

Spring 2018

IMR Kickstart Facility Grants Awards



Ten new research projects were awarded by the IMR for a total investment of \$25,000 in support of innovative materials research. These ten projects support seventeen researchers from eight different departments within the College of Engineering, College of Arts and Sciences, College of Public Health and College of Food, Agricultural, and Environmental Sciences.

Quantification of the Susceptibility to Ductility Dip Cracking in Austenitic Alloys

Principal Investigator: Boian Alexandrov, Materials Science and Engineering; Co-Investigator: Samuel Luther, Materials Science and Engineering

Ductility dip cracking (DDC) in face-centered cubic (FCC) alloys, such as nickel-based alloys and 300 series stainless steels, is a challenge facing several industries, and a unified mechanism for DDC has been elusive. One key industry experiencing DDC problems is nuclear power generation, where aging reactors need to be repaired via large, multipass weld overlays designed to mitigate underlying damage from primary water stress corrosion cracking (SCC). DDC often occurs in the first few layers of these overlays, and a high-risk industry like nuclear has very low flaw tolerance, making even small DDC subject to costly repair and rework. Basically, materials susceptible to DDC experience an anomalous intermediate temperature (~ 0.6 - $0.8T_M$) ductility loss that can result in cracking if sufficient restraint is applied. There are several damage mechanisms sometimes associated with these alloys that may need to be balanced with DDC, including solidification cracking and SCC. The ideal alloy would have resistance to all three types of failure. The prevailing theory describing DDC is based on observations of grain boundary (GB) sliding, microvoid formation, and the effect of GB tortuosity. However, it is mostly phenomenological, and there is not yet a firm consensus on the role that impurities play, whether they initiate or exacerbate DDC. This work aims to advance fundamental understanding of DDC by clarifying the role of impurities and further develop a more mechanistic theory. To expand on this, several experiments have been devised to test the hypothesis that GB sliding is initiated by a critical strain level and temperature leading to localized thermal faceting and decohesion which may be influenced by the impurities sulfur and/or oxygen. Experimentation began with initial Gleeble™-based testing procedure designed to replicate the thermo-mechanical histories in multilayer overlays. 52M Ni-based filler metal and 310 stainless steel (SS) were both tested to demonstrate applicability of the test procedure across two different DDC-susceptible alloy systems. Thermal faceting has been observed on DDC fracture surfaces produced in preliminary testing. The features are small, necessitating the use of high-resolution electron microscopy to observe them. Samples from

this testing as well as previous experiments carried out at OSU will be used in characterization work to produce new microstructural results. Failed samples from laboratory work as well as actual failed samples will be used in failure analysis and fractography for validation. Future work will involve the development of a computational model to assist in strain quantification and continuing to develop the experimental procedure utilizing both high-purity and sulfur/oxygen-containing austenitic alloys. Additional characterization of the fracture surface is needed. To aid in assessing the role impurities play in DDC, chemical analysis of the fracture surfaces will be completed. Furthermore, the literature has shown impurities may induce crystallographic changes in localized GB regions, which is verifiable through EBSD and TEM SAD.

Tailoring Catalyst Surface Morphology for Highly Efficient Ethanol Steam Reforming

Principal Investigator: Robert Baker, Chemistry and Biochemistry

The design of highly selective catalysts for use in complex, multipath chemical reactions is a pressing challenge with important applications in energy conversion and storage. To accomplish this goal requires the ability to engineer surfaces to optimize a catalytic reaction based on detailed understanding of the surface reaction mechanism. Ethanol steam reforming (ESR) refers to the process by which ethanol is oxidized by water to produce CO₂ and H₂. Efficient catalysts for this reaction would enable energy to be stored at high volumetric densities in the form of liquid ethanol and then converted onsite to H₂ gas for fuel cell applications. Nickel is the catalyst of choice for this reaction but suffers from poor selectivity and fast deactivation. The performance of nickel can be improved by the addition of a CeO₂ co-catalyst, but the mechanism for observed performance enhancement remains unclear. We propose to demonstrate that the kinetics of this reaction depend strongly on the morphology of the Ni–CeO₂ interface, opening exciting possibilities for the tailored design of engineered surfaces to optimize this reaction. We have recently demonstrated the ability to synthesize CeO₂ nanocubes that serve as co-catalysts for surface chemical reactions of interest, including ESR. These catalyst/co-catalyst systems consist of 2-dimensional films of CeO₂ nanocubes deposited on a planar metal surface. Surprisingly, we find that the long-range order of these 2D films has a dominate effect of the net performance of the catalyst system. Mesoscale refers to features of a material that range in size from tens to hundreds of nm. Because this is length scale is much large than the molecular scale it has been largely ignored in mechanistic studies. Additionally, many spectroscopic probes are blind to features of this size range, making this structural length scale a relatively unexplored frontier in catalysis science. Recent observations by our group reveal that this length scale can have an unexpectedly dramatic effect on material performance for selective catalysis, motivating further studies of this phenomenon for additional energy conversion reactions. ESR is one such reaction that is expected to depend strongly on mesoscale morphology but which has not yet been investigated. Here we propose to combine existing expertise in the patterning of surfaces on the nano and mesoscale with state-of-the-art surface spectroscopy uniquely available at Ohio State to answer critical questions about the mechanism of ESR on bifunctional surfaces. This Kickstart Award is requested to support

