8th Annual ChEGSA Research Symposium

List of Speakers

Advanced Materials and Catalysis

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Advanced Materials and Catalysis

Jia Quan Su - 9:45 to 10:00 AM

Copper is an essential material used in Nano and microelectronics. Electromigration failure is a major challenge on the reliability of interconnection copper lines. Electromigration stress causes void formation and merging in the copper line, which eventually leads to the line failure phenomena with an abrupt increase of the line resistance. However, copper lines without a passivation layer are subject to oxidation in air. Therefore, passivation is usually applied in complicate interconnection structures. In this research, authors studied the electromigration phenomena of copper lines with a self-aligned copper oxide passivation layer. A smooth copper oxide passivation layer is generated by plasma oxidation in a parallel plate plasma reactor under plasma etching mode. Reliability of copper lines with and without passivation layer are evaluated by the electromigration stress method. Void formation is analyzed by dark field microscopy. Grain boundary depletion and grain thinning are the main pathways of void formation. In addition, bulk copper film thickness is a critical factor which affects the lifetimes of copper fine lines. Copper oxide passivation layer could getter copper atoms from diffusing to adjacent layers. Copper oxide has the potential to be an important passivation material for copper interconnection in electronic devices.

Anubhav Sarmah - 10:00 to 10:15 AM

Our research demonstrates a new method for curing thermosetting resins using localized Radio-Frequency heating in a thermosetting resin bath. Multi-walled carbon nanotubes are used as fillers in the resin to make it responsive to an RF field, thus allowing for heating and curing of the resin. The RF power can be modulated to maintain a target epoxy curing temperature. An RF applicator generates a fringing electric field, which heats and cures the nano-filled resin exposed to the field and allows for localized curing of the resin. The RF applicator was moved relative to the resin bath at a calculated scan speed to print simple 1D and 2D structures. Thermal and mechanical properties of these RF printed samples were compared against: (i) RF-printed samples followed by post-curing in an oven, and (ii) samples conventionally cured in an oven. Characterization of cured samples showed comparable Glass Transition Temperatures and Storage Moduli for the samples cured using the mentioned three methods. This method of curing thermosetting resins using RF heating allows for rapid, free-form processing of such resins without a mold, in contrast to conventional oven curing.

Nagat Elrefaei - 10:15 to 10:30 AM

The most commercial routes to convert natural gas (mainly methane) to chemicals start with the steam methane reforming or partial oxidation of methane, which produce a substantial amount of CO2 mainly as a product of the reaction stoichiometry. Thus, it is important to identify a conversion route that does not produce CO2 as a main product from the reaction stoichiometry. One promising route is the direct conversion of natural gas to aromatic products which is known as the methane dehydroaromatization process (MDA). The catalytic reaction takes place over a heterogeneous catalyst (the commonly used is Mo/ZSM-5). During the reaction, a high reaction temperature is required to break the methane C-H bond followed by C-C coupling to produce aromatics; mainly benzene, naphthalene, and hydrogen. However, this process is hindered from commercialization by many limitations. A major one is the thermodynamic challenge which allows a single-pass methane conversion of about 10-20% at a very high reaction temperature (700-800℃). Another limitation is the rapid deactivation due to coke accumulation on the catalyst which inhibits the continuity of the process. One way to overcome the deactivation challenge is to introduce other molecules to the system to balance the rate of deactivation with the rate of regeneration simultaneously to ideally reach a continuous operation process. In this work, we will present the results of our studies on the effect of introducing different molecules into the system through various feeding modes (continuous, periodic, and pulse) and identify the most effective reaction conditions.

Niranjan Sitapure - 10:30 to 10:45 AM

Li metal anode is the 'Holy Grail' material of advanced Lithium-ion-batteries (LIBs). However, it is plagued by uncontrollable dendrite growth resulting in poor cycling efficiency and short-circuiting of batteries. This has spurred a plethora of research to understand the underlying mechanism of dendrite formation. While experimental studies suggest that there are complex physical and chemical interactions between heterogeneous solid-electrolyte interphase (SEI) and dendrite growth, most of the studies do not reveal the mechanisms triggering these interactions. To deal with this knowledge gap, we propose a multiscale modeling framework which couples kinetic Monte Carlo and Molecular Dynamics simulations. Specifically, the model has been developed to account for (a) heterogeneous SEI, (b) dendrite-SEI interactions, and (c) effect of electrolyte on Li electrodeposition and potential dendrite formation. This allows the proposed computational model to be extended to various electrolytes and SEI species and generate results consistent with previous experimental studies. –

