Greetings from the Department of Chemical Engineering and Materials Science (ChEMS) at Michigan State University! We have had a very busy and productive year and I would like to share with you some of the exciting highlights and achievements of our faculty, staff, and students.

**NEW FACULTY**
With programs in both chemical engineering and materials science and engineering, research in ChEMS spans a remarkably wide range of topics, including the metallurgy of lightweight alloys, materials for energy storage and conversion, polymers and composites for structural and functional applications, new materials and nanotechnology, bio-based and biorenewable products, and biomedicine. This expertise and range of interests have been further enhanced this past year as we have again welcomed new faculty to the department:

- **Ray Boeman** joined us as a Research Professor and Associate Director of the Vehicle Technology Area Scale-Up Facility for the Institute for Advanced Composites Manufacturing Innovation (IACMI) in Corktown, Detroit.

- **Robert Ferrier**, a postdoctoral fellow at The University of Texas at Austin, joined us as an Assistant Professor in the fall. Dr. Ferrier brings synthesis and chemistry expertise to our growing polymers and composites program.

**PARTNERSHIPS**
In addition to research activities in ChEMS, our faculty are further strengthening and enhancing collaborative activities on campus and across the globe. For example:

- Four of our faculty have joint appointments with the [Fraunhofer Center for Diamond and Coating Technologies](https://www.fraunhofer.org), and several of our graduate students are involved in research in the Fraunhofer facility in the Engineering Research part of campus.

- A cohort of our faculty working in the biomedical arena continue to interface and collaborate with scientists in the [Institute for Quantitative Health Science, and Engineering](https://www.ihse.msu.edu).

- The new dual-PhD degree programs with the [Institute of Chemical Technology](https://www.che.mtu.edu/ict), Mumbai, and the [Indian Institute of Technology](https://www.iitm.ac.in), Madras have brought students from these institutions to MSU for research.

**FACULTY AWARDS & HONORS**
Our faculty members continue to excel in their work, and their success in doing so is reflected in the numerous prestigious awards and honors they have received this past year. Some highlights include:

- **Yue Qi** became the first associate dean for inclusion and diversity in the College of Engineering;

- **Jason Nicholas** is among the 12 current fellows in the Academy for Global Engagement (AGE);

- **Thomas Bieler** was elected a Fellow of The Minerals, Metals and Materials Society (TMS);

- **Shiwang Cheng** was awarded the Peter Debye Prize for Young Investigators in Dielectric Research by the International Dielectric Society;
The MSU Innovation of the Year Award was presented to Donald Morelli for his work in thermoelectric technologies;

Lawrence Drzal received the MSU Innovation Center Technology Transfer Achievement Award for his work in graphene and composite materials;

Alexandra Zevalkink was the recipient of the 2018 Withrow Teaching Excellence Award.

In Memoriam
On a sad note, the Department, College, and University suffered a major loss with the passing of Professor Kris Berglund. Kris, who was on the faculty at MSU for 35 years and advised countless graduate and undergraduate students, was an expert in alternative uses of agricultural and forest materials and a pioneer in fermentation and distilled beverage technology. His knowledge, enthusiasm, wit, and gentle personality will be greatly missed.

Student Achievements
Students, of course, are the lifeblood of the academic enterprise, and once again this year several of them at both the undergraduate and graduate levels have received accolades for their outstanding work, including:

Evan Draplin and James Wortman, ChEMS department seniors, both won national awards in the individual category in the 2018 Annual AIChE competition;

William Killian, a ChEMS PhD student in Carl Lira’s group, was recognized with the 2nd place award for student presentations at the 2018 Midwest Thermodynamics and Statistical Mechanics Conference.

Killian’s talk presented a new technique developed with PhD student Aseel Bala for quantifying the O-H band in spectroscopy and demonstrated quantification of the entire O-H band for the first time;

Students in Kris Berglund’s Brewing and Distilled Beverage Technology course, led by graduate student Nicole Shriner, won a bronze medal for their “Toucan Sam’s Milk Stout” at the U.S. Open College Beer Competition.

Distinguished Alumni
Finally, our alumni continue to make us proud of our programs and their graduates. A few highlights for this year include:

Jadel Hughes-Davis, a 2017 ChEMS graduate, currently working at General Motors, is writing a children’s book to boost girls confidence to explore a future in a STEM field.

In May, the 2019 Red Cedar Circle Distinguished Alumni Award will be presented to outstanding ChEMS PhD alumnus Kathleen Fish, Chief Research, Development, and Innovation Office at the Procter & Gamble Company.

While we leave the last year behind, the doors of tomorrow beckon us toward the future, and we are excited about the possibilities and opportunities that we will encounter. I hope you will enjoy reading the research highlights contained in this brochure, and I look forward to updating you on our progress in the future.

Donald Morelli
Chairperson and Professor
The Michigan State University Department of Chemical Engineering and Materials Science (ChEMS) has vibrant research programs in both chemical engineering and materials science and engineering.

- **OUTSTANDING FACULTY**

Among our 30 faculty members, we have:

- Four NSF CAREER Award winners
- Three University Distinguished Professors
- Five MSU Distinguished Faculty/William J. Beal Outstanding Faculty winners
- Six MSU Teacher-Scholar Award winners
- Four Withrow Distinguished Scholar Award winners
- Three Withrow Junior Scholar Awards winners
- Nine Withrow Teaching Excellence Award winners (several have won multiple times)
- The first Excellence in Diversity Award winner

Also included among the faculty ranks are multiple society Fellows:

- National Academy of Inventors
- American Institute of Chemical Engineers
- American Institute of Chemists
- American Institute for Medical and Biological Engineering
- Society of Plastics Engineers
- ASTM International
- American Ceramic Society
- ASM International

Many faculty members have also received national and international recognition for their academic and research achievements.

- **DEPARTMENT ACHIEVEMENTS**

- Total research expenditures were about $13.5 million in FY 2018
- Approximately 120 refereed publications and 8 patents per year
- Total undergraduate student population to nearly 675 (as of Fall 2018)
- Graduate enrollments of more than 100 students, including 95 PhD and 13 MS (as of Fall 2018)

- **RESEARCH CENTERS**

The department operates a number of major research centers, including:

- The Composite Materials and Structures Center
- Department of Energy (DOE)-funded Institute for Advanced Composites Manufacturing Innovation (IACMI)

- **PARTNERSHIPS**

In today’s world, partnerships with industry and global institutions play an ever-increasing role in research and innovation, and our department has been active in seeking and developing these connections.
The Institute for Advanced Composites Manufacturing (IACMI) is rolling into its fifth year and includes a host of industry partners working closely with ChEMS faculty and on lightweight polymer composites for vehicles at the prototyping facility in the Corktown area of Detroit.

On the international front, we have established two new dual-PhD degree programs: one with the Institute of Chemical Technology, Mumbai, and a second with the Indian Institute of Technology, Madras. Industrial and international programs such as these further broaden the experiences of our students and help prepare them for tomorrow’s world.

**MISSION & GOALS**

The Department of Chemical Engineering and Materials Science pursues a mission of growing national recognition as a center of excellence in research, teaching, and service. In support of this mission the department has four goals:

- Attaining leadership and excellence in conducting nationally recognized, innovative, and cutting-edge research
- Recruiting high-performing students and delivering modern, high-quality graduate and undergraduate programs that produce top-notch graduates serving the needs of industry, government, and academia
- Providing outstanding professional and outreach services
- Cultivating support from the private sector, state, and federal sources, and providing stewardship in support of research, instruction, and service.

**STRATEGIC INITIATIVES**

As we look to the future, the department has established strategic initiatives to ensure our continued ascension in productivity and prominence:

- Continued faculty growth to complement and supplement our research priorities
- Recruitment of a growing pool of high-quality PhD students
- Increased recruitment of highly qualified undergraduate students, and matriculation of bachelor’s degree graduates that are prepared to solve the problems of both today and tomorrow
- Enhanced support of endowments for fellowships, scholarships, professorships, and the discretionary excellence fund.
**RESEARCH INTERESTS**

Grain boundaries, crystallographic texture, crystal plasticity, microstructure evolution, damage nucleation

**LAB(S)/GROUP(S)**

Solder Research Group, Niobium Research Group, Titanium Research Group

**WEBSITE**

http://www.egr.msu.edu/~bieler/

**SPECIAL EQUIPMENT AVAILABLE**

Orientation imaging microscopy™ (OIM, aka EBSP mapping) is used to quantitatively examine the relationships between microstructure and localized deformation processes that ultimately control heterogeneous deformation, recovery and recrystallization mechanisms, and damage nucleation. Combined with other experimental and analytical tools, such as 3D x-ray diffraction, new insights on formability and damage nucleation mechanisms are found. This will enable development of optimal material processing strategies to gain more predictable and reliable properties. Four examples follow:

**Damage nucleation in titanium and titanium alloys.** Figure 1 shows computational deformation of a bicrystal that is oriented to enable slip transfer from a prism slip system (blue grain) that is perfectly aligned with a pyramidal slip system (red grain). While uniaxial tension is applied to the bicrystal, the restrictions of the anisotropic slip systems causes the stress state to deviate significantly from uniaxial tension. The left grain sees a stress state closer to uniaxial tension and the right crystal is closer to biaxial tension. Normal crystal plasticity models allow slip transfer across grain boundaries by all slip systems. When slip is restricted on all except the one that is well-aligned, the magnitude of the stress is actually reduced (color scale on the right) and the shape of the stress tensor changes (glyphs). This provides evidence that more physically realistic deformation at grain boundaries can be installed into larger scale simulations.

**CURRENT RESEARCH**

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**DOE/BES SISGR Grant, with M.A. Crimp, C.J. Boehlert, and P. Eisenlohr (MSU).**

**Microstructural impact on the machinability of titanium alloys.** Machining of titanium is often the most expensive part of the process to make titanium parts, due to excessive tool wear. This grant will reveal underlying mechanisms that cause tool wear, and how tool-work piece interactions affect the properties of the machined surface. Relationships between microstructural evolution in the titanium work piece, the chip, and wear of the tool will be quantified. Recent results prove that the high tool wear rates with high speed machining are correlate with high temperatures that cause transformation to a softer (beta) phase that attacks the tool more severely. NSF CMMI MEP, with P. Kwon (ME)

**Microstructural evolution during thermo-mechanical cycling in lead-free solder joints.** Combined electromigration and thermal cycling is a normal aspect of functioning electronics. Solder joints were examined with just electromigration, just thermal cycling, and combined electromigration and thermal cycling. This particular joint in

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**FIGURE 1.** Simulation of internal strain history in two differently oriented grains during cooling of CP Ti.
Figure 2 completely changed its crystal orientation during this process; a twinned orientation grew into the original grains to alter the orientations within the joint. Much of the accelerated testing done by industry to validate products does not consider coupled phenomena that ultimately leads to damage, and this example shows behavior that is not observed with either kind of validation test strategy alone.

With visiting PhD student Yong Zuo (advised by Fu Guo at Beijing University of Technology)

**Characterization and modeling of deformation of defects in high-purity Nb for particle accelerators.** High-purity Nb is used for radio frequency superconducting particle accelerator cavities (the structures that accelerate particles), but the fundamental physics of deformation and surface modification processes (which includes strong acid etching) and microstructure evolution are not well understood. Figure 3 illustrates how preferential magnetic flux penetration (red arrow) occurs along low angle grain boundaries, and may result from hydride precipitates that form during cooling. Hydrides leave scars when they dissolve upon reheating to room temperature. The hydride scars are misoriented by as much as 10° from the surrounding material, indicating that significant local straining occurred.

DOE/OHEP, with P. Eisenlohr and N.T. Wright (MSU), F. Pourboghrat (OSU), K. Solanki (ASU), and C. Compton (FRIB).

**Figure 3.** Upon cooling Nb to about 8K, magneto optical imaging reveals preferential flux penetration sites (red arrow, upper left image), which is correlated with low angle boundaries. Niobium hydrides form on the surface, and dissolve upon heating, but they leave scars revealed in an orientation map. It is unknown how they affect magnetic flux penetration.

**RECENT PUBLICATIONS**


Professor Carl Boehlert
boehlert@egr.msu.edu | 517.353.3703 | 428 S. Shaw Lane, Room 3529

- **RESEARCH INTERESTS**
  Physical metallurgy

- **LAB LOCATION**
  Engineering Bldg., 428 S. Shaw Lane, Room B338

- **WEBSITE**
  www.egr.msu.edu/~boehlert/GROUP

- **SPECIAL EQUIPMENT AVAILABLE**
  Thermomechanical testing machine

- **GROUP MEMBERS**
  PhD STUDENTS: Aida Amroussia, JoAnn Ballor, David Hernandez Escobar, Geeta Kumari, Uchechi Okeke.