electron microscopy analysis of these materials in CEMAS in order to correlate these reaction kinetics and surface spectroscopy with detailed characterization of surface morphology. We anticipate that these results will reveal key parameters in the design of tailored surfaces for catalytic ESR applications and lead to one or more externally funded research projects in this exciting area.

Evaluation of fungal growth in household products

Principal Investigator: Karen Dannemiller, Civil, Environmental and Geodetic Engineering, Environmental Health Sciences; Co-Investigators: Natassia Brenkus, Civil, Environmental and Geodetic Engineering; Marcia Nishioka, Civil, Environmental and Geodetic Engineering; Chad Rappleye, Microbiology; Thomas Mitchell, Plant Pathology

We spend 90% of our time indoors where we are exposed to diverse microbial communities. This exposure can impact our health and - potentially - the structural integrity of our homes. For instance, exposure of asthmatics to mold in housing costs \$3.5 billion in the US each year. Additionally, home damage due to flooding and fungal growth cost \$9.1 billion in insurance claims from 2007 to 2009, and this number may rise with increased extreme events due to climate change. Additionally, microbes may interact with products in our home to release harmful chemicals. However, the mechanisms and consequences of this growth are often unknown. Our recent work has demonstrated that fungal growth in dust has the potential to be a substantial source of human exposure to harmful organisms¹, but this growth has been under-characterized. Additionally, more research needs to be done to characterize fungal growth rates on wood to determine the impact on structural integrity. The goal of this work is to collect preliminary data to support future proposal to study fungal growth in the home environment. We will achieve this through the following objectives: (1) Characterize fungal growth in house dust, (2) Characterize fungal growth on polyurethane foam and release of carcinogenic 2,4-DAT, and (3) Identify the impact of fungal growth on wood structures in the home after flooding events. We will utilize the SEM in the CEMAS facility to collect images of fungal colonization of substrates in all these systems. Materials will be incubated to support growth in the laboratories in Hitchcock and brought to CEMAS for analysis by students. Solutions to ameliorate fungal growth and their effects in the home environment will likely involve innovations in materials research. However, prior to development of new materials, we need to better understand how this fungal growth will impact any proposed systems.

Insight into liquid metal embrittlement in the Fe-Zn and Fe-Cu systems

Principal Investigator: Carolin Fink, Materials Science and Engineering; Co-Investigators: Dean Sage, Materials Science and Engineering

Liquid metal embrittlement (LME) can be described as grain boundary penetration of a high melting point metal by a liquid metal with a lower melting point. The subsequent ductile-to-

brittle transition can result in brittle intergranular cracking, occasionally through the thickness of the material. LME has been reported to occur in a wide variety of solid metal/liquid metal couples, and can severely interfere with the service integrity of metallic parts. Prominent examples exist in energy and traffic infrastructure. The central problem in LME is the role of solute atoms interfering with cohesion of the grain boundary interface. The majority of work has been done on embrittling solutes at room temperature (Al-Ga, Ni-Bi). Gaining mechanistic insights into cases of LME occurring at elevated temperatures, such as in the Fe-Zn and Fe-Cu systems is much more challenging, and the focus of in-situ investigations pursued in an upcoming grant proposal to an external funding source. IMR facility funding is sought for initial ex-situ advanced characterization on iron (steel) grain boundaries with zinc and copper solute penetration. The goal is to identify the ensuing changes to grain boundary structure, melting behavior, and grain boundary phase transitions. This serves as a critical first step towards fundamental knowledge of the embrittling process.

