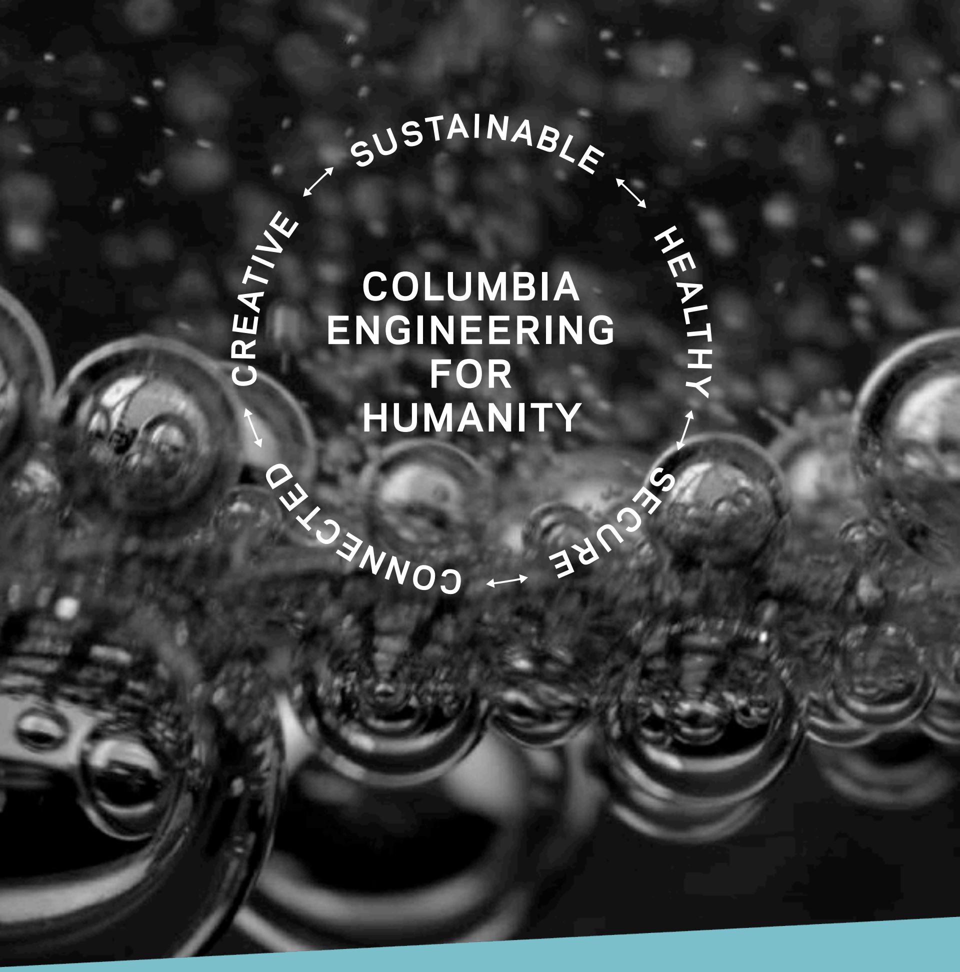


COLUMBIA ENGINEERING FOR HUMANITY

Department of Chemical Engineering
Columbia University

2021 Research Symposium

TRANSCENDING DISCIPLINES, TRANSFORMING LIVES

Schedule

SESSION 1

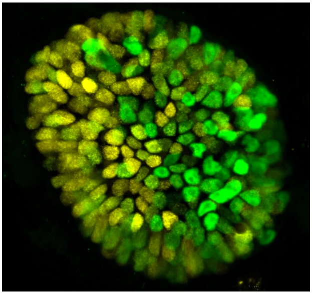
Friday, October 1

2:30 pm	*Welcome*
2:36 pm	**Azin Padash**
2:54 pm	**Zhengyan Zhang**
3:12 pm	**Dimitri Livitz**
3:30 pm	**Deboleena Dhara**
3:48 pm	*Break* (10 min)
4:00 pm	**Do Young Maeng**
4:18 pm	**Dong An**
4:36 pm	**Emma Willett**
4:54 pm	**Salomon Vainstein**
5:15 pm	*Adjourn*
5:30 pm	*Department Reception*

SESSION 2

Friday, October 8

2:30 pm	*Welcome*
2:36 pm	**Richard May**
2:54 pm	**Robert Mohr**
3:12 pm	**Karthik Mayilvahanan**
3:30 pm	**Jianzhou Qu**
3:48 pm	*Break* (10 min)
4:00 pm	**Akash Neal Biswas**
4:18 pm	**Xueqi Pang**
4:36 pm	**Robert Tannenbaum**
4:54 pm	**Nikhil Rampal**
5:15 pm	*Adjourn*
5:30 pm	*Department Reception*