- **PATENT**

- **CURRENT RESEARCH**
  The research group of Materials Science and Engineering Professor Carl Boehlert 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 components used in commercial applications. In situ testing methods have been developed which allow for characterizing the evolution of surface features during deformation in order to understand the deformation mechanisms. Boehlert’s group also researches severe plastic deformation processing effects on nanostructured zinc-magnesium hybrids targeted for biomedical absorbable implant applications, where the zinc-magnesium components are intended to degrade safely in the body after completing their function.

Below provides a brief description of one of the research programs in Boehlert’s group:

The search for absorbable metal systems, showing a good combination of mechanical properties, uniform corrosion behavior, and biocompatibility, remains to be an open challenge. Magnesium (Mg) and zinc (Zn) have been identified as the most suitable elements to explore the next generation of biodegradable medical implant devices. However, none of the current Zn-Mg alloys is yet able to simultaneously meet those three benchmarks: adequate mechanical performance (i.e., tensile strength > 300 MPa, elongation-to-failure (εf) > 20%) for structural support, biocompatibility to prevent an inflammatory response, and a corrosion rate matching that of the healing tissue.

It is well established in the field of physical metallurgy that the refinement of grain size increases the yield strength of polycrystalline materials. This has led to a continuing tendency for designing metallic materials with fine microstructures that generally exhibit superior strength, hardness and wear resistance. In addition to high strength, adequate εf and toughness are also required for engineering materials to prevent catastrophic failure during service. However, strength and εf tend to be mutually exclusive properties, and there is usually a trade-off between both, which complicates the development of advanced materials for structural and functional applications.

Unlike conventional metal forming processes, i.e., rolling, forging, or extruding, severe plastic deformation (SPD) techniques have shown potential to achieve a high strength while maintaining a good εf. In particular, Boehlert’s research group is focused on high-pressure torsion (HPT), as it is considered the most effective SPD technique in terms of grain refinement, and has been used for synthesizing new metal systems that can promote additional strengthening mechanisms. In collaboration with Professor M. Kawasaki (Oregon State University), Zn-Mg hybrid disks have been HPT-processed under 6 GPa applied pressure at room temperature (RT) under different conditions (1, 5, 15, and 30 turns) to evaluate their performance as potential absorbable biomedical candidates, see Figure 1.

Microstructural characterization via SEM revealed the development of a sub-micron multilayered structure embedded in a Zn-rich matrix with an average grain size of ~ 600 nm at the disk periphery after 30 turns. The central regions of the disks consisted of relatively larger Mg-rich and Zn-rich phases after 1 and 5 turns. At least 15 turns were needed to achieve a relatively homogenous microstructure. A general tendency for decreasing the grain size and the scale of the multilayered structure was observed with...
increasing radial distance and number of HPT turns.

Electron backscattered diffraction (EBSD) analysis showed that the grain size refinement of the Zn-rich phase, from 1 to 15 turns, was accompanied by a significant increase in the volume fraction of high-angle boundaries (HABs). A strong basal texture developed after 5 turns, however, the maximum intensity value of the corresponding (0001) pole figure decreased gradually from 5 to 30 turns, suggesting the occurrence of DRX during HPT.

X-ray diffraction along with transmission electron microscopy (TEM) demonstrated that HPT was able to induce the nucleation of the intermetallic compounds, Mg₂Zn₁₁ and MgZn₂, identified close to the disk edges after 15 and 30 turns, see Figure 2. The volume fraction of these intermetallics increased consistently with the number of turns, as determined from Rietveld refinement. Similarly, an exceptional increase of the hardness values was recorded with increasing number of turns, with values over 250 HV after 30 turns at the disk periphery. These values are among the highest hardness values ever reported for the Zn-Mg alloy system, and it is due to the contribution of several strengthening mechanisms: Hall-Petch effect and hard intermetallic compounds.

Overall, these results have demonstrated that HPT exhibits potential for the development of Zn-Mg hybrid systems (at RT) with ultrafine-grained metal-matrix structures having enhanced hardness that may open a window towards the research of a new generation of medical device applications.

**Figure 2.** (a) X-ray diffraction patterns taken from the mid-thickness plane at the periphery of the Zn-Mg HPT disks, (b) Bright-field TEM image and (c) corresponding selected area diffraction pattern from the periphery of the Zn-Mg HPT disk after 30 turns. The phases associated to the diffraction rings and their reflection planes are labeled in yellow.

**Recent Publications**


**RESEARCH INTERESTS**
Electrochemistry and electrocatalysis, from theory to experiment

**LAB**
Electrochemical Energy Lab (Engineering Bldg., 428 S. Shaw Lane, Room 3250)

**WEBSITE**
www.msu.edu/~scb

**GROUP MEMBERS**
STUDENTS & COLLABORATING FACULTY: Carolina Carbray, Kanchan Chavan, Manali Dhawan, Alex Mirabal, Nick Quebbeman, Yan Xie, James Woodworth (PhD).

**PATENT**

**CURRENT RESEARCH**
Our research addresses engineering and materials issues in fuel cells, particularly mass transport within high-rate catalytic electrodes. We focus on non-precious metal catalysts based on redox enzymes and transition metals, which have low cost but often introduce transport limitations. We study these issues using experimental and multi-scale modeling approaches. Below are brief descriptions of current projects.

**Bio-inspired design of adaptive catalysis cascades.** As new catalytic systems are created for the production of advanced materials, energy conversion and harvesting, and human/machine interfaces, it is clear that natural pathways provide essential clues that will inspire novel designs. In this collaboration, we are developing integrated catalytic cascades created from different catalytic modalities to optimize selectivity, electron transfer, diffusion, and overall pathway flux. The contribution of our laboratory is to quantitatively model the coupling of these novel catalytic steps and to study the transport of intermediates between steps (figure 1).

We are currently studying the ability of electrostatic channeling to enhance cascade throughput and efficiency. We use multiscale simulations combined with advanced sampling techniques to understand the channeling mechanism, quantify cascade kinetics and design future cascades. Figure 2 shows an example of a cascade structure, synthesized by our collaborators, containing two enzymes joined by a positively-charged polypeptide. The negatively charged intermediate (G6P2−) is guided by electrostatic forces from one enzyme to the next. Molecular dynamic (MD) simulations demonstrate a hopping mechanism on the cascade surface, and we quantify energy barriers for hopping and desorption using techniques such as umbrella sampling and Markov state modeling. We are able to show clear ionic strength dependence of long-range and short-range interactions. We are currently developing experimental capability to monitor intermediate distributions experimentally, using scanning electrochemical microscopy.

We have extended this approach to channeling by molecular confinement, exemplified by reactions within a carbon nanotube. Using continuum and molecular modeling techniques, we have demonstrated the geometric and

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**FIGURE 1.** (a) Tartronic acid oxidation to mesoxalic acid at TEMPO catalyst; (b) facilitated transport of mesoxalic acid along DNA; (c) oxidation of mesoxalic acid to oxalic acid via catalysis by PtRu nanoparticle – AldDH adduct.

**FIGURE 2.** Electrostatic cascade structure and modeling approaches.
transport parameters that will allow high retention and reaction of intermediates inside the CNT. Sponsor: U.S. Army; Collaborators: Universities of Utah and New Mexico, Columbia, UC Riverside

**Metal nitrogen carbon (MNC) oxygen reduction catalysts for automotive fuel cells.** 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 (figure 3). Activity approaches that of precious-metal platinum in acid and alkaline electrolytes.

We study the performance of these catalysts within a fuel cell cathode layer using numerical modeling techniques. Using our model, we have identified opportunities to optimize the design for improved performance, including reduced catalyst layer thickness and increased hydrophobicity of catalyst layer materials (figure 4).

Sponsor: DOE; Collaborators: Pajarito Powder LLC, U.C. Irvine

**Electrocatalytic hydrogenation using low-cost metal catalysts.** The advent of low-cost electricity creates an opportunity to convert biomass to value added fuels and chemicals by electrochemical hydrogenation at low temperatures and pressures. Furfural, for example, can be converted to furfural alcohol and methyl furan by hydrogenation, with applications in perfumes, polymers, and pharmaceuticals. We are developing high surface area and low-cost metal supported carbon catalysts for these reactions, wherein Ni, Cu, Fe are supported on activated carbon in molecular and nanoparticle form and their performance is screened on the basis of conversion and selectivity towards the desired products. Successful catalysts will enable new pathways for chemical products from renewable sources. Collaborator: Inst. Chemical Technology, India

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**RECENT PUBLICATIONS**


RESEARCH INTERESTS
Disease mechanisms, system biology, drug delivery, tissue engineering

WEBSITES
https://www.egr.msu.edu/people/profile/krischan
http://www.egr.msu.edu/changroup/

LABS
Cellular & Molecular Laboratory, Integrative Systems and Computational Biology Laboratory

GROUP MEMBERS
CO-ADVISED WITH S. PATRICK WALTON: Chelsie Boodoo, Kevin Chen, Harrison Lawson, Amrita Oak, Chauncey Splichal, Ryan Thompson, Daniel Vocelle. BMS ROTATION STUDENT: Melanie Bernard. UNDERGRADUATE STUDENTS: Kayla Csapo (Visiting student), Grace Jansen, Ryan Jin, Shay Ladd.

PATENT

CURRENT RESEARCH
Biophysical mechanisms of palmitate-induced signaling and cytotoxicity. Numerous diseases, including non-alcoholic fatty liver disease, cardiovascular disease, type 2 diabetes, metabolic syndrome, neurodegenerative diseases, and cancer, involve malfunction of the endoplasmic reticulum (ER) stress response. Physiological conditions such as elevated levels of saturated long chain-FFAs, e.g., palmitate, have been shown to induce ER stress in many types of cells, and to contribute to the development of these ER stress-associated diseases. We found that palmitate promotes the dimerization of inositol-requiring enzyme (IRE1α), an ER stress sensor protein, through the Trp457 residue in the transmembrane domain of IRE1α (figure 1). This study will impact the design of therapeutics that target the ER stress response in treating metabolic dysfunction, as well as the design and development of drug therapies that target ER stress-associated diseases, including cancers, Alzheimer’s disease and many other diseases.

Delivery of siRNAs by polymeric nanoparticle
(COLLABORATOR: S. Patrick Walton). The overall goal of the proposed research is to design vehicles with optimal chemical and physical characteristics. 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.

Neural transdifferentiation of MSCs through down-regulation of the NRSF. Mesenchymal stem cells (MSCs) are multipotent adult stem cells exhibiting a high proliferation rate and plasticity as compared to other adult stem cell lines. MSCs naturally serve as precursors for adipocytes, chondrocytes, and osteocytes, and provide trophic support for cells of the immune system in the bone marrow. In vitro experiments have shown that MSCs can be induced to gain characteristics of neural cells including generation of Na⁺K⁺ currents, expression of neural specific structural proteins, and exhibition of neuronal morphology upon induction. Previously, we demonstrated that the cAMP-elevating agents, forskolin and IBMX, induced neural-like differentiation of MSCs, including expression of neural markers and increased sensitivity to neurotransmitters. However, due to the broad range of effects that forskolin and IBMX can elicit through the intracellular second messenger, cAMP, a better mechanistic understanding is required. Recently, we show that neural induction by forskolin and IBMX is dependent on downregulation of expression of the master transcriptional regulator, neuron restrictive silencer factor (NRSF), and its downstream target genes. Since silencing of NRSF is known to initiate neural differentiation, we found that forskolin and IBMX result in transdifferentiation of MSCs into a neural lineage (figure 2).

FIGURE 1.

WT

W457A

BSA

PA
CRISPR to increase the homogeneity and efficiency of stem cell differentiation. Stem cells are a promising cell source for the regeneration of aged, injured and diseased tissues and organs, but to realize their therapeutic potential challenges remain, including restricting the growth of unwanted cell types and improving the efficiency of converting them to a specific cell type, and thereby render them safer to use. The heterogeneous nature of stem cells presents challenges in inducing them into a specific cell type. Early transplantation studies to treat Parkinson’s disease successfully regenerated lost dopamine-producing neurons but also resulted in involuntary movements caused by the expression of other types of neurons. Therefore, reducing unwanted cell lineages by genome editing several genes through multiplexing via CRISPR would greatly enhance the efficiency of stem cell differentiation to a specific cell type, decrease probability of mutagenesis and render its use safer. Thus, the overall aim of the project is to increase the efficiency and specificity of stem cell differentiation by reducing off-target cell types through CRISPR. CRISPR/Cas9 mediated knockout of transcription factors involved in the maturation of serotonergic, glutamatergic and GABAergic phenotypes will be performed. We show that MSCs exhibit heterogeneous differentiation during dopaminergic differentiation. We aim to create Tbr1−/− MSCs that could potentially yield a more homogeneous dopaminergic population after induction with forskolin and IBMX.

**RECENT PUBLICATIONS**


A. Nath, C. Chan, “Genetic alterations in fatty acid transport and metabolism genes are associated with metastatic progression and poor prognosis of human cancers,” Scientific Reports 6, 18669 (2016).