Preparation and Characterization of Magnetic Tips for Spin Polarized Scanning Tunneling Microscopy

Principal Investigator: Xun Liu, Welding Engineering Program, Material Science and Engineering

Multi-material structure is one of the key enablers for modern lightweight vehicles. Accordingly, development of reliable, economical and efficient dissimilar material joining technologies is of great practical value. Ultrasonic welding as a solid state joining method has several inherent advantages, particularly in restraining formation of brittle intermetallic compounds. However, due to the limited power of generally available ultrasonic transducers, currently its application is restricted to thin gage sheets and the welded materials are relatively soft. Moreover, the ultrasonic vibration can only be applied in a lateral configuration. In this study, resistance spot welding is proposed to be combined with ultrasonic spot welding process. The additionally introduced electrical current softens the material and allow effective delivery of ultrasonic energy into the weld zone. This greatly enhance the capability of current ultrasonic welding process and favorably maintains the solid-state nature of the process. In this project, the proposed innovative ultrasonic resistance spot welding (URSW) process will be applied for joining aluminum alloy to advanced high strength steel. To understand the combined effects of ultrasonic vibration and electrical current on formation of the dissimilar material joints, multi-scale characterization of the weld will be performed, particularly at the interface. Scanning electron microscope (SEM) with energy dispersive spectroscopy will be employed for analyzing the morphology and compositions of the interfacial layer. More intricate features unresolved by SEM will be further analyzed using transmission electron microscope. Finally, a comprehensive relationship between process conditions, weld microstructure and joint properties will be established.

Organic Redox Relay Flow Batteries for Energy-Dense, Grid-Scale Storage

Principal Investigator: Christo Sevov, Chemistry and Biochemistry

Large-scale penetration of electricity from renewable sources into the electrical grid has yet to be realized because technologies that can modulate the intermittence and variability of solar or wind energies are lacking. Redox flow batteries (RFBs) have attracted attention as a solution to grid-scale storage because they can be inexpensively scaled by simply adding redox liquids to large reservoirs. Because of this flow architecture, identifying redox-active solutions that are inexpensive, yet energy dense, is critical to the deployment of RFBs. However, RFBs remain nearly an order of magnitude more expensive than what is necessary for cost-competitive energy storage. The proposed work addresses fundamental limitations to current grid-scale batteries by conceptually redesigning energy storage in flow. Here, redox-active organic solids (ROSs) will serve as storage materials. Rather than forcing these solids to undergo redox directly at the electrode, small quantities of solvated redox-active organic molecules (ROMs) will relay electrons between the ROSs and the distal current collectors. This redox *relay* flow battery will be scalable, have high energy density, and be tunable because of the organic materials. Moreover, this design will provide the disruptive advance to flow storage that years of RFB research has failed to yield.

Measuring Tumor Extracellular Matrix Dynamics with Molecular Scale Force Spectroscopy

Principal Investigator: Jonathan Song, Mechanical and Aerospace Engineering; Co-Investigator: Carlos Castro, Mechanical and Aerospace Engineering

The mechanical properties of the tumor extracellular matrix (ECM) play an important role in cancer progression. Hence, dynamically measuring the local changes in the mechanical and rheological properties of the ECM is crucial for the prognosis and diagnosis of cancer. Despite previous efforts that have been made to monitor these changes using different techniques, such as Atomic Force Microscopy (AFM) and Multiple Particle Tracking (MPT), reliably measuring the local changes from the same sample in 3D space remains very challenging. In order to address this challenge, we developed a DNA origami-based nanorheology sensor (NRS) to monitor the changes in the mechanical and rheological changes in the ECM. The readout of the NRS is obtained by Förster resonance energy transfer measurements and we have previously demonstrated that the devices are sensitive to sub-piconewton changes in depletion forces in poly(ethylene glycol) (PEG) hydrogel. Here, we propose to broaden the application of our NRS by verifying the stability, distribution, and performance of our NRS in biological 3-D ECM such as collagen and hyaluronan using transmission electron microscopy and confocal reflectance microscopy. These studies will help enable dynamic rheological characterization of the ECM with potentially unprecedented time and length scales.