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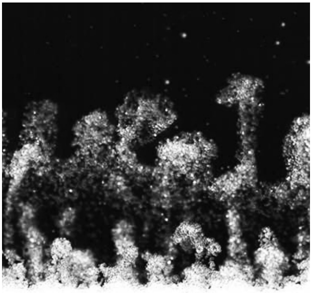

Cover by D. Esposito

SESSION 1

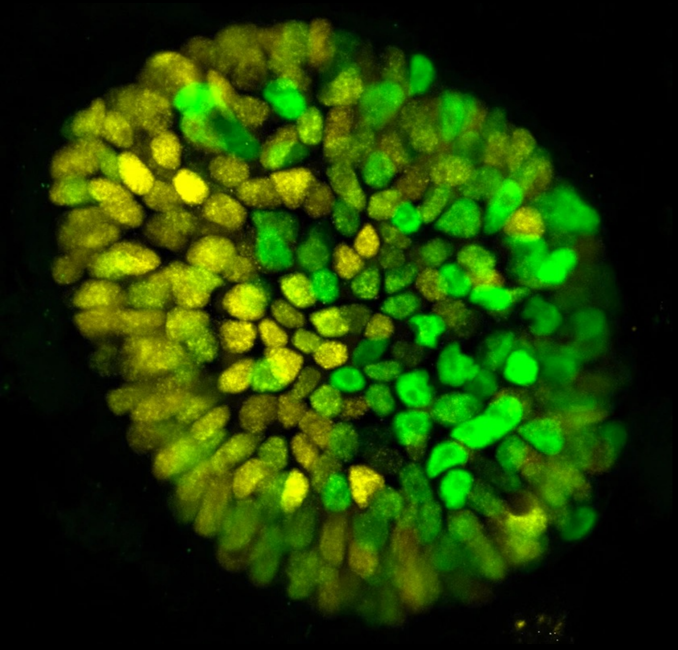

Image by M. Simunovic

Azin Padash

Periodically Repeating Structured Coalescence of Bubbles in a Cornstarch-Water Suspension

Abstract. We report periodic coalescence of bubbles at the same points in space from a single gas jet injected vertically into a 40 vol% cornstarch-water suspension at a specific Froude number. This regular coalescence is not observed at other conditions, such as different Froude numbers, volume fractions of cornstarch, density-matched suspension, or in a Newtonian fluid with comparable viscosity. We were also able to create this structured bubble coalescence by injecting bubbles in a consecutive fashion using solenoid valves. In this method, we kept the bubble injection frequency the same as the first method, but changed the bubble area by tuning the injection time. We attribute the regular bubble coalescence to the rheology of the suspension where the leading bubbles entering a shear-thickening regime, while trailing bubbles are in a shear-thinning regime, leading to coalescence.

Advisor: Chris Boyce

Zhengyan Zhang

Quincke oscillations of colloids at planar electrodes

Abstract. Dielectric particles in weakly conducting fluids rotate spontaneously when subject to strong electric fields. Such Quincke rotation near a plane electrode leads to particle translation that enables physical models of active matter. Here, we show that Quincke rollers can also exhibit oscillatory dynamics, whereby particles move back and forth about a fixed location. We explain how oscillations arise for micron-scale particles commensurate with the thickness of a field-induced boundary layer in the nonpolar electrolyte. This work enables the design of colloidal oscillators.

Advisor: Kyle Bishop

Dimitri Livitz

Predictive modeling of magneto-capillary systems through optimal Bayesian experimental design

Abstract. Time varying, uniform, magnetic fields can drive motion of particles at curved liquid interfaces. Different particles' geometry, size and surface properties require different physical considerations when modelling this motion, and experimental data is required to infer which effects are dominant. In this work we apply the principles of optimal Bayesian experimental design to the behavior of a magnetic Janus sphere at the interface of a water droplet in order to provide a template of how to effectively and precisely model behavior of similar systems. We show that in addition to each Janus sphere's ferromagnetic moment, we must quantify its buoyant mass and paramagnetic moment to accurately predict the particle's motion. While large numbers of experiments can be collected, analyzing data from a dense grid of experiments is prohibitive due to the computational burden. We show that when analyzing batches of four experiments, the Laplace approximation is appropriate. This approximation enables us to apply Bayesian experimental design to only select the most informative experiments, greatly reducing the computational workload of fitting and model selection.