**RESEARCH INTERESTS**

Bioactive glasses and glass-ceramics for combating resistant bacteria and regenerative lost, damaged or diseased tissue. Sol-gel (solution-gelation) derived bactericidal and bioactive nano-particles, injectable composites with natural and synthetic hydrogels, 3D scaffolds, nanopatterned coatings on metallic implant substrates.

**LAB**

Biomaterials laboratory (Engineering Bldg., 428 S. Shaw Lane, Room 3531)

**GROUP**

PHD STUDENTS: Natalia Pajares Chamorro, Adam Marsh.
UNDERGRADUATE STUDENTS: Kayla Chuong, Mikayla Lowell, Logan Soule.

**CURRENT RESEARCH**

**Bioactive and bactericidal particles in nano and micro size.**

In this project, we apply the sol-gel method to fabricate bioactive glass-ceramic particles at micro and nano size. Different compositions with various antibacterial agents such as Ag, Zn, Cu, Se will be fabricated and compared in terms of their bacteriostatic or bactericidal activity. The particles will be further functionalized with antibiotics and the synergistic effect with the heavy metal ions will be studied. The bactericidal action will be observed against Methicillin-resistant *Staphylococcus aureus* (MRSA) and Vancomycin Resistant Enterococci (VRE). Their cell-material interaction will be studied in contact with hard and soft tissue for bone and dental tissue regeneration.

**Injectable bioactive composites for minimal invasive applications in orthopedics and dentistry.**

The aim of this project is to develop systems that could accelerate the translation of the bactericidal and bioactive particles to the clinical practice. Synthetic microbeads made by alginate or collagen/fibrin as well as thermosensitive naturally derived extracellular matrix hydrogels (ECMs) will be applied as the delivery vehicle for the bioactive and antibacterial agents. The microstructural characteristics, antimicrobial action, regenerative properties and cytotoxicity of the developed injectable bio-composites will be studied in vitro and in vivo.

**Nanopatterned coatings on implants.**

Sol-gel nanopatterned bioactive coatings releasing metal ions and antibiotics will be fabricated on metal substrates, used currently as implants in different applications both in orthopedics and dentistry. The aim is to develop advanced bioactive and antibacterial coatings on the surface of implants. Dip and spin coating techniques are the applied methods. The bond strength and the microstructural properties of the fabricated coatings at the interface are studied. The loading and delivery properties of the therapeutic drugs are also measured. Finally, the capability of the fabricated coatings to exhibit antimicrobial (ISO 22196:2011) properties and the cell-coating interaction are studied.

**Nanopatterned 3D scaffolds.**

Different techniques are applied for the fabrication of 3D scaffolds with macroporous structure ~300μm and interconnected porous ~100μm. The microstructural, morphological, mechanical, and bactericidal
properties are tailored to achieve excellent bioactive, antibacterial and mechanical properties. The biological properties are studied both in vitro and in vivo. The goal of this work is to fabricate advanced bioactive and antibacterial glass-ceramic scaffolds that can provide a 3D hierarchical porous structure to better attract and regenerate lost or damaged tissue, while it can combat bacteria using a mechanism of action that bacteria cannot resist.

FIGURE 4 (right, top). 3D-bioactive and antibacterial structures for tissue engineering.

FIGURE 5 (right, bottom). Sol-gel derived coating on metal substrates, for applications in dentistry and orthopedics.

Recent Publications


RESEARCH INTERESTS
Dynamics of polymers at interfaces and its relationship to their rheological properties, polymer nanocomposites (including bio-based polymers) design, glass transition and glassy dynamics

WEBSITE
https://www.egr.msu.edu/people/profile/chengsh9

LABS
Dynamics and Mechanics of Soft Materials Group (Engineering Bldg., 428 S. Shaw Lane, Room 3535)

SPECIAL EQUIPMENT AVAILABLE
Broadband dielectric spectroscopy, Anton Paar MCR 302, Fabry-Pérot interferometer, Rheo-optics, Rheo-dielectrics

GROUP MEMBERS
GRADUATE STUDENTS: Matthew Melton, Quinn Sun.
COLLABORATORS: Dr. Yangyang Wang (ORNL).

PATENT

Figure 1. LEFT: A sketch of chain conformations (microstructures) of polymer nanocomposite with low molecular weight. Short trains, loops, and tails can be expected in this case. RIGHT: A sketch of chain conformations (microstructures) of polymer nanocomposite with high molecular weight. Large loops, long tails, and possible bridges can be anticipated in this case. The red and blue beads represent segments of adsorbed polymers. The olive beads represent segments of non-adsorbed polymers.

Figure 2. Rheo-dielectrics to probe the dynamics of interfacial polymers under active deformation. Special attention will be paid to the two types of events here: (i) forced polymer-nanoparticle detachment, (ii) force disentanglement between adsorbed polymers and their adjacent chains.

CURRENT RESEARCH
Polymers are promising candidates to address emerging challenges in environment, food, and energy. Understanding the structure-property relationships of polymeric materials are crucial to design novel polymeric materials on demand. The Dynamics and Mechanics of Soft Materials group are interested in the dynamics of multicomponent polymeric materials at different times and lengths scale, and their correlation to the microscopic properties. Currently, we are pursuing the structure-property relationship of multi-component polymeric materials from dynamics and mechanics perspective of view.

Dynamics and mechanics of polymers at interfaces. Polymers adsorbing onto a surface can form a variety of different microstructure such as trains, loops, and tails. Structurally, the population of each microstructure at the interfacial region varies with the polymer molecular weights, the polymer-nanoparticle interactions, and so forth. The complicated surface conditions have strong impacts on the structure and dynamics of interfacial polymers. For example, the polymer adsorption is typically known as an irreversible process with extremely long lifetime. So far, there are no experimental methods that enable one to effectively study the dynamics of polymers at the interface, especially the slow modes like the Rouse, sub-Rouse, and diffusion of interfacial polymers. In this project, we focus on the polymer structure and dynamics at the polymer/nanoparticle interface. With a combination of dielectric spectroscopy and rheology, we aim to understand the correlation between the properties of the interfacial layer of a few nanometers and the macroscopic properties of polymer nanocomposite, i.e., the mechanism of nano-reinforcement.

Advanced polymer nanocomposites design. Recently, we have demonstrated that small nanoparticles are much more effective in tuning macroscopic properties of PNCs than conventional big nanoparticles, suggesting a potential paradigm shift in PNCs design (Fig. 3). The advanced macroscopic properties of small nanoparticle PNCs (s-PNCs) include a large shift in glass temperature (~10× larger than conventional nanoparticle PNCs (c-PNCs)), an unexpectedly high fragility index (up to 270), a high threshold of kinetic gelation (> 40 vol%), an apparent “fully disentanglement” of polymers with molecular weight of 100 kg/mol, and a processing favorable zero-shear viscosity. We proposed the origin of the large effects as (i) a finite desorption time between the small nanoparticle and polymer segment; (ii) the high mobility of the nanoparticles; (iii) the small sizes. This discovery opens new routes of tuning the macroscopic
properties of PNCs. In this project, we aim to extend the newly discovered strategy to design novel high-performance polymer nanocomposites through precisely tuning the polymer matrix and the size and polymer-nanoparticle interactions through polymer chemistry.

**Dynamics of polymer glasses under active deformation.**

The search and design of new polymer glasses with high modulus, high toughness, and high resistance to failure that can replace metals and ceramics is a long-lasting topic. Despite decades of intensive study, our understanding of the mechanics of polymer glasses is still limited, far behind market demands. It is generally believed that rational design of polymer glasses cannot be reached before the establishment of a molecular deformation mechanism of glassy polymers. In this project, we plan to apply *in situ* rheo-spectroscopy measurements during mechanical tests to characterize the changes of the local vibrations (the “free volume”), the elastic heterogeneity length scale, and the activated segmental hopping during deformation. These details are all critical to illustrate the nature of the high mechanical stress, the origin of the shear yielding and toughening, and the molecular mechanism of the fracture of polymer glasses.

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### RECENT PUBLICATIONS

**RESEARCH INTERESTS**
Deformation and fracture mechanisms, substructure characterization, nanoindentation, grain boundary strain transfer, electron diffraction and channeling, dislocation mapping, scanning electron microscopy, transmission electron microscopy

**LABS**
Electron Microscopy and Characterization (Engineering Bldg., 428 S. Shaw Lane, Room 3507), Sample Preparation Facilities (Engineering Bldg., 428 S. Shaw Lane, Room 3510)

**WEBSITE**
http://www.chems.msu.edu/people/profile/crimp

**SPECIAL EQUIPMENT AVAILABLE**
Three field emission scanning electron microscopes with electron backscattered diffraction (EBSD) orientation mapping capabilities, including one dual column focused ion beam (FIB)/FEG-SEM; tensile, bending, and high cycle fatigue in situ deformation stages; heating and cooling stages

**GROUP MEMBERS**
PHD STUDENTS: Hank Han, Yang Su.
UNDERGRADUATE STUDENT: Alex Hughes.

**CURRENT RESEARCH**
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, based on 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.

**Characterization of deformation structures using scanning electron microscopy.** Enhancing the performance of metals and alloys used in structural applications requires an understanding of the mechanisms that lead to strength, toughness, and in particular, damage nucleation that leads to failure. For many years these mechanisms have been characterized using TEM, but this approach is limited by the need to use very thin samples with small fields-of-view. Here at MSU, we have been at the forefront in the development of SEM approaches that allow the direct imaging and crystallographic characterization of deformation structures in the near surface regions of bulk samples using electron channeling contrast imaging (ECCI) (figure 1). Recently, we have worked on extending this approach to 3D analysis of structure using serial imaging/tomography approaches based on both electropolishing and focused ion beam sectioning.

**Characterization of heterogeneous deformation in polycrystalline arrays using ECCI.** The reliability of engineering structures is often limited by the development of local damage during processing or service. Such damage can often be traced back to the heterogeneous deformation that is inherent in polycrystalline metals. Thus, in order to optimize the performance of structural materials, it is critical to characterize the nature of deformation in these polycrystals, particularly at in grain boundaries. We have recently developed a new ECCI-based approach for such characterization that allows identification of grain boundary dislocation nucleation sites as well as the manner in which dislocation slip bands interact with grain boundaries (figure 2). Using this approach, we are identifying how different polycrystalline arrays may be more or less susceptible to damage nucleation, with an aim towards identifying optimum microstructures for structural applications. Using this approach, we are identifying how different polycrystalline arrays may be more or less susceptible to damage nucleation, with an aim towards identifying optimum microstructures for structural applications. Recent 3D ECCI results have demonstrated how mis-aligned slip systems at grain boundaries can effectively transfer shear by nucleating small numbers of dislocations on a variety of planes, often with high critical resolved shear stresses (figure 3). These small packets of dislocations then merge with the dominant slip bands to carry shear through the interiors of the grains.
**Dislocation interactions at grain boundaries.** Grain boundary engineered materials display enhanced strength and ductility over other polycrystalline materials. Many of these engineered microstructures contain large numbers of crystallographic twins. Understanding how dislocation slip interacts with the resulting twin boundaries is critical to further development of these materials. Working with Professor Yue Qi, we have been combining experimental observations of the dislocation interactions with twin boundaries with molecular dynamics atomistic simulations of the same processes (figure 4). Matching the simulations with the nature of the experimentally observed dislocation pile-up allowed the barrier stress associated with the boundary to be determined.

**RECENT PUBLICATIONS**


RESEARCH INTERESTS
Energy, wealth, and human well-being. Integration of bioenergy generated using sustainable agricultural practices with electricity from solar and wind

FACULTY COLLABORATORS
Dr. Seungdo Kim, Professor Wei Liao, Professor Chris Saffron

PATENTS

CURRENT RESEARCH
Current global trajectories for food and energy production are not sustainable. There are currently over seven billion people on the planet and another two billion are expected in the next few decades. Therefore, food production must expand significantly and soon. But current food production practices tend to deplete soil and degrade water supplies. Modern agriculture uses large quantities of fossil energy both directly and indirectly and is thereby a major greenhouse gas emitter. Modern agriculture also depends heavily on synthetic pesticides and herbicides with many resulting adverse environmental effects.

Lack of energy access is at the root of human poverty. To provide energy services that will lift people from poverty we must also rapidly expand energy production. But about 85% of current energy use is based on fossil energy. If we expand energy production based on fossil energy resources, we will accelerate buildup of atmospheric greenhouse gases at the very time when we should instead be removing large quantities of carbon from the atmosphere and sequestering it in stable forms.

Agriculture is an industry, and like other industries, agriculture must be financially healthy if it is to innovate and become more sustainable. But prices of crop commodities are at historically low levels and many farmers are going bankrupt. How will agriculture innovate and become more sustainable?
sustainable if it does not have the required cash flow? Large scale, sustainable bioenergy production might provide the additional income.

However, we will not solve linked problems by addressing them in isolation. We must address linked problems as an integrated whole, using “win-win” approaches.

