows them to achieve extremely high volumetric mass transfer coefficients.


Fig. 6. 300 L MBI reactor retrofitted for µbubble sparging.

Group Members

Visiting Scientist: Serban Peteu; **Graduate Students**: Bhushan Awate, Yangmu Chloe Liu, Ying Liu, Paul Sharpe.

Example Research Publications

1. Liu, Y.; Worden, R. M. "Biomembrane disruption by silica-core nanoparticles: effect of surface functional group measured using a tethered bilayer lipid membrane," Biochimica et Biophysica Acta-Biomembranes 1838, 429-437, (2014).

2. Brandenberger, C.; Rowley, N. L.; Jackson-Humbles, D. N.; Zhang, Q.; Bramble, L. A.; Lewandowski, R. P.; Wagner, J. G.; Chen, W.; Kaplan, B. L.; Kaminski, N. E.; Worden, R. M.; Harkema, J. R. "Engineered silica nanoparticles act as adjuvants to enhance allergic airway disease in mice," Particle and Fibre Toxicology, 10(1), 26, (2013).

3. Negoda, A., Kim, K. J., Liu, Y., Crandall, E. D., and Worden, R. M., "Polystyrene nanoparticle exposure induces ion-selective pores in lipid bilayers," Biochimica et Biophysica Acta - Biomembranes, 1828(9):2215-2222 (2013).

4. Negoda, A.; Liu, Y., Hou, W. C.; Corredor, C.; Moghadam, B. Y.; Musolff, C.; Li, L.; Walker, W.; Westerhoff, P.; Mason, A. J.; Duxbury, P.; Posner, J. D.; Worden, R. M. "Engineered Nanomaterial Interactions with Bilayer Lipid Membranes: A Screening Platform to Assess Nanoparticle Toxicity " International Journal of Biomedical Nanoscience and Nanotechnology 3(1/2), 52-82, (2013).

5. Huang, Y.; Liu, Y.; Hassler, B. L.; Worden, R. M.; Mason, A. J. "A Protein-Based Electrochemical Biosensor Array Platform for Integrated Microsystems," Biomedical Circuits and Systems, IEEE Transactions on 7(1), 43-51, (2013).

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