Advisor: Kyle Bishop

Deboleena Dhara

Dynamic Properties of Filled Elastomers

Abstract. Crosslinked rubber materials reinforced with nanofillers are important to many technologies that have a broad impact on the economy and environmental sustainability, especially in the tire industry. During 1990's, widespread replacement of carbon black with silica contributed significantly to improving rolling resistance without compromising on the grip and wear resistance of tires. The incorporation of nanoparticles into rubber is usually carried out during processing. The resulting dispersion state and mechanical properties are controlled by a poorly understood combination of filler chemistry, agglomeration state and processing conditions. In this study, we use polymer grafted silica particles to get better control over the dispersion of the particles in an elastomeric matrix. Previous work in the group has shown that tuning parameters such as grafting density and the ratio of matrix to graft chain length result in various dispersion states, which in turn have a direct correlation with reinforcement. Mechanical analysis on melt nanocomposites show that reinforcement is maximized by the formation of a percolating network. On the other hand, the crosslinked composites showed notable enhancement in reinforcement at low grafting density in which the sample exhibits sheet-like aggregated morphology. Our ultimate goal is to understand the microscopic mechanisms of rubber reinforcement, examine the origin of rolling resistance in rubber tires and eventually design filled rubber materials that will improve the fuel efficiency of tires.

Advisor: Sanat Kumar

Do Young Maeng

Indoor Air Quality: Hydrolysis of Man-Made Esters, and Room-Level Ventilation

Abstract. Man-made esters (MMEs) are ubiquitous indoor pollutants due to their widespread use in consumer products and building materials. MMEs have been detected on indoor surfaces, in household dust, and in indoor air. Besides the adverse health effects of direct MME exposure, the hydrolysis degradation products of these species in the indoor environment pose additional health concerns. We have made laboratory measurements of the alkaline hydrolysis kinetics of 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TMPD-MIB), butylparaben (BP), bis(2-ethylhexyl) adipate (DEHA), and butyl benzyl phthalate (BBzP) in bulk aqueous solutions at room temperature, using UPLC-QToF-MS to detect the reactants over the course of the reactions. The determined rate constants are incorporated into GAMMA-CIE, our multiphase indoor chemistry model which enables us to quantify and predict the impacts of MMEs and MME hydrolysis on indoor air quality under different conditions. Experimental and preliminary modeling results will be presented.

In addition to the hydrolysis of MMEs discussed above, room-level ventilation measurements will also be highlighted in this talk. Amid the COVID-19 pandemic, ensuring adequate ventilation on a room-level basis has become a key strategy in reducing the spread of COVID-19. In support of the reopening efforts by the university, we have investigated the ventilation rates in classrooms, conference rooms, and elevators in campus buildings to help administrators and building managers in assessing the risk of airborne transmission of SARS-CoV-2.

Advisors: V. Faye McNeill

Dong An

Breaching cell membranes for neurotransmission in the brain and for drug delivery

Abstract. Compartmentalization is essential to life. To make compartments, cells use phospholipid membranes to enclose the cells, and to enclose vesicles and other organelles within cells. Membrane-enclosed vesicles containing neurotransmitters, insulin or other bioactive molecules are vital for processes such as neurotransmission in the brain or regulation of blood sugar levels whose malfunction leads to diabetes. For these functions, membranes must be secure boundaries, not easily breached. Thus: (A) cells have evolved specialized machineries to make openings in membranes so vesicles can release contents in response to a signal, and (B) traversal of cell membranes requires particular strategies for vital medical applications involving delivery of drugs such as vaccines (e.g. against the CoV-2 virus).

We use computational molecular simulations to study (A) and (B). (A) I studied the molecular machineries used by cells to open synaptic vesicles at nerve terminals in response to action potential-evoked calcium injection. On millisecond timescales, this remarkable multi-component machinery makes a fusion pore, a connection between the vesicle and neuronal plasma membranes for neurotransmitter release. We discovered membrane fusion is driven by entropic forces among the core SNARE proteins. (B) I describe my studies of cationic cell-penetrating peptides that enter cells by making simple pores in the cell membrane. We find simple pores must expand beyond a critical size for membrane breaching. Importantly, the simple pore is also the last step on the pathway to membrane fusion, (A), and the pore expansion requirement explains the observed pathway to fusion which is via an expanded hemifusion diaphragm.