These unsustainable, strongly linked trends in food and energy production must be addressed now. We do not have decades to wait for “perfect” solutions. We need proven, scalable, sustainable approaches now. We can improve and innovate on these approaches as we proceed, but it is time to implement large scale, sustainable, “no-regrets” approaches to integrated food and energy production.

I am currently contributing to two efforts to sustainably integrate food and energy production. One is using the ammonia fiber expansion (AFEX™) process to produce high quality ruminant animal feeds from low quality straws and hay. AFEX-treated straws can also be used as feedstocks for producing biofuels such as ethanol. With support from the Gates Foundation, the AFEX process is now being scaled up to produce dairy animal feeds in India. The additional milk production enabled by the AFEX treatment will provide enough income to potentially lift millions of poor Indian families from poverty.

The second approach to integrated food and energy production is called Biogasdoneright™, or BDR. BDR is a set of linked practices for sustainable on-farm production of food linked with both production and conservation of energy. BDR depends on double-cropping to produce energy crops for anaerobic digestion. These energy crops represent additional carbon extracted from the global carbon cycle. Energy crops, plus crop residues, manures and agrowastes, are converted to biogas, electricity or biomethane. Stable carbon and plant nutrients are recycled to the soil through the residual digestate stream to reduce farmer costs and sequester carbon in the soil. The BDR approach with its many linked “win-win” outcomes is summarized in figure 1.

Bioenergy systems modeling is supported by the Department of Energy, Great Lakes Bioenergy Research Center

### RECENT PUBLICATIONS


RESEARCH INTERESTS
Polymer–fiber composite materials, nano-composites (graphene, halloysite, silica), bio-composites (bass fibers, cellulose nano-fibrils, cellulose nano-whiskers), fiber-polymer interfaces (carbon, glass uhmwpe, aramid), adhesion, adhesive bonding, nanostructured electrodes for batteries and supercapacitors

LAB
Composite Materials and Structures Center

WEBSITES
http://www.chems.msu.edu/people/profile/drzal
www.egr.msu.edu/cmsc

SPECIAL EQUIPMENT AVAILABLE
Specific instrumentation available for the fabrication, evaluation, characterization and testing of polymer, fibers, nanoparticles and their polymer composite materials:

- COMPOSITE MATERIALS EVALUATION AND ANALYSIS

- COMPOSITE MATERIALS FABRICATION

GROUP MEMBERS

PHD STUDENTS: Mariana Batista, Christopher Cugini, Zeyang Yu

SELECTED PATENTS (37 TOTAL)

CURRENT RESEARCH

Nanostructuruing of multifunctional graphene nanoplatelet composites for structural, energy generation and energy storage applications. The Drzal research group is in general conducting research in 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 Michigan-based start-up company to produce graphene nanoplatelets. Specific ongoing projects include:

Investigation into the enhancement of polymers with graphene nanoplatelets. The objective of this project is to develop the next generation of aerospace structural multifunctional materials (polymer + fiber + nano particle) that will provide a balance between processing and performance. It is envisioned that an aerospace polymer composite compound will be developed which is modified...
with graphene nanoplatelets at various concentrations to provide a material optimized for: (1) strength and modulus, (2) electrical conductivity, (3) thermal conductivity, and (4) thermal expansion. This will involve extrusion processing and nanostructuring of the nanoparticles into highly aligned films for integration into composites.

**Nano-structured materials for Li ion battery and supercapacitors.** The objective of this research project is to: (1) gain a fundamental understanding of the atomic and molecular level processes that govern the operation, performance and failure mechanisms of energy storage systems; (2) design and investigate nanostructured materials with the goal of increasing the performance, durability and reliability of batteries and supercapacitors; (3) explore nanostructuring of materials for battery and supercapacitor materials to facilitate fast electron and ion transport with an emphasis on high-power and high-capacity batteries for electric vehicles.

Drzal’s portion of the project involves the nano-structuring of graphene nanoplatelets in the anode to improve capacity, re-charging rate and durability.

**Multifunctional composite materials.** The objectives of the research are: (1) to demonstrate a new approach to improving composite fracture and impact toughness by surface modification and coating with functionalized elastomeric coatings of nanoparticles and (2) to impart flammability improvement and flame resistance by the incorporation of xGnP 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. The insertion of xGnP nanoparticles around fibers and between lamina in a composite can deflect blast and impact energy laterally away from the impact point and provide a safety margin by preventing structural collapse.

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**RECENT PUBLICATIONS**


RESEARCH INTERESTS
Deformation mechanisms of crystalline solids, multi-physics simulation of microstructure mechanics

LAB
Computational Materials Mechanics (Engineering Bldg., 428 S. Shaw Lane, Room 1105)

WEBSITE
compmatermech.wordpress.com

GROUP MEMBERS
MS STUDENT: Mingwan Zhu. UNDERGRADUATE: Kieran Nehil-Puleo.

CURRENT RESEARCH
Computational prediction of advanced structural material performance by considering interactions of microstructure and plasticity in crystalline solids. In our daily life, we heavily rely on the mechanical capacity and integrity of many different materials. For most structural materials of technological relevance, the mechanical behavior is intricately influenced by their chemistry (alloying in the case of metals) but even more importantly, by their microstructure. The latter is strongly impacted by processing conditions and, hence, can be substantially manipulated through processing. This complexity makes the prediction of the (thermo-) mechanical behavior of existing materials and the design of new materials and their required microstructures for targeted properties a remarkable challenge that is addressed at the Computational Materials Mechanics (CMM) lab by Eisenlohr and his group. We tap into the resources offered by the High Performance Computing Center (HPCC) and the Division of Engineering Computing Services (DECS) to simulate material deformation with commercial and homemade open-source software. In our simulations, we investigate the mechanisms of deformation occurring at mesoscopic scales and connect them to the material microstructure. By this we seek, for instance, to (1) understand basic aspects of plastic deformation in crystals, (2) identify critical configurations in polycrystals or multiphase materials that might trigger nucleation of internal damage, and (3) predict the inherently anisotropic behavior of structural materials with complex microstructure at the scale of engineering components.

As an overarching theme, we seek to advance the forward modeling and associated simulation methodologies necessary to understand the properties of materials with (complex) microstructure and by that facilitate the solution of the inverse problem posed by the search for a microstructure that meets a given property demand.

A current example of ongoing research is:

Identifying the origins of whisker formation in tin films. The spontaneous growth of tin (Sn) whiskers from tin coatings, which are frequently used due to their favorable properties such as excellent solderability, ductility, electrical conductivity, and corrosion resistance, is a serious concern to the electronic industry as these long filament-like structures pose a major risk of short-circuiting. Especially after lead (Pb), an alloying element that previously suppressed whisker growth, was banned in consumer electronics due to environmental hazards, understanding and mitigating whisker formation is of renewed interest. Current models of whisker formation simplify the film geometry into one dimension, partly consider plastic relaxation mechanisms, prescribe the stress condition surrounding a predetermined whisker grain, and are fitted to reproduce observed whisker growth rates. Yet none of those models can be regarded as predictive, since many open and critical aspects of whisker formation are not explicitly addressed by them. First and foremost, the specific conditions that trigger particular grains to grow a whisker are ignored and cannot be deduced from the simulation results. Secondly, the long-range stress

\[ p \approx -40 \text{ MPa} \]

**Figure 1.** Spatial variability of hydrostatic stress \( p \) in the vicinity of grain boundaries at three different film depth (surface to substrate from left to right). Substrate is not shown while part of the columnar grain structure of the tin film is illustrated at the far back and is colored according to the crystallographic direction that is parallel to the surface normal (close to \( \{100\} \) in this example, see color code in standard stereographic triangle).
gradient that is predicted to develop around a whisker grain has not been observed in highly resolved x-ray diffraction studies. Moreover, geometrically simplified models disregard the elastic and plastic anisotropy of Sn, hence, cannot account for measured influences of the global grain orientation distribution (crystallographic texture) on whisker propensity. Since whisker nucleation is ultimately a local phenomenon, specifics of the whisker grain neighborhood in terms of geometry and crystal orientations are very likely decisive factors.

We perform thermo-mechanically coupled full-field crystal plasticity simulations of tin films on an isotropic rigid substrate to investigate the influence of crystallographic texture, grain size distribution, and presence of oblique grains on the development of hydrostatic stress within the film, in particular within the network of grain boundaries, as that is the path for atom redistribution considered to be ultimately decisive for whisker formation. The exemplary results illustrated in Figures 1 and 2 demonstrate that a highly fluctuating hydrostatic stress field emerges under thermal strain that is influenced by the texture but essentially independent of the grain size distribution or the presence of non-columnar grain shapes. The results are consistent with the hypothesis that a whisker nucleates where low compressive stress relative to its immediate grain neighborhood occurs, a condition that appears to be predominantly determined by the crystallographic orientation distribution of the film.

**RECENT PUBLICATIONS**

“DAMASK—The Düsseldorf Advanced Material Simulation Kit for modelling multi-physics crystal plasticity, damage, and thermal phenomena from the single crystal up to the component scale,” *Comp. Mater. Sci.* 158, 420–478 (2019).


**RESEARCH INTERESTS**
Hierarchical material structure, electronic materials, scanning microscopy

**LAB**
Measurement and Analytics (1449 Engineering Research Ct., Rooms C24D and C14)

**WEBSITE**
msudag.wordpress.com

**SPECIAL EQUIPMENT AVAILABLE**
Rigaku micro x-ray diffraction system, deep ultraviolet photoluminescence microscope

**GROUP MEMBERS**
STUDENTS: Shengyuan Bai, Karli Deutscher (PA student), Yvonne Hsiung (intern), Erik Vyhmeister-Cancel.
COLLABORATORS: Fraunhofer Center for Coatings and Diamond, the Advanced Photon Source, the Center for Integrated Nanotechnology, and Drs. Martin Crimp, Qi Hua Fan, Timothy Grotjohn, Aljoscha Roch.

**CURRENT RESEARCH**
The aim of this group is to use hyperspectral imaging to understand the process-structure-property relationships of materials. Current efforts focus on using microscale x-ray diffraction (μ-XRD) to map crystal orientation, domain, and stress in single crystal diamond grown using microwave plasma-assisted chemical vapor deposition. This understanding can translate to the development of new methods to control growth parameters and manipulate lattice orientations of diamond to yield electronics-grade large single crystal wafers.

Diamond growth. Our goal in studying diamond is to understand the physical mechanisms which lead to diamond wafer outgrowth and fracture. For diamond to be realized in devices such as power converters, heat spreaders, or radiation detectors their lateral dimensions need to expand beyond the typical 10×10 mm.

Much is already understood about the diamond lattice structure. Growth is understood to take place as a combination of surface etching and rebuilding, creating favorable, highly stable lattice points exposed by etching on which constituent atoms of CH₃ may attach, propagating overall growth along specific lattice planes. In this highly dynamic environment, researchers have noted the formation of 1D and 2D defects is not uncommon but have learned to suppress them through surface engineering, i.e., miscuts relative to the primary growth facets of (100) or (110) resulting in a step-flow overgrowth scheme. Surface engineering of diamond now offers a path forward to growing wafer-sized diamond through converging lateral surfaces, however, the interaction of crystals at these junctures is not well understood.

Our group works closely with the Fraunhofer Center for Coatings and Diamond to conduct research to leverage their expertise with industrial scalable growth techniques. The primary method to grow electronics grade diamond is with microwave plasma-assisted chemical vapor deposition reactors, of which the Fraunhofer center houses eight separate reactors for doped and un-doped single crystal diamond growth. In the reactor, a transverse standing wave is established with a node directly above the substrate crystal surface. Within the same volume, methane and hydrogen gasses are pressurized in a quartz bell jar and the interaction of the pressurized gases and microwaves produces a 2000°C ball of hydrogen and carbon dimers. At the surface of the substrate, these particles interact to actively etch and attach to the surface, forming covalent carbon bonds ultimately resulting in a diamond crystal lattice.

μ-XRD. Crystal structural information can be obtain in a variety of ways using electron, x-ray, neutron, and ion probes at multiple length scales. To gain insight into how large, scalable processes like microwave plasma-assisted chemical vapor it is ideal to collected microstructural information of millimeter and larger length scales.

Structural information typically derived from XRD comes from bulk samples at millimeter length scales with a millimeter-sized x-ray beam spot. This inhibits the ability to probe structural information such as domain size and orientation relative to the surrounding microstructure, essentially averaging out this information within the probe spot size on target. μ-XRD follows conventional XRD except the ultimate beam spot on target is only hundreds of microns.

**FIGURE 1.** Single crystal diamond sample during growth in microwave plasma reactor. Diamonds grown this way have the lowest defect and impurity concentrations of any method.
in diameter, a condition created through strong anisotropic beam scattering to reduce beam spread and subsequent collimation. A five-axis Eulerian cradle with $\phi$ and $\chi$ rotation and XY scanning enables us to render 2D spatial maps of the crystal domain, orientation, texture, and stress and strain. Further, the modularity of the system allows for swapping of different components, giving us an extremely sensitive and versatile tool. The applications of the system promise to expand far beyond diamond materials.