Muhammad Anas - 10:45 to 11:00 AM

Silicon carbide (SiC) is a valuable material due to its low density, high thermal stability, and semiconducting properties. Preceramic polymers, such as polycarbosilane (PCS), are now being used to make SiC due to the ease of processing and low synthesis temperature requirements. However, polymers need to go through several steps such as crosslinking, pyrolysis, and sintering before SiC is formed which can be time consuming and energy intensive. In this work, we show one-step rapid synthesis of β-SiC using laser-induced pyrolysis of PCS. We confirm using experiments and molecular dynamics simulation that the oxide impurities can be reduced by lasing in the inert environment. We also show formation of patterned dense and hard SiC and SiC-SiC coatings as well as electrically conductive SiC-graphene composites. The findings are important for nuclear as well as energy applications.

Ahmed Badreldin - 11:00 to 11:15 AM

Hydrogen gas (H2) is a clean fuel that produces only water when combusted and it can be produced by utilizing renewable energy sources such as geothermal, solar, or wind energy to split water. The continuous decrease in cost of electricity produced by solar PV and wind combined with the urgent need for reduction of CO2 emissions, creates a vast economic opportunity for H2 production by water and saline water electrolysis. A few well-defined challenges, predominantly sluggish oxygen evolution reaction (OER) kinetics and competing chlorine evolution reaction (CER) at the anode, still limit the applicability of this green hydrogen technology commercially. Herein, we report the facile and swift fabrication of a S,B-codoped bimetallic (CoFe) oxyhydroxide guided by the solution combustion synthesis (SCS) for the OER with apparent CER suppression abilities. The as-prepared S,B-(CoFe)OOH-H attained ultra-low overpotentials of 161 and 278 mV for achieving current densities of 10 and 1000 mA cm-2, respectively, in alkaline saline (1M KOH + 0.5M NaCl) electrolyte; making this electrocatalyst the second-most active reported to date amongst thousands others developed in literature. A low Tafel slope of 46.7 mV dec-1 correlates to the fast kinetics of the electrocatalyst. Chronoamperometry (CA) testing of the c-doped bimetallic oxyhydroxides showed very stable behavior in harsh alkaline saline (4M KOH + 0.5M NaCl) and in neutral saline (1M PB + 0.5M NaCl) environments. Chloro-reaction products were quantified during CA testing at 470 mV of overpotential in order to be over the thermodynamic triggering limit for CER in neutral saline media. The S,B-(CoFe)OOH-H oxyhydroxide showed a notable decrease in CER production in comparison with its other S,B-codoped counterpart. Moreover, systematic testing in electrolytes from pH values of 14 to 7

yielded promising results which bring closer the realization of direct seawater electrolysis at near-neutral pH conditions. This study provides a simple and straightforward approach towards rationally designing and thoroughly testing anodic electrocatalysts which we believe can aid in future works pertaining to saline and seawater electrolysis. It is our belief that this is a pivotal step towards the advancement and realization of seawater electrolysis as a viable commercial technique for hydrogen production.

Purbjoa Purkayastha - 11:15 to 11:30 AM

The physical properties of biomaterials – such as stiffness or nanostructure- are commonly tailored to direct cell functions in diverse applications. While biochemically induced laboratory cellular evolution is well established, no studies have examined whether population of cells can evolve in response to selection pressure imposed by the physical properties of biomaterials. Here we found that genetically variable populations of fibroblasts increased in fitness upon sustained culture on novel soft biomaterial substrates, whereas clonal populations did not. Whole exome-sequencing combined with simulations of experimental evolution revealed that cells evolved by natural selection and not random drift. Novel cell phenotypes were observed on the soft substrate upon evolution, and different replicate lines evolved the same phenotypes through distinct patterns of gene expression. These results suggest that laboratory cellular evolution on biomaterials is a powerful untapped approach that can be used to generate cell populations with novel genetic and phenotypic properties.

Suyash Oka - 11:30 to 11:45 AM

Structural energy storage requires batteries with good energy storage properties as well as mechanical properties. This technology may lead to substantial mass and volume savings in electric automobiles, cube satellites, and aerospace applications by storing energy within the body panels of the vehicle. However, most studies on structural energy storage focus on conventional cathode materials such as lithium iron phosphate (LFP), lithium cobalt oxide (LCO) or nickel manganese cobalt oxide (NMC). These materials possess potential hazards to the environment and are significantly reliant on the volatile metal market that leads to economic fluctuations commercially. Organic radical polymers are a promising alternative because they are environmentally benign, recyclable, and their availability is independent of the metal markets. They also exhibit rapid charge transfer ability, and good cycling stability. In this work, we report for the first time, structural cathodes using organic redox active polymers such as PTMA (poly (2,2,6,6-tetramethyl- piperidenyloxyl-4-yl methacrylate)) as the electrochemically active material. A one-step, carbon-compatible thermal cross-linking method is carried out to significantly inhibit PTMA's dissolution in the electrolyte. PTMA slurries are coated on reduced graphene oxide (rGO)/branched aramid nanofiber (BANF) supports. The rGO/BANFs composites provides structural support and improved adhesion while also acting as current collector. The effect of cross-linking agent content on the electrochemical and mechanical performance is investigated. This work provides a pathway for utilising environmentally benign polymers in structural lithium-ion batteries.