Advisor: Ben O’Shaughnessy

Emma Willett

Membrane-less ATP Regeneration Enzyme Cascade Using a Reversible NAD Kinase and NADH Oxidation

Abstract. ATP regeneration is an important bioengineering topic for cell-free protein synthesis (CFPS), pseudocells, and other in vitro applications. Methods for regenerating ATP in industry include expensive phosphate donors and synthetic ATP-synthases that require membranes. In this talk, a membrane-less ATP-generating enzyme cascade that utilizes NADH oxidation is proposed. A membrane-less cascade is ideal for CFPS applications to avoid complicated protein purification. The 4 enzymes chosen for the cascade are good candidates for ATP production in synthetic pseudocells because the enzymes use polyphosphate and formate, which are cheap fuel sources, and NAD(P)H, a prevalent cellular cofactor. At the center of the proposed cascade is the ATP-NAD + kinase (NADK). All of the commonly investigated isoforms of NADK (human, S. cerevisiae, Arabidopsis and E. coli) have been measured, or assumed, to be irreversible and can only accept ATP as a reactant. Only one group, in 1977, has reported a reversible NADK obtained from pigeon livers. First, we confirmed the recombinant pigeon NADK was reversible. Additionally, we identified 2 other isoforms (duck and cat) that use ATP as a substrate and a product. Then, we constructed the membrane-less enzyme cascade with the reversible pigeon NADK, a polyphosphate NADH kinase, a formate dehydrogenase, and an NADPH oxidase. This cascade proved to produce ATP for several hours when coupled with firefly luciferase. To show the efficacy of the cascade, the purified enzymes were implemented into a CFPS system and demonstrated protein expression of both sfGFP and HRP. Finally, the cascade was powered with monophosphate, providing an even cheaper phosphate donor alternative.

Advisor: Scott Banta

Salomon Vainstein

Engineering Protein Activity with Non-Canonical Cofactors

Abstract. Engineering enzymes and cofactors can benefit a variety of fields, such as the food industry, oil and gas, and pharmaceuticals. Some enzymes require cofactors to function, which adds additional transport steps and may pose additional challenges if other enzymes require the same cofactor, leading to competition and crosstalk. There has been an increasing interest in designing enzymes to use non-canonical cofactors, which are cofactors that are seldom used by enzymes in the natural pathway. In this work, we focus on the non-canonical cofactor nicotinamide adenine dinucleotide 3-phosphate (3'-NADP+) and nicotinamide adenine mononucleotide (NMN+), which have both been found to be naturally produced in some species. The end goal is to design enzymes to be able to use naturally occurring NAD+ capped RNA in vivo. We explored a variety of mutation methods, including computational design and rational mutagenesis, to mutate the formate dehydrogenase enzyme from Candid boidinii (CbFDH) in an attempt to increase activity with the non-canonical cofactors. No mutant thus far has shown activity with NMN+, but a double mutant (D195SY196H) led to an increased activity with 3'-NADP+. Additionally, we are working at developing a kinetic based enzyme capture (KBEC) platform to screen mutants in directed evolution by selecting mutants that are able to form a stable intermediate with a bound cofactor and substrate. KBEC would allow for a high throughput screening during the various cycles of directed evolution, and we plan to create a universal platform to screen various enzymes with various cofactors.