**Optical microscopy.** Beyond x-rays, photons offer a number of unique ways to probe the structural and compositional information contained in crystals. Through correlative measurements with XRD and other techniques, both visible white light and UV range, offer the ability to detect optically active centers contained in crystal lattices (composition), lattice strain along specific crystallographic directions, and surface topography.

Birefringence is a well-known technique to study the quality of materials for transmission of electromagnetic radiation. Incident light is initially polarized, then passed through the target material and an analyzing polarizer before finally detected. For imperfect crystals, light interaction will result in a rotation of the polarization vector during its transit through the crystal, resulting in detection of the rotated light. When combined with knowledge of the crystal orientation, this method can reveal in seconds the relative anisotropy of crystal strain relative to specific lattice orientations.

Instrumentation expected to be added this year will include photoluminescence. A technique by which the excitation of lattice atoms using light can reveal compositional information about the material.

**FIGURE 2.** The $\mu$-XRD instrument pictured above during measurement. The instrument is designed to adjust sample position in real time to track diffraction peak shifts in a rocking curve measurement. Such maps are rendered as shown in the countour map above and can be correlated with optical microscopy techniques to understand microstructure of the material relative to specific crystal planes.

**FIGURE 3.** A birefringence image taken from a cross-sectioned diamond sample. While the sample is a single monolithic piece, the heterogeneity of its growth is obvious from this image. Strain along the direction (311) from the seed layer (A) diminishes as growth proceeds. Beginning with the second growth cycle at (b), strain appears aligned along (101) before decaying towards the top face of the crystal (100).

### RECENT PUBLICATIONS


CURRENT RESEARCH

Transparent high-barrier films (BOPP) with nanostructured additives. The application of interest here is packaging dried foods with transparent film, which requires high barrier to water vapor without using metallization. Biaxially oriented polypropylene-clay nanocomposite (BOPP-NC) films have been prepared and compared with other BOPP films without additives. The nanocomposite sheets were stretched biaxially in a Karo IV apparatus to area stretch ratios of 40 to 50, similar to neat PP sheets. Transmission electron microscopy on the stretched films confirmed the maintenance of exfoliation and dispersion quality. The biaxially oriented nanocomposite films showed significant improvement in mechanical property without sacrificing clarity. Oxygen and water vapor permeability of 1 mil thick BOPP-NC films were both reduced by 40% compared with BOPP. The latest results were obtained in collaboration with the Innovia Films R&D Group at Wighton, UK. Three-layer packaging film trials are also planned.

Thin and strong tapes of porous composite. We have shown that the solid phase die-drawing process can be used to produce porous strips or tapes as thin as 1 mm (which is thin for this process) and with 40% void fraction from polypropylene-talc composites, especially when using lower die temperatures. Two different composites with different talc particle size distributions were drawn under similar conditions. The porosity, crystalline orientation and texture and the mechanical strength of the drawn composite with smaller mean particle size was found to develop differently with increasing strain rate than for the other composite. The final porosity and mean aspect ratio of pores was found to be the same with both composites at different limiting conditions; however greater tensile strength (170 MPa) and puncture strength were achieved for the porous tapes with smaller particles after die-drawing at a higher strain rate. The greater tensile strength and the leveling off in puncture strength with increasing draw ratio was seen to be a result of the greater extent of crystalline rearrangement to fibrils achieved with the composite having smaller particles, as revealed by x-ray diffractometry. The enhancement in

PACKAGING FILM

Packaging film with nanocomposite layer

FIGURE 1. Additives for high barrier transparent packaging film.
puncture strength of this tape may be attributed also in part to the smaller mean pore dimensions.

**Wall slip and friction in processing highly filled polymer melts with lubricants.** Lubricants must be used to process highly filled polymer melts into gel-free products. The action of lubricant is typically to migrate to the wall and form a low viscosity slip layer. Another effect may also be produced in two-phase flow of particulate suspensions or rubber suspensions: the friction between the particles and the wall may be reduced by lubricant. The objectives of this research were to evaluate lubricant action in two-phase flow of highly filled polymer melts through (1) capillary rheometry with nonlinear Bagley correction and Tikhonov regularization for further analysis; (2) slip velocity curves for lubricated flow of rubber-free and rubber-filled melts and (3) AFM imaging of the morphology of DVA extrudate at the surface and in the core.

**Figure 2.** Solid-phase die-drawing apparatus.

**Figure 3.** Blowing of inner liner for tires.

**Figure 4.** Lubricated two-phase flow in a channel.

### Recent Publications


Wei Lai
Associate Professor
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**RESEARCH INTERESTS**
Advanced materials and electroanalytical methods for energy conversion and storage technologies

**LAB**
Advanced Energy Materials Lab

**WEBSITE**
http://weilaigroup.org

**GROUP MEMBERS**

**CURRENT RESEARCH**
Research interests in our lab have been broadly focused on the study of advanced materials and electroanalytical methods for energy conversion and storage technologies. Recently our research effort has centered around Solid-state Ionic Conductors (SIC) and Solid-state Mixed Ionic and Electronic Conductors (SMIEC) as battery electrolytes/electrodes and thermoelectric (TE) materials. SIC, SMIEC, and TE compounds are all complex materials with a framework-guest structure and unique ionic and electronic properties. The guest atoms in SIC and SMIEC are able to diffuse or conduct, while the framework is insulating (SIC) or semiconducting (SMIEC) for electrons, respectively. The guest atoms in TE are rattlers while the framework is semiconducting for electrons. 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 to understand their fundamental structure-property relationships.

Ongoing projects include:

**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 non-flammable solid electrolytes with high lithium ionic conductivities. The framework of the materials is composed of LaO\(_8\) dodecahedra and TaO\(_6\) octahedra. There are two types of cages, tetrahedral (Td) and octahedral (Oh), to host lithium ions. Each Td cage is surrounded by four Oh cages and each Oh cage is surrounded by two 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\(_3\)Zr\(_{2-x}\)Ta\(_x\)O\(_{12}\) (x = 0-2). The scientific goal is to understand structure and dynamics of lithium disorder in these complex materials. **FUNDING:** National Science Foundation.

**Structure and dynamics of thermoelectric materials.** Currently around two-thirds of energy produced in US is rejected mainly in the form of waste heat. Such unused heat can be recovered by thermoelectric processes that directly convert thermal energy into electricity. Robust and cost-effective thermoelectric devices could have

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**Figure 1.** (a) La-Ta-O framework, (b) Td-Li, (c) Oh-Li, (d) 2D schematic.
significant impact on the energy production and utilization of the society. Tetrahedrites are a class of TE materials based on Cu$_{12}$Sb$_4$S$_{13}$ containing earth-abundant and environmentally friendly elements. The structure consists of a 3D framework of CuS$_4$ tetrahedra and SbS$_3$ polyhedra. Another type of Cu atoms (Cu$_{12e}$) behave as rattling guests inside a cage formed by three S and two Sb atoms. The interaction between Cu$_{12e}$ and Sb atoms is mitigated by the Sb lone pairs. We are currently investigating the relationship between atomic and electronic structure and thermoelectric properties of undoped and doped Cu$_{12}$Sb$_4$S$_{13}$ tetrahedrites.

**FUNDING:** National Science Foundation (in collaboration with Donald Morelli).

**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$_{x}$Ti$_{1-x}$]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.”

**FUNDING:** National Science Foundation.

**RECENT PUBLICATIONS**


RESEARCH INTERESTS
Electronic packaging materials, solidification of materials, high-temperature polymers and their composites, phase, and synchrotron characterization

LAB
Inorganic-Organic Synthesis and Processing (3545 Engineering Bldg.)

SPECIAL EQUIPMENT AVAILABLE
Confocal Raman spectrometer with environmental control deformation chamber, high-pressure differential scanning calorimeter, rheometer, dynamic solid analyzer

GROUP MEMBERS
UNDERGRADUATE STUDENTS: Eric Egedy, Risa Hocking.
PHD STUDENTS: Yang Lu, Aditya Patil, David Vogelsang, Yueline Wu. COLLABORATING FACULTY: Prof. Robert Maleczka (Chemistry).

PATENTS

CURRENT RESEARCH
Electrochemical behavior of Cu-Al intermetallics in Cu wire bonding packages. Wire bonding is a key packaging technology to achieve the electrical and mechanical interconnections between integrated circuit and the metal frame in printed circuit board. Recently, copper (Cu) has gained popularity over gold (Au) as the wire material based on cost reduction and higher performance. Two major intermetallics (IMCs), CuAl2 and Cu2Al, are often found in the Cu-Al interface after the as-bonded structure undergoes thermal aging for extended period of time. Galvanic corrosion for this Cu/Al interface may take place when dissimilar metals are brought into electrical contact in the presence of an electrolyte containing corrosive species. In the service environment, moisture absorbed by the molding compound can dissolve a small amount of halogens (Cl, Br) used in the synthesis of molding compound and act as the electrolyte to initiate galvanic corrosion. Several studies have reported that the mechanical failure resulted from the disappearance of γ and failure occurred at the wire side. The use of Pd-coated Cu wire had shown to enhanced service reliability. It was suggested that the enhanced service reliability maybe due to the nobility of Pd addition, however, no systematic electrochemical characterization has been carried out for each of the entities in Cu(Pd)-Al interface, which is essential to understand corrosion behavior of Cu(Pd)-Al bonding interface.

Using open circuit potentials and potentiodynamic polarization measurements systemic investigate were performed on all the undoped/Pd-doped samples (Cu, γ, θ) in different pH, Cl concentration and temperatures to provide a complete picture of electrochemical behavior needed to understand the service reliability of wire boned electronic packages. Electrochemical characteristic of metals were examined using cathodic and anodic polarization curves. Both Ecorr and icorr are determined by the thermodynamics (reversible potentials: E(M/M°), E(O2/OH−)) and kinetics (exchange current densities: i0(M/M°), i0(O2/OH−), Tafel constants) of the two half-cell reactions. The addition of Pd increases the cathodic current density by increasing the exchange current density for ORR, and reduces the anodic current density by the induced passivation. This upward shift on the cathodic polarization curve, as well as the downward shift on the anodic polarization curve, led to an increase in Ecorr. However, the change in the value of icorr depends on the relative amount of shift between cathodic and anodic polarization curves. As shown in Figure 1(a), the upward shift in the cathodic polarization curve was more than the downward shift in the anodic polarization, the value of icorr will increase, which meaning a faster rate of corrosion. This was the case when only small amounts of Pd addition in Cu.
nucleation sites during solidification as grain refiner, and also serve as obstacles for preventing coarsening at elevated temperatures for microstructural stability of Al alloys.

A4047 and A4047 powders with and without POSS trisilanol added were used to make ingots for metallographic study. Figure 2 shows the optical micrographs of the ingots made of 325 mesh A4047 powders without and with POSS trisilanol addition, respectively. A4047 has a near-eutectic Al-Si composition with primary Al phase and eutectic Si-Al phase. Figure 2 (left) displays the microstructure of A4047 without POSS trisilanol, which is typical from a slow-cooled ingot with Al dendrite and lamellar Si cuboids. With the addition of POSS trisilanol, under the same casting and cooling configurations, the Si platelets are broken down to very fine spheroidized phase, as shown in figure 2 (right).

The microstructure modification with POSS trisilanol added also leads to significant benefit in the mechanical property of A4047. Tensile tests were conducted on the tensile bars machined from the ingots. It was found that the elongation to failure had increased with POSS trisilanol addition, with percentage increase from 23% to 250% over the control sample (without POSS trisilanol added). In addition, the ultimate tensile strength did not decrease with the benefit of increases in the elongation to failure. Currently we are exploring different approaches for produce master alloys with different Si contents from hypoeutectic to hypereutectic Al-Si casting alloys.

Influence of nano-structured silanols on the microstructure of Al-Si casting alloys. Aluminum (Al) based casting alloys have been used as light-weighting materials in the automotive industry for decades. Further weight reduction has been introduced in the automotive body construction recently with the use of structural aluminum. However, without modification, most of Al casting alloys have poor ductility, and does not meet the structural application requirement, i.e., at least 12% elongation to failure. Although, the addition of Na or Sr can spheroidize Si cuboids, and the addition of Ti and B reduce the grain size of primary aluminum phase in Al-Si based casting alloys. However, these modifications had some drawbacks needed to overcome, such as coarsening with aging as well as fading with repeated melting. Polyhedral oligomeric silsequioxanes (POSS) are silsequioxane-based nano-structural chemicals. These chemicals are cage like structures with repeated monomer units of RSiO$_{1.5}$ where Si is the element silicon, O is oxygen and R is hydrocarbon group, e.g., ethyl, isobutyl, phenyl etc. Partial cage-like POSS have the thermal stability in the molten aluminum and the silanol (Si-OH) functionalities form thermodynamically stable Si-O-M bonds with metals (e.g., Al). These nano-sized silanol compounds provide nucleation sites during solidification as grain refiner, and also serve as obstacles for preventing coarsening at elevated temperatures for microstructural stability of Al alloys.