Safety Engineering

Zhuoran Zhang - 2:10 to 2:25 PM

Liquefied natural gas (LNG) is widely used to cost-effectively store and transport natural gas. However, a spill of LNG can create a vapor cloud, which can potentially cause fire and explosion. High expansion (HEX) foam is recommended by the National Fire Protection Association (NFPA) 11 to mitigate the vapor hazard and control LNG pool fire. In this study, the parameters that affect HEX foam performance were examined using lab-scale testing of foam temperature profile and computational fluid dynamics (CFD) modeling of heat transfer in vapor channels. LNG leakage was simulated using liquid nitrogen due to the similar boiling point of liquid nitrogen compared to methane (i.e., the main component of LNG). A lab-scale foam generator was used to produce HEX foam and carry out experiments to develop the temperature profile in the foam. Based on the experimental results, the heat balance between HEX foam and vaporized gas was determined, and a heat transfer model using ANSYS Fluent® was developed to estimate the minimum HEX foam height that allows the vapors from LNG spillage to disperse rapidly. Finally, we performed a sensitivity analysis on the effect of the vaporization rate, the diameter of the vapor channel, and the heat transfer coefficient on the required minimum height of the HEX foam using the heat transfer model. It can be observed that at least 1.2 meters of HEX foam in height are needed to achieve risk mitigation in a typical situation. The simulation results can be used not only for understanding the heat transfer mechanisms when applying HEX

foam but also for suggesting to the LNG facility operator how much HEX foam they need for effective risk mitigation under different conditions.

Bhavana Bhadriraju - 2:25 to 2:40 PM

Fault prediction has arisen as a basic monitoring strategy that predicts an abnormal event occurring in near future based on the current symptoms observed in a process. Such a proactive approach helps in taking an appropriate action beforehand so as to mitigate the impact a fault can have on a process. Recently, data-driven modeling techniques have been widely used due to an increased accessibility to process data. Though the offline trained models are successful in modeling complex dynamics, they have limited ability in capturing the dynamic process behavior, especially under abnormal conditions. In particular, chemical processes do not necessarily operate within the pre-characterized conditions and can undergo various abrupt changes such as throughput fluctuations and parametric drifts. In such circumstances, it is useful to implement an adaptive predictive monitoring scheme that can cope with any dynamical changes and predict the process accurately. Therefore, we utilize an adaptive modeling technique called operable adaptive sparse identification of systems (OASIS) that can cope with abrupt system changes. Based on the forecasted process behavior using OASIS, we perform risk-assessment to predict faults and assess risk. In the proposed method, risk is used as a criteria to monitor and manage process operation. For demonstration purposes, we consider two case studies, a non-isothermal continuous stirred tank reactor (CSTR) and a gas-phase polyethylene reactor. The proposed method successfully predicted a process fault earlier than it becomes functional.

Pallavi Kumari - 2:40 to 2:55 PM

Computational fluid dynamics (CFD) models have been widely used in the chemical process industry to analyze various aspects of high-consequence rare events. Since CFD models solve a set of coupled differential equations, they are computationally intensive in nature. Therefore, several developments have been made in building computationally efficient models. The existing computationally efficient models in the field of high-consequence rare events are temporally static in nature and do not represent system evolution with time, which is crucial for consequence modeling of rare events. Further, the consequences depend on various parameters in addition to inputs. It is to be noted that the input may vary with time, while the parameter is fixed during operation and may vary with different rare events. To capture the effect of both the inputs and parameters, it is not affordable to develop a new model for every parameter value. Hence, incorporation of inputs and parameters is an additional challenge in developing a consequence model. To address the aforementioned challenges, this work develops a dynamic k-nearest neighbor (kNN)-based parametric reduced-order model (PROM), which can replace computationally intensive CFD models for consequence modeling and handle any changes in parameters. Specifically, the proposed approach interpolates local (with respect to parameters) ROMs constructed for a range of parameters. First, local ROMs are constructed using multivariable output-error state space (MOESP) algorithm. Then, the consequences for a new parameter value is obtained by interpolating the consequences obtained from k-nearest local ROMs. The applicability of the proposed kNN-based PROM is demonstrated for a case study of supercritical carbon dioxide release rare event.