Analysis of the chemical compositions of tomato fruit cuticle by using UPLCMS and GC-MS for plant health and quality

Principal Investigator: Ye Xia, Plant Pathology

The plant cuticle is the outermost layer of the plants and provides the physical barrier to protect plants from the biotic and abiotic stress, such as the UV light, drought, cold, pathogens, and pests. The cuticle includes two main components-cutin and wax. The cutin of most plants contains the C16 and C18 esterified and oxygenated fatty acids and small amounts of glycerol, phenyl-propanoids, etc. The cuticular waxes are complex mixtures, which consist of different kinds of primary and secondary alcohols, ketones, alkanes, aldehydes, and esters derived from very-long-chain fatty acids (VLCFAs; C20–C34). More and more research has been carried out to discover the active roles of plant cuticle in plant defense against bacterial and fungal pathogen infections, which includes both basal and systemic defense. However, the detailed mechanisms are still not well known. Recently we find one member of hydrolase family (GHR) of tomato plants, which plays critical roles in tomato cuticle formation for both leaves and fruits and protects the tomato plants from bacterial and fungal pathogen infection and water loss. The goal of this proposal is to apply different metabolomics approaches including UPLC-MS and GC-MS to test the chemical compositions of the fruit cuticle peel of the tomato GHR RNAi silencing plants that have defects in this gene function related with the cuticle formation, water retention, and disease resistance compared with wild type plants. Our study will include both targeted and untargeted metabolites test through comparative metabolomics analyses. The outcome of the project will significantly improve our understanding of the related gene function and metabolites involved in tomato fruit cuticle formation and related plant resistance to pathogen and drought stress. The result will be very informative for us to identify certain specific targeted metabolites and related pathways, so that make more precise hypothesis. And the data will be used as preliminary data to apply for external larger grants. Ultimately, the project will also provide valuable information to develop the breeding and biotechnology approach to improve tomato plant cuticle function and defense against both biotic and abiotic stress during plant growing season and also at the post-harvest transportation and storage stage, which may significantly reduce the tomato yield and economic losses and improve the tomato health, yield, quality, and economic values as a very important crop with high nutrient levels and \$2 billion in the annual sale in USA.

Fast Charging Thiazyl Radical Battery

Principal Investigator: Shiyu Zhang, Chemistry and Biochemistry

Conversion and storage of renewable energy to electrical power are key challenges across the world for realizing net zero carbon emission. While modern electrical energy technologies have led to significant breakthroughs in generating energy from renewable sources, the storage of this energy generated by renewable means fails to progress at the same rate. The mismatch between

energy generation and storage results in considerable inefficiency in the handling of energy. On a smaller scale, further breakthroughs of secondary batteries are required to fulfill the future desires for hybrid electric vehicles (HEV) and full electric vehicles (EV). Powering electric vehicles for long-distance travels remains difficult with the sluggish charging rate of 30-80 miles/hour, almost two orders of magnitude slower than a gas- or diesel-engined car (ca. 300 miles / 3 minutes filling time). With the driving range of commercial EV now approaches 270-300 miles, the slow charging rate, rather than the specific energy capacity of secondary batteries, has become the most pressing problem that electric vehicle industry faces today. The objective of this proposal is to increase the charging rate of secondary batteries by developing alternative electrode materials. The central hypothesis is that intrinsic conductivity organic radical electrode material will significantly enhance the charging rate of lithium ion battery. This project will provide fundamental science required for more economical routes to various alternative battery materials. Potential discoveries from the proposed research will interest the battery manufacturing industry as well as funding agencies including the National Science Foundation (NSF) and Department of Energy (DOE).

Structural Characterization of Silver-DNA Supramolecular Assemblies and Nanoparticles

Principal Investigator: Yuyuan Zhang, Chemistry & Biochemistry

Nucleobase monomers can self-assemble in aqueous solution to form long fibers with diameter of tens of nanometers and length on the scale of micrometers in the presence of silver ion (Ag(I)). Ag(I) associates two nucleobases to form a dimer, which in turn stack with other subunits via π -interaction, forming a supramolecular structure. Upon chemical reduction of Ag(I) , DNA-mediated Ag(0) nanoparticles which have tunable plasmonic resonance can be prepared. We seek to understand how the structure influences the photophysics of these supramolecular assemblies and nanoparticles using femtosecond transient absorption spectroscopy probing the electronic and vibrational resonances. Obtaining information on the structure of these assemblies is the crucial first step towards our goal. We plan to alter the experimental conditions such as temperature, pH and alcohol concentration, as well the identity of the nucleobases, in order to break the large structure into smaller subunits. By “peeling the layers of the onion”, we aim to identify the fundamental interactions that control the photophysics. We plan to utilize the imaging capabilities in IMR facilities to thoroughly characterize the materials prepared under different conditions. Obtaining information on length, diameter, morphology, and possibly stacking motif(s) of the Ag-nucleobases assemblies are the goal of this proposal.