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RECENT PUBLICATIONS


RESEARCH INTERESTS
Nanotechnology, polymers, adhesion, particles, biomimetics, self-assembly, nanomixing, nanodispersion, separation, renewable bioenergy, fluid flow

LAB
Polymer Surface, Interface, Nanotechnology Research Group (Engineering Bldg., 428 S. Shaw Lane, Room 2522)

WEBSITE
http://www.egr.msu.edu/~leeil/

SPECIAL EQUIPMENT AVAILABLE
Brookheaven ZetaPALS dynamic light scattering particle size analyzer/zeta potential analyzer; Primix TK Filmix ultra high-speed, thin-film mixer designed to produce stable nanodispersions; fluorescent and phase contrast optical micrographs with a digital camera connected to a computer (Nikon Eclipse ME 600 and ME 400 microscopes); layer-by-layer assembly and microcontact printing facilities; programmable slide stainer (Zeiss), spin coater, centrifuge, plasma cleaner (Harrick)

GROUP MEMBERS
Dr. Joung Sook Hong, Brooke Meharg, Chris Tawfik, Jing Yu

PATENTS


RECENT ACHIEVEMENTS
- The poster “Development of Layered Multi-scale Porous Thin Films by Tuning Deposition Time and Molecular Weight of Polyelectrolytes” by J. Yu, O. Sanyal, A.P. Izbicki, I. Lee won the First-Place Poster Award ($500) in the Materials Science and Engineering Division (MSED) at the AIChE 2015 Annual Meeting in Salt Lake City, UT (November 8–13, 2015).
- Affordable production of cellulose nanowhiskers (MIIE); Solar-Bio-Nano Based Wastewater System for the Production of Energy and Potable Water (DOD- SERDP); Understanding and Modulation of Electrostatic and Hydrophobic Forces within; Plant Cell Walls to Facilitate Enzymatic Deconstruction and Conversion to Biofuels (NSF); Prevention of Bacterial Biofilm Formation on Surfaces (SPG).

CURRENT RESEARCH
Dr. 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. 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:

FIGURE 1. This work focuses on the design of porous polymeric films with nano- and micro-sized pores existing in distinct zones.
Prevention of bacterial biofilm formation on surfaces
Solar-bio-nano based wastewater system for the production of energy and potable water
Hybrid nanostructured metal foam material systems for blast impact (and wrinkle-free films)
Fabrication of functional nanoparticles and delivery system
Fast and efficient production of cellulose nanowhiskers and the use in the composite materials
Understanding and modulation of interfacial properties within plant cell wall pores to facilitate enzymatic deconstruction and conversion to biofuels.

Recent Publications

- **RESEARCH INTERESTS**

- **LABS & LOCATIONS**
  Properties Lab (Engineering Bldg., 428 S. Shaw Lane, Room 2255), Reactive Distillation Pilot Facility (3900 Collins Rd.).

- **WEBSITE**
  https://www.egr.msu.edu/reactivedist/

- **SPECIAL EQUIPMENT AVAILABLE**
  Vapor-liquid equilibria measurements, flash point, cloud point, densitometry, low- and high-pressure speed-of-sound, IR and NMR measurements of hydrogen bonding.

- **GROUP MEMBERS**
  Bill Killian, Renming Liu, Andrew Norfleet, Lars Peereboom, Jackson Storer

- **RECENT PATENTS**

- **CURRENT RESEARCH**
  The Lira Thermodynamics Research Facility measures and correlates vapor-liquid equilibria (VLE), liquid-liquid equilibria (LLE), and solid-liquid equilibria. For VLE, the lab has a Fisher T-xy recirculating apparatus, a custom P-xy apparatus, and a miniature ebulliometer. We also have capabilities for density and viscosity measurements. An example of P-x measurements are shown in figure 1, for ethyl levulinate + water.

  **A new modeling approach.** Separation operations are generally the most expensive components of chemical processes. Therefore, it is especially important to optimize separations to accelerate the concept-to-implementation timeline of a project. Designing these operations requires accurate and flexible thermodynamic models, but existing tools often fall short when applied to systems with polar components. The hydrogen bonding which occurs between these components has a dramatic effect on chemical properties and the phenomenon is poorly represented in traditional models. This work aims to address this limitation by: (1) developing a thermodynamic model which incorporates a statistical mechanics approach (Wertheim’s perturbation theory) to calculate the extent and effects of association; (2) evaluating parameters for the model by leveraging a combination of IR and NMR spectroscopy as well as molecular and quantum simulations; and (3) delivering the resulting model as a commercial tool (an Aspen Plus user model) to be utilized by industrial partners and the broader engineering community.

  Activity coefficient models permit accurate fitting of pure component vapor pressures independently of mixture parameters, but traditionally the models don’t represent association effects of hydrogen bonding. Adding the Wertheim association term addresses the deficiency. The approach adds the association term to the typical residual and combinatorial terms,

  \[ \ln \gamma = \ln \gamma^{\text{res}} + \ln \gamma^{\text{comb}} + \ln \gamma^{\text{assoc}} \]

  Figure 2 shows the improvement for the methanol + cyclohexane system compared to the traditional NRTL.

  **Quantum mechanics to guide spectroscopy.** A unique feature of the MSU associating fluid project is the incorporation of quantum calculations to guide interpretation of the spectra. In literature, the peak at 3640 cm\(^{-1}\) has been speculated to be both alpha and beta hydroxyls. Our calculations confirm the empirical assumptions. Our dedicated 28 supercomputer cores with 512 GB RAM on the MSU Institute for Cyber-Enabled Computing permit us to run quantum calculations on medium-sized clusters.

  In our approach, we run molecular simulations to generate realistic molecular environments and save frames.
We analyze the frames to locate a hydroxyl and classify the hydrogen bonding type as alpha, beta, gamma, or delta (as shown by the inset in figure 3). After classifying a hydroxyl, we capture the surrounding molecules to create a realistic cluster. We pass the cluster to Gaussian for quantum calculations. We minimize the hydroxyl and nearby atoms using PM6 and then run minimization and frequency calculations at the B3LYP/6-31G* level of theory. Finally, we verify the classification of the hydroxyl after the quantum calculations because the classification sometimes changes during the quantum calculations.

Figure 3 shows that the predicted extinction coefficient for absorption of radiation changes significantly with the bonding of hydrogen for both the ethanol + cyclohexane and n-butanol + cyclohexane systems. We show that the free hydroxyl alpha and beta hydroxyls vibrate and absorb similarly. The gamma hydroxyls vibrate at intermediate frequencies and absorb more strongly. The delta bonds vibrate at lower wavenumbers and absorb very strongly, as shown by the large absorption coefficient.

Spectroscopic determination of association. We are developing a method to scale the experimental spectra before determining population distributions used for quantifying the association constants. A raw spectra is shown as the inset in figure 4. The alpha and beta contributions are the small peak to the left. Because the bonded hydroxyls absorb so strongly, the shape of the absorbance is misleading in terms of populations. If we divide by the theoretical extinction coefficient from the quantum calculations, we obtain the curves shown in figure 4. After scaling, the integrated areas are invariant with temperature so that quantification can be performed from the scaled spectra. The integrated areas after scaling are linear with concentration as expected by Beer’s law. We are currently working to determine association constants.

**RECENT PUBLICATIONS**


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 research interest as it may enable substantial reductions in PV installation costs and facilitate wider market penetration. Ultimately, we aim to further evaluate and exploit these new materials in thin-film architectures to realize ubiquitous and low-cost solar energy.

**Excitonics for building integrated transparent PVs and solar concentrators.** We are pioneering transparent molecular photovoltaics that can retain a high degree of visible-transparency, while absorbing ultraviolet 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 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.

**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.

**Understanding organic epitaxy.** The presence of excitons in organic semiconductors at room temperature distinguish them from traditional semiconductors, providing exceptional opportunities for manipulating energy in a range of structures from light emitting diodes, lasers, transparent photovoltaics, and optical switches. However, control over crystalline order, orientation, and defect formation are crucial to the fabrication and optimization of these excitonic electronics. The overarching goal of understanding organic epitaxy is to explore bottom-up vapor-deposition routes to the growth of large-area organic and molecular crystalline films with enhanced properties.

**RECENT PUBLICATIONS**


**RESEARCH INTERESTS**
Materials physics, new semiconductors for energy applications, thermal and electronic transport in solids

**LAB**
Electronic Materials Laboratory (Engineering Research Complex, 1497 Engineering Research Court, Room E172)

**WEBSITE**
www.egr.msu.edu/morelli-research

**SPECIAL EQUIPMENT AVAILABLE**
Equipment for synthesis of materials, including vacuum melting, arc-melting, and powder processing; x-ray diffractometer for crystal structure and phase identification; electrical and thermal transport property characterization from 80–1000K

**GROUP MEMBER**
Daniel Weller

**CURRENT RESEARCH**
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 the following:

*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 combined state-of-the-art computational approaches with thermal and electronic transport characterization to study the relationship between crystal structure and properties 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.

*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$_4$S$_{13}$, 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$_2$Si$_2$. 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**


RESEARCH INTERESTS
Design and engineer biobased and biodegradable-compostable plastics, develop environmentally responsible end-of-life options for plastics and bioplastics materials, conduct carbon footprint and life cycle assessment (LCA) of materials, studies in reactive extrusion processing and biofiber composites

LAB
MBI, 3815 Technology Blvd., Lansing, MI

WEBSITE
www.msu.edu/~narayan

PATENT

GROUP MEMBERS
POSTDOCTORAL & VISITING RESEARCH FELLOWS: Professor Philippe Dubois (Univ. of Mons, Belgium), Dr. Elodie Hablot (Univ. of Strasbourg, France), Dr. Weipeng Liu (Green Star Company, China), Dr. Mohan Patil (UICT, India), Dr. Jean Marie (Ben) Raquez (Univ. of Mons, Belgium), Dr. Yuya Tachibana (AIST, Japan), Professor Y.Z. Wang (Sichuan Univ., China). STUDENTS: graduated 19 PhD and 20 Master’s students; currently 5 graduate students and 8 undergraduates work in the group.

CURRENT RESEARCH
Biobased Materials 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, and The group’s biobased materials technology platform is covered by 29 patents; 200 peer reviewed publications, and several technologies have been licensed or resulted in a spin-off company. 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), a $150 million NASDAQ traded company
- 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 a Michigan agri-business, Zeeland biobased products (www.zfswinc.com)
- licensing four patents on thermoplastic modified starch and its copolymers with biopolymers to Ingredion Inc., a $2.3 billion international company.

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.zfswinc.com). ZFS is Michigan’s largest soybean processor servicing about 2,500 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. The plant oils are being converted into biobased polyls 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. Figure 2 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.

Our biobased and biodegradable-compostable hybrid materials technology platform is based on poly(lactide) (PLA) resins derived from plant-biomass feedstock like corn and sugarcane. Funded by NSF SBIR Phase I and II grants, the technology is being commercialized by Natur-Tec, a business unit of Northern Technologies (NASDAQ:NTIC). The company currently supplies biodegradable-compostable bags to global companies such as Levi Strauss & Co. About 76,000 m.t./yr of plastic packaging resins are used for packaging 5 billion garments in South Asia alone (figure 3), translating to about $200 million in economic value.

The group is working towards addressing the major issue of microplastics in the ocean environment. In a recent paper published in the journal Science (February 2015, 347:6223, 768), we reported that 4.8 to 12.7 million tons of plastics entered into the oceans in 2010 and without any intervention would increase to 10.4 to 27.7 million tons by 2025. The paper shows that reducing 85% of waste from the top 35 mismanaged waste countries would result in a 75% reduction of plastic waste going into the oceans. We are working towards developing and implementing compostable plastics technology in conjunction with composting and anaerobic digestion systems to prevent “mismanaged plastic waste” from entering into the oceans. These efforts along with along with educational and consumer awareness messaging can clearly advance the goal to “a cleaner ocean environment.”

**RECENT PUBLICATIONS**


times lower than conventional power plants. Unfortunately, widespread SOFC commercialization is limited by the high operating temperatures (>600°C) required to incorporate oxygen into the device. Further, attempts to engineer the oxygen surface coefficient, $k$, have been complicated by the large $k$ discrepancies in the literature for nominally identical materials under nominally identical conditions (such as the 10,000 times discrepancy in the 650°C $k$ of the model material $La_0.6Sr_{0.4}FeO_{3-x}$).