Process Systems Engineering

Prasad Bandodkar - 2:55 to 3:10 PM

The feed-forward loop (FFL) network motif is commonly observed in several biological networks. Most studies on the FFL motif have focused on its response to variations in the input signal either in space or in time. However, in morphogen-mediated tissue patterning, the input signal varies both spatially and temporally. We studied the behavior of a coherent FFL in two contexts: - a generic oscillating morphogen gradient, and - patterning the dorsal-ventral axis of early Drosophila embryos by the NF-kappaB homolog, Dorsal, with its early target Twist. We found features in the dynamics of the intermediate node - phase difference and noise filtering - that were a consequence of the structure of the FFL itself, and were largely independent of the parameterization in the models. Furthermore, in the Dorsal-Twist model, we found that proper target gene expression was not possible without including the effect of the maternal pioneer factor, Zelda.

Chistopher Gordon - 3:10 to 3:25 PM

This research provides a framework for safety-aware fault-aware and maintenance-aware process control. It leverages ensemble classification via machine learning models for fault detection, mixed-integer nonlinear programming for integrated safety-aware production and maintenance scheduling, as well as hybrid multiparametric model predictive control for fault-tolerant setpoint tracking. The approach can be used to help improve the safety, productivity, as well as resilience of industrial processes, and is illustrated with a reaction network, and cooling water system.

Dustin Kenefake - 3:25 to 3:40 PM

Air separation via cryogenic distillation is the basis for most industrially produced air products such as pure oxygen, nitrogen, and argon. These products are heavily used in the chemical industries for inert blanket gases in process vessels and feedstocks. Air Separation Units (ASU) typically involve cryogenic distillation processes and highly interconnected material recycle loops to minimize utility cost. This process is highly complex and energy-intensive, with ASUs in the US accounting for more than 2% of all US manufacturing sectors' electrical energy consumption. A 1% improvement in the energy efficiency of ASU plants leads to approximately 10 million dollars per year savings industry-wide. In this work, we apply smart manufacturing techniques for the online monitoring and optimal operation of industrial-scale ASUs. Specifically, this work focuses on developing model-based methodologies, tools, and platforms for real-time optimization. The approach aims (i) to create a digital twin of a real-life ASU and (ii) provide implementable policies and controls on for the real-life unit. The PAROC framework is followed for the development of multiparametric Model Predictive Controllers (mpMPC).

Niranjan Sitapure - 3:40 to 3:55 PM

Inorganic lead halide perovskite quantum dots (QDs) have emerged as a promising semiconducting nanomaterial candidate for widespread applications, including next-generation solar cells, displays, and photocatalysts. The optoelectronic properties of colloidal QDs are majorly dictated by their bandgap energy (related to their size). Thus, it is important to fine-tune the size while having fast and continuous production of QDs. However, the mass and heat transfer limitations of batch reactors with batch-to-batch variations have hindered precise control over the size-dependent optoelectronic properties of QDs. Thus, to address this knowledge gap, we propose a multiscale model for continuous flow manufacturing of colloidal perovskite QDs. Specifically, a first-principled kinetic Monte Carlo model is integrated with a continuum model to describe a plug-flow crystallizer (PFC). The PFC has two manipulated inputs, precursor concentration and superficial flow velocity, to fine-tune the size of QDs. Furthermore, a neural network based surrogate model is designed to identify an optimal input trajectory which will ensure that the desired QD size is achieved, thereby taking a step towards controlled and reliable nanomanufacturing of QDs

Akhilesh Gandhi - 3:55 to 4:10 PM

Representations of crystal frameworks are important for structure description, design, and discovery of new frameworks. Traditional cartesian coordinate-based representation of crystal frameworks are inefficient in the sense that they require more information to describe the framework. We propose a novel Hamiltonian graph-based representation that identifies unique tetrahedral nodes within the framework based on their structure and utilizes these to capture positions and connectivity. The smallest repeating unit (SRU) is proposed that can represent the crystal framework with less information and provide added benefits of describing the ring size within the representation. We propose both, an algorithmic approach and an optimization-based approach towards identification of the SRU in large crystal structures. We demonstrate the benefits of this proposed representation on 158 zeolite structures where-in fewer than 4 times reduced T-nodes can represent the crystal. For example, Chabazite framework can be represented using only 12 T-nodes in the Hamiltonian graph-based representation as opposed to 36 T-nodes in the traditional unit cell. We envision this representation to enable new avenues for design and discovery of novel zeolite frameworks.