Advisor: Scott Banta

SESSION 2

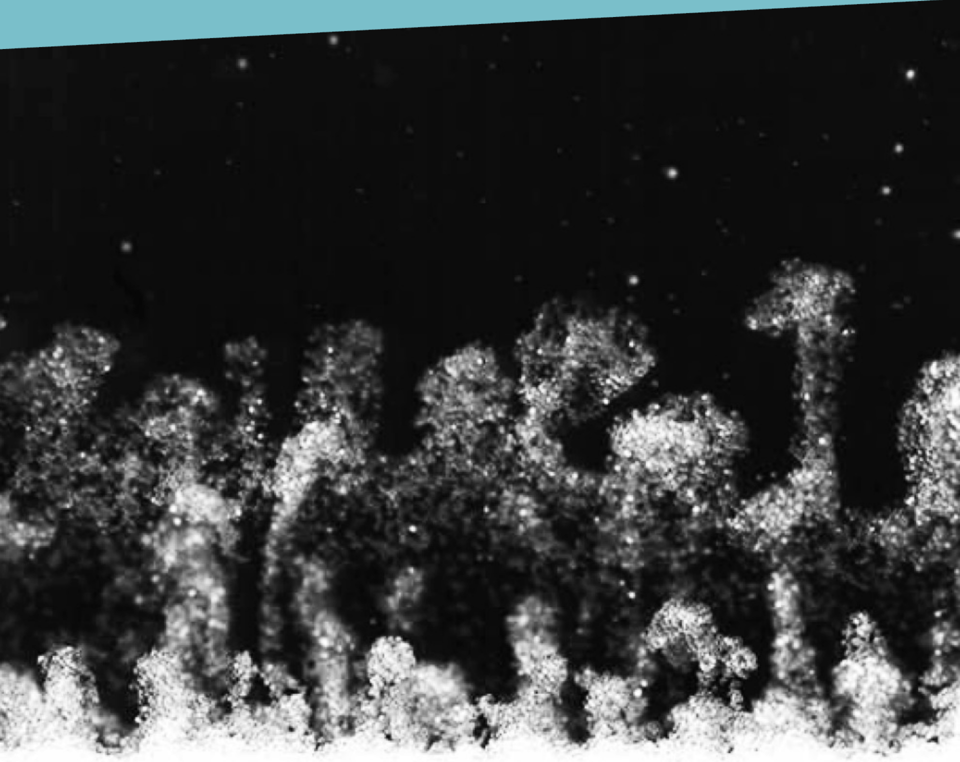

Image by C. Boyce

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Richard May

Decoupling bulk and interfacial contributions to performance in localized high concentration electrolytes for Li metal batteries

Abstract. Localized high concentration electrolytes (LHCEs) are a promising class of electrolytes to enable stable cycling of the lithium metal anode. Here, we report the use of operando nuclear magnetic resonance (NMR) spectroscopy to observe electrolyte decomposition during Li stripping/plating and identify the influence of individual components in LHCEs on Li metal battery performance. Data from operando 19F solution NMR indicates that both bis(fluorosulfonyl)imide (FSI–) salt and bis(2,2,2-trifluoroethyl)ether (BTFE) diluent molecules play a key role in solid electrolyte interphase (SEI) formation, in contrast to prior reports that suggest diluents are inert. Using solution 17O NMR , we assess differences in solvation in LHCEs and compare to low concentration electrolytes (LCEs). We find that BTFE diluents are chemically reduced during Li metal battery operation, which can be detected with operando NMR, but not conventional electrochemical methods. Solid-state NMR (SSNMR) and X-ray photoelectron spectroscopy (XPS) measurements confirm that LHCEs decompose to form a SEI on Li metal that contains organic BTFE reduction products as well as high quantities of lithium fluoride from both BTFE and FSI– reduction. Insight into the (electro)chemical reduction mechanisms underpinning SEI formation in LHCEs suggests that fluorinated ethers exhibit tunable reactivity that can be leveraged to control Li deposition behavior.

Advisor: Lauren Marbella

Robert Mohr

Using Density Driven Flow to Design Low-Cost Passive Flow Batteries

Abstract. Low cost energy storage is an important part of decarbonization and stabilization of next generation power grids around the world. However, existing technologies are still too expensive to fit many important use cases. Flow batteries have been proposed as a potential solution because they enable the use of extremely low cost, highly reversible electrochemical couples. They introduce many operational and transport benefits from their usage of an actively pumped electrolyte, but in practice they have been unable to meet cost targets due to a multitude of engineering and materials challenges. Here we show that for common flow battery chemistries, density changes at the electrode surfaces are large enough to drive substantial flow without active pumping. In long duration energy storage applications this density driven flow can act as a substitute for a pump resulting in a system of drastically reduced complexity and cost. This convection resulting from density change is characterized through non-dimensional analysis and compared among different flow battery chemistries. A simple system utilizing this principle is constructed using the zinc-bromine chemistry and is characterized through electrochemical testing and optical imaging techniques.

Advisor: Alan West & Dan Steingart

Karthik Mayilvahanan

Quantifying Uncertainty in Tortuosity Estimates for Porous Electrodes

Abstract. Measuring tortuosity in porous electrodes is important for understanding rate capability and optimizing design. Here, we describe an approach to determine electrode tortuosities and quantify the associated uncertainties by fitting a multiscale model to discharge profiles from a standard rate capability test. A dimensionless current is identified as a design-of-experiment parameter that can be used to identify experiments that return confident estimates of tortuosity, even when other model parameters are not known with certainty. This approach is applied to analysis of $Li_xV_3O_8$ (LVO) electrodes and $Li_xNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) electrodes. The details of the assumptions made in these measurements and their impact on the reported uncertainties are discussed. We also perform an uncertainty analysis on the standard method for quantifying tortuosity in the literature: electrochemical impedance spectroscopy collected under blocking electrolyte conditions. We find that confident estimates can be obtained using this approach even when uncertainties in equivalent circuit model parameters are considered.

Advisor: Alan West

Jianzhou Qu

Modeling Hydrogen Evolution Reaction at the Interface of Silica Coated Platinum Electro-Catalysts from First Principles

Abstract. Current technology for water electrolysis requires highly purified water, which increases the overall energy requirements and thereby cost. It has recently been reported