Recently, the Nicholas group developed a new in situ, non-contact, current collector-free wafer curvature technique that simultaneously measures the oxygen surface exchange coefficients and biaxial stress state of thin film oxygen reduction reaction (ORR) or oxygen evolution reaction (OER) catalysts. Further, the Nicholas Group demonstrated that some of the $k$ variation in the literature is caused by Pt current collector enhancement and Si surface impurity impairment of the oxygen surface exchange reaction. The hypothesis of the present work is that differences in grain size, surface structure, and stress state are responsible for the rest of the $k$ variation and can be used to tailor the performance of $La_0.6Sr_{0.4}FeO_{3-x}$. This will be evaluated by (1) performing curvature relaxation measurements on samples with varying grain sizes and intentionally varied surface structures, (2) comparing global $k$ values from curvature relaxation to local $k$ values from secondary ion mass spectroscopy depth profiling, and (3) comparing the observed behavior to density functional theory–based models. This work will hopefully lead to improved solid oxide fuel cell, solid oxide electrolysis cell, gas-sensing, catalytic converter, water splitting, water purification, and other ion-exchange-enabled devices.

**Thin film diamond anvil cell studies to determine how deviatoric stress alters subducting slab phase transformations.** The mechanism(s) responsible for deep focus earthquakes are important for understanding the dynamics of mantle convection, subduction, and seismic hazards within the Earth. Although multiple mechanisms have been proposed to explain the existence, frequency, and source characteristics of deep focus earthquakes, no one mechanism is consistent with all the observations. The objective of the present work is to evaluate the hypothesis that a combination of geologically-relevant deviatoric stresses, preferred crystallographic orientation, and/or new metastable phases stabilize the olivine-structured $Mg_2SiO_4$ found within subducting oceanic crust. This will be achieved by using (1) using pulsed laser deposition to produce $Mg_2SiO_4$ thin films with intentionally varied crystallographic orientations, grain sizes, and deviatoric

**RESEARCH INTERESTS**
Solid state ionics, mechano-chemical coupling, solid oxide fuel cells, ceramic-metal joining, mineral physics

**LAB**
Solid State Ionics Laboratory (Energy and Automotive Research Laboratory, 1497 Engineering Research Court, Room 172)

**WEBSITE**
https://www.egr.msu.edu/nicholasgroup/index.php

**SPECIAL EQUIPMENT AVAILABLE**
Thin film deposition, controlled atmosphere/high temperature wafer curvature measurement

**GROUP MEMBERS**
Genzhi Hu, Yuxi Ma, Yubo Zhang, Quan Zhou

**RECENT PATENTS**


**CURRENT RESEARCH**
Understanding the factors controlling ion surface exchange in electrochemical devices. Solid Oxide Fuel Cells (SOFCs) have energy densities five times higher than the world’s best battery, efficiencies three times higher than the world’s best internal combustion engine, and NO, and SO$_2$ emissions 100

**FIGURE 1.** The Nicholas Group’s in situ wafer curvature measurement setup.
stress levels, (2) using in situ wafer curvature measurements to measure the deviatoric stress in each thin film sample outside of a diamond anvil cell versus temperature, and (3) using externally heated diamond anvil cell thin film Raman spectroscopy to observe the impact deviatoric stress and temperature have on the kinetics and thermodynamics of the Mg$_2$SiO$_4$ olivine to spinel phase transformation. In addition to providing new insights into the mechanisms responsible for deep focus earthquakes, the techniques developed here will allow mineral physicists to perform optically-accessible experiments under previously inaccessible stress states, demonstrate a new class of thin film pressure sensors, and show how geologically relevant high-pressure phases can be stabilized in thin film form for use in everyday devices.

**High performance circuit pastes for solid oxide fuel cell applications.** SOFCs are a unique green technology capable of providing improved efficiencies for today’s hydrocarbon-based economy while also providing a pathway to a CO$_2$-neutral future. Unfortunately, SOFC circuit paste degradation and delamination, especially upon thermal and/or redox cycling, is a major problem that can shorten SOFC lifetimes. Recently the Nicholas Group discovered that porous nickel interlayers could be used to promote the wetting and spreading of silver on a variety of ceramic substrates.

The objective of the present work is to find ways to modify that approach to produce resilient silver-based electrical circuits. If successful, this work will result in a new, cost-effective class of thick-film circuit pastes with lower sheet resistance, lower contact resistance, better redox cycling stability, better rapid thermal cycling stability and better adhesion to a variety of SOFC materials than today’s best commercially available contact pastes.

**Degradation and performance studies of ald-stabilized nano-composite solid oxide fuel cell cathodes.** Nano-composite SOFC cathodes produced by the infiltration and subsequent firing of nitrate solutions exhibit excellent performance. Unfortunately, significant amounts of high temperature infiltrate particle coarsening results in unacceptably high nano-composite cathode degradation rates. The objective of the present work is to use atomic layer deposition (ALD) to stabilize the performance of La$_{0.6}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$-Ce$_{0.9}$Gd$_{0.1}$O$_{1.95-\delta}$ (LSCF-GDC) cathodes developed by the Nicholas Group and previously shown to exhibit the world’s best low-temperature SOFC cathode performance of ~0.1 Ω cm$^2$ at 550°C.

**Figure 4.** Patterned Ag-Ni circuits on sapphire.

**Figure 5.** Microstructure of a LSCF-GDC nanocomposite cathode showing Mixed Ionic Electronic Conducting (MIEC) oxygen exchange catalyst on an Ionic Conducting (IC) scaffold.

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**Recent Publications**


RESEARCH INTERESTS
Transport phenomena (single phase and multiphase); rheology of suspensions, turbulent flows in rotating and nonrotating frames, hydrocyclone classifiers and separators, animal orientation and navigation, computational transport phenomena for undergraduates

CURRENT COLLABORATING STUDENTS
Andrew Bowden (Chemical Engineering, Undergraduate Professorial Assistant), Abdul Motin (PhD Candidate, Mechanical Engineering, A. Bénard, Advisor), Devinda Wijewardena (Chemical Engineering, Undergraduate Professorial Assistant).

CURRENT COLLABORATING FACULTY & COLLEAGUES
Dr. André Bénard (Mechanical Engineering, MSU), Dr. Farhad Jaberi (Mechanical Engineering, MSU), Dr. YoChan Kim (PhD 2006, MSU, Bechtel National), Dr. Karuna Koppula (PhD 2009, MSU, Rochester Institute of Technology), Dr. Vlad Tarabara (Environmental Engineering, MSU).

NSF INDUSTRY/UNIVERSITY COOPERATIVE RESEARCH CENTER, 2004–2011
C. Petty and A. Bénard, Founders and Co-Directors, Michigan State University, University of Tulsa, Central Florida University, University of Akron, Ansys, Bechtel, BP, CD-adapco, Chevron, ConocoPhillips, M-I Swaco, Petrobras, Pfizer, National Science Foundation, Department of Interior (MMS).

PATENT

CURRENT RESEARCH
Multiphase transport phenomena research and education. Multiphase fluids (i.e., drilling fluids, foodstuffs, pharmaceuticals, blood, liquid crystalline polymers, aerosols, fuel sprays, oil/water dispersions, solid/liquid suspensions, liquid/gas mists, and bubbly liquids) occur ubiquitously in many applications in engineering, polymer science, human medicine, and biology. Computational methods can provide significant insights related to the behavior of these fluids in extreme conditions and in complex geometries. Examples include hydrate formation in subsea pipelines; oil/water spills in the ocean; dust storms on Earth and on Mars; circulation of large scale ocean currents; mixing of pollutants in lakes and rivers; ice formation in the atmosphere; particle deposition in the lungs; and, effluent flows from hydrocyclone separators.

Flows of multiphase fluids 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 the further development and experimental validation of next generation multiphase transport phenomena closure models and the further development of computational transport phenomena methods for rapid analysis and design of processes with an emphasis on safety.

Turbulent fluctuations and bird navigation. The solution of the Reynolds-Averaged Navier-Stokes equation is the only viable means for simulating high Reynolds number flows typically encountered in engineering practice and in the troposphere. Research at MSU for the past 20 years has developed a realizable, algebraic Reynolds stress closure for rotating and nonrotating turbulent flows. The theory predicts the redistribution of turbulent kinetic energy among the three components of the velocity in simple mean shear flows (figure 1). The new approach is being used to analyze atmospheric scintillation of electromagnetic waves induced by the local coupling between the angular velocity of Earth and fluctuations in the turbulent velocity field. The relationship between scintillation phenomena and bird migration may provide an explanation of a longstanding question in biology: How do birds navigate over global scales?

Cross flow filtration hydrocyclone for liquid/liquid separation. A cross flow filtration hydrocyclone (CFFH) combines the desirable attributes of a vortex separator

| Turbulent Energy Distribution |

**FIGURE 1.** Redistribution of turbulent kinetic energy among the three components of the velocity in rotating shear flows (K. Koppula, PhD, Chemical Engineering, 2009, MSU).
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 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.

Multi-phase flows. 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 (figure 2) and flow through a bend (figure 3), deposition of particles on the walls is influenced significantly by streamlines curvature of the flow field.

**FIGURE 2 (right, top).** 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. (NSF/Combined Research and Curriculum Development Case Study. D. Eldein, S. Teich-McGoldrick, J. Roth, and C. Trainer. “CFD Simulation of a Pulsed-Jet Mixer,” Second Place Ribbon: Undergraduate Poster Session, Annual AIChE Meeting, 3–8 November 2002, Indianapolis, Indiana)

**FIGURE 3 (right, bottom).** Flow patterns through a bend (180°) 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 (P. Zhang, PhD, Mechanical Engineering, 2012, MSU).

**Recent Publications**


**RESEARCH INTERESTS**
Computational Materials Science, especially for Li ion batteries, oxide fuel cells, lightweight materials

**LAB**
Materials Simulation for Clean Energy (MSCE) Lab (Engineering Bldg., 428 S. Shaw Lane, Room 1105)

**WEBSITE**
http://researchgroups.msu.edu/msce

**SPECIAL EQUIPMENT AVAILABLE**
Dedicated computer clusters at the MSU High Performance Computing Center

**GROUP MEMBERS**
CURRENT: Min Feng, Yuxiao Lin, Jiyun Park, Hong-Kang Tian, Yuqin Wu, Dr. Michael W. Swift, Dr. Chi-Ta Yang.
RECENT ALUMNI: Tridip Das (Intel), Christine James, Kwang Jin Kim (Dongjin Semichem, Korea), Jialin Liu (3M), Joe, T. Phongpreecha (Stanford), Dr. Yunsong Li (Northwestern Polytechnic University, China).

**PATENT AWARDED**

**CURRENT RESEARCH**
At the Materials Simulation for Clean Energy (MSCE) Lab, Qi and her group develop multi-scale simulation methods to design materials atom by atom. We are interested in materials that deliver clean energy. In the last several years, research grants from NSF, DOE, MSU, and GM allow the MSCE lab to study anode and cathode materials for lithium ion batteries, design brazing alloys for solid oxide fuel cells, and predict the role of oxides in aluminum casting.

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). The multi-scale simulation tools we use and develop include: Density Functional Theory (DFT), large-scale molecular dynamics, reactive force field, parallel computing, phase field model, Mesodyn, coarse graining schemes, COMSOL, and finite element method. 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.

Currently, the ongoing projects include:

**Electron and ion transport in complex materials and interphases.** Defect-mediated diffusion greatly affects the power performance of battery and fuel cell devices. Using DFT informed thermodynamics formulation, we developed a systemic approach to predict ionic conductivity as a function of voltage, pressure, temperature in single and polycrystals. Recently, we developed a half-cell model for complex electrode/electrolyte interfaces enabled a bottom-up multiscale modeling approach for ion-transfer electrochemical reactions. Currently, these methods were used to understand and design high energy density cathode materials for Li-ion batteries, high energy density Li-metal batteries, all-solid-state batteries, catalysts for biomass production, and cathode with high concentration of oxygen vacancies to reduce the operating temperature of solid oxide fuel cells.

**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. We have used DFT to predict the elastic and fracture properties of electrode materials and their interfaces, then integrated these properties into continuum...
model to predict the lithiation-induced stress and failure of composite electrodes. Many of our predictions have been confirmed by in situ experiments.

For example, while silicon is highly desired as a high-energy anode, it poses severe degradation problems due to its large 300% volume expansion upon full lithiation. Thin protective layers are a promising approach to mitigate the resulting fracture mechanisms problems. Using continuous reactive molecular dynamics simulation of silicon nanowires and nanofilms coated by either Al2O3 or SiO2, we have shown that fast delithiation leaves appreciable lithium inside the nanowire and imposes a radial gradient in mechanical properties, while slow delithiation allows the nanowire to shrink and expel most of the lithium, but leaves defect structures that accelerate subsequent lithiation. These results provide guidelines for design and operation of silicon nanowire-based battery anodes.

**The impact of environment on forming and machining lightweight materials.** The environment (air, water, solution, electrolyte) can have a profound impact on deformation processes for lightweight metals (Al, Mg, Ta, Li …) that have a high affinity to oxygen. Similar impacts of the environment are seen for electrode materials. By developing a reactive molecular dynamics method, we are able to track chemical reaction and mechanical deformation simultaneously and investigate their competing effect.

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**RECENT PUBLICATIONS**


L. Nation, Y. Wu, C. James, Y. Qi, B. Powell, B.W. Sheldon, “Si-Doped high-energy Li2Mn0.54Ni0.46Co0.13O2 cathode with improved capacity for lithium-ion batteries,” *Journal of Materials Science* 33:24, 4182–4191 (2018).


A.P. Wang, S. Kadam, H. Li, S.Q. Shi, Y. Qi, “Review on modeling of the Solid Electrolyte Interphase (SEI) for lithium-ion batteries,” *npj Computational Materials* 4:15 (invited review, highlighted as one of the 10 ionizing papers in March 2018 by Research Interfaces)


RESEARCH INTERESTS
Biomolecular engineering and biotechnology, engineering education

LAB
Applied Biomolecular Engineering Laboratory (Engineering Building, 428 S. Shaw Lane, Room 2125)

WEBSITE
http://www.egr.msu.edu/abel/

SPECIAL EQUIPMENT AVAILABLE
Fluorescent and chemiluminescent imaging, cell culture facilities

GROUP MEMBERS
GRADUATE STUDENTS: Kevin Chen, Harrison Lawson, Chauncey Splichal, Daniel Vocelle. UNDERGRADS: Hannah Cavagnetto, McKenna Coskie, Emma Smith.

RECENT GRANTS
EAGER: “Biomanufacturing: CRISPR to increase the homogeneity and efficiency of stem cell differentiation.” AWARD #1547518, p.i.: Christina Chan; co-p.i.: Stephen Walton, organization: Michigan State University, CBET start date: 01/01/2016, award amount: $263,584.

CURRENT RESEARCH
One achievable goal of the 21st century is “personalized medicine,” the design of diagnostics and therapeutics specifically for a single patient. Reaching this goal depends on the development of new diagnostic approaches that can acquire vast quantities of data simultaneously, improving our understanding of the behavior of diseased cells, and therapeutics that can be delivered specifically to the diseased cells and can target the molecular-scale causes of the disease with exceptional activity and specificity.

The Applied Biomolecular Engineering Laboratory (ABEL), led by S. Patrick Walton, is currently working in both these areas, specifically on technologies that rely on nucleic acids (i.e., DNA and RNA). Areas of investigation include: (1) designing nucleic acid-based therapeutics based on understanding their mechanism of action, and (2) applying

FIGURE 1.
Confocal microscopy of delivery vehicle mediated silencing. Confocal images of cells (green) and fluorescently labeled siRNA (red) delivered by (A) a commercial reagent or (B) our nanoparticles.
genome editing to improve the understanding of cellular responses to stimuli. Recent work involves investigating how proteins interact with a new class of therapeutics, short, interfering RNAs, moving towards guidelines for designing these molecules. Additionally, the ABEL is applying CRISPR/Cas9 genome editing to manipulate stem cell responses to differentiation signals.

In collaboration with colleagues from the College of Education, Dr. Walton is examining how to apply the science of motivation to better understand engineering student success. It is his goal to expand the research on engineering student success beyond the typical metrics of persistence and GPA. Dr. Walton’s research will examine student success by many metrics to help the broader engineering community better understand how to support students with different short and long-term ambitions, ultimately enhancing the diversity of individuals and skills in the engineering workforce.

### RECENT PUBLICATIONS


RESEARCH INTERESTS
Multiphase biocatalysis, nanobiotechnology, biomimetic interfaces, biosensors, bioelectronics

LAB
Nanobiotechnology and Biomimetic Interfaces (Engineering Bldg., 428 S. Shaw Lane, Room 2525)

WEBSITE
http://www.chems.msu.edu/people/profile/worden?user=worden

GROUP MEMBERS
Serban Peteu, Neda Rafat, Paul Sharpe, Ziwie Wang

PATENTS

CURRENT RESEARCH
Multiphase biocatalysis. Focus includes developing cost-effective and carbon-neutral methods to produce biofuels and chemicals from high-energy gases such as hydrogen and carbon monoxide. His group has been funded by the NSF and DOE to use microbubbles to enhance gas mass transfer. In a recent project funded by DOE’s ARPA-E Electrofuels program, Dr. Worden’s lab collaborated with the group of Dr. Anthony Sinskey at MIT to develop a bioprocess for continuous conversion of the gaseous reactants \( \text{H}_2 \), \( \text{CO}_2 \), and \( \text{O}_2 \) into the biofuel isobutanol (IBT). To address the three significant bioreactor-design challenges: (1) extremely high demands for gas mass transfer; (2) safety issues resulting from the simultaneous use of by \( \text{H}_2 \) and \( \text{O}_2 \) gases, which form explosive mixtures; and (3) biocatalyst inhibition by the IBT, Dr. Worden’s group developed a novel Bioreactor for Incompatible Gases (BIG). The BIG features a hollow fiber module that allows the \( \text{H}_2 \) and \( \text{O}_2 \) gases to be kept on opposite sides of the membrane and transferred to the cells without forming unsafe gas mixtures. In addition, product inhibition is controlled by continuous removal of the IBT as it is formed. A prototype bench-scale BIG has been assembled in a walk-in hood, and an automatic process control system has allowed the bioreactor stably for up to 19 days. These experiments have demonstrated for the first time continuous IBT production from \( \text{H}_2 \), \( \text{CO}_2 \), and \( \text{O}_2 \).

Nanobiotechnology and biomimetic interfaces. This focus has recently been used to better understand cell toxicity caused by engineered nanomaterials (ENM). The approach uses an artificial bilayer lipid membrane (BLM) to mimic a cell membrane. When ENM interact with a BLM, pores are formed in the BLM, and the resulting leakage of ions through the pores can be measured. Dr. Worden’s group recently used electrochemical impedance spectroscopy to provide a sensitive method to measure ENM’s potency in disrupting biomembranes. One study showed that the method could discern differences in the potency of polystyrene nanoparticles (PNP) having different in size and surface charge. Negatively charged, carboxyl modified PNP 20 nm in diameter were more potent in disrupting BLM than positively charged PNP.
those 100 nm PNP. However, positively charged amidine modified nanoparticles, 120 nm PNP were more potent than 23 nm PNP.

**Biosensors and bioelectronics.** This focus is exemplified by a project funded by the NSF Accelerating Innovation Research program to advance a biosensor patent toward commercialization. The project addresses the need for more high-performance, inexpensive biosensors able to detect toxic organophosphorus pesticides and nerve agents. The objectives are (1) to adapt the redox-cycling biosensor interface to nanoparticle-functionalized electrodes, (2) to develop a redox-cycling biosensor interface for alkaline-phosphatase-linked antibodies, and (3) to adapt redox-cycling biosensor interfaces to three commercial biosensor platforms. Conductive nanomaterials are being incorporated into the bioelectronic sensor interface and functionalized to measure activity of a organophosphate as an electric current. Additional bioelectronic sensors are also being developed that use a redox-recycling mechanism to amplify biosensor signals that measure binding of enzyme-linked antibodies to their target antigen. A portfolio of potentially commercializable prototype bioelectronic immunosensors is being developed in collaboration with an original equipment manufacturer.

Dr. Worden has been active in leveraging research in these areas to develop novel educational programs that integrate multidisciplinary research with pedagogy. He has served as PI on two grants by the Department of Education’s Graduate Assistance in Areas of National Need (GAANN) program to develop graduate Ph.D. training programs entitled, “Interdisciplinary Training Program on Bioelectronics” (seven co-Is) and “Multidisciplinary Graduate Training Program on Technologies for a Biobased Economy” (seven co-Is). He also served as PI of a grant from the NSF Combined Research and Curriculum Development program to develop a novel “Multidisciplinary Bioprocessing Laboratory” course (five co-PIs). He and a colleague from the Michigan Biotechnology Institute were funded by the US State Department to co-develop a fermentation scale-up training program for Russian bioscientists entitled “Fermentation Pilot-Plant Training for Sibbiopharm Staff.”

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**RECENT PUBLICATIONS**


RESEARCH INTERESTS
Crystal growth; crystallography; thermal properties of materials, including thermal expansion, sound velocity, bond anharmonicity

LAB
Advanced Materials for Thermal Energy Conversion and Storage (Engineering Bldg., 428 S. Shaw Lane, Room 2530)

WEBSITE
https://alexzevalkink.wordpress.com
YouTube channel: “Zevalkink Research Group”

SPECIAL EQUIPMENT AVAILABLE
Optical floating zone furnace for crystal growth up to 2200°C; resonant ultrasound spectroscopy for measurement of elastic constants and sound velocity up to 500°C in controlled atmosphere; high-resolution, high-speed x-ray diffractometer with 2D pixel array detector, and high-temperature stage with controlled atmosphere up to 1400°C.

GROUP MEMBERS

RECENT GRANTS
NASA-JPL: High-temperature structure and bonding in Zintl thermoelectrics, $203,000, start date 01/08/18.

NSF-DMR SSCM, Traveling solvent crystal growth of anisotropic Zintl thermoelectrics, $328,750, start date 8/16/17, award #1709158

CURRENT RESEARCH
Out research leverages crystal growth and high-temperature characterization techniques to study the relationship between atomic structure, bonding and the electronic and thermal properties of functional materials. Ultimately, we aim to apply this understanding to engineer improved functional materials for energy applications. Our recent efforts have focused on crystal growth using optical floating zone, flux, and Bridgman methods, and on measurements of the high-temperature sound velocity and lattice expansion in materials used for thermoelectric energy conversion.

Crystal growth of anisotropic materials. Our current aim is to develop improved thermoelectric materials for use in radioisotope thermoelectric generators designed and tested at NASA’s Jet Propulsion Laboratory. The thermoelectric materials used in this application must be semiconductors with very high melting temperatures, optimized electronic properties, and low thermal conductivity. They must also be mechanically robust over a large temperature gradient.

Many candidate materials have atomic structures that are extremely anisotropic, and are therefore predicted to have more favorable electronic properties along specific crystal orientations, as illustrated in figure 1 for Ca₅Al₂Sb₆. This anisotropy is expected to lead to improved thermoelectric properties along the high conductivity direction. One of the most significant barriers, however, to understanding the intrinsic electronic and thermal properties of complex semiconductors is the scarcity of large single crystal samples. This is particularly limiting in the case of anisotropic materials, for which measurements of bulk, single crystalline samples yield only “averaged” properties.

In our laboratory, we are utilizing several high-temperature techniques to grow single crystals of semiconducting and ceramic materials from the melt. Our main focus is optical floating zone growth, illustrated in figure 2, which is a powerful method for materials with very high melting temperatures and relatively low vapor pressures. An optical floating zone furnace consists of several halogen lamps set in elliptical mirrors (four, in our case). The mirrors focus the light on the center of the chamber, where two polycrystalline rod-shaped samples are suspended inside of an inert gas-filled quartz tube. A stable “floating” molten zone is established where the two rods meet. During growth, both rods are moved downwards, so that the floating zone
slowly progresses up the length of the feed rod. This method can also be adapted to materials with incongruent melting behavior by employing a molten flux (i.e., solvent material) instead of melting the target compound.

**Resonant ultrasound spectroscopy.** The thermal and elastic properties of materials are critical in a wide range of applications. Resonant ultrasound spectroscopy (RUS) is an elegant approach to characterize the elastic constants of bulk and single crystal samples by measuring the vibrational resonant frequencies. This method is also ideal for measuring the full elastic tensor of anisotropic single crystals, as the entire tensor is obtained in a single measurement. High-temperature RUS measurements coupled with high temperature x-ray diffraction—also available in our laboratory—gives us an extremely sensitive set of tools to investigate structural changes in materials, including gradual softening of bonds, order-disorder transitions, and structural phase changes.

**FIGURE 2.** (A) Screen-shot from the growth of a TiO$_2$ crystal using the optical floating zone method. (B) Schematic of the interior of a floating zone furnace showing the sample mounted inside of an evacuated quartz tube. Light from four halogen bulbs is focused on the center of the sample, creating a floating molten zone.

**FIGURE 3.** The resonant ultrasound method uses a piezoelectric transducer to emit acoustic waves over a range of frequencies. Certain frequencies will resonate strongly in the sample, yielding a vibrational response that is detected by a second transducer. This method allows us to study the elastic tensor of single crystals and polycrystalline materials at room temperature and at high temperatures.

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**RECENT PUBLICATIONS**


A. Zevalkink, M. Bobnar, U. Schwarz, Y. Grin, “Making and breaking bonds in superconducting $\text{SrAl}_{4-x}\text{Si}_x$ ($0 \leq x \leq 2$),” *Chem. Mater.* 29, 1236–1244 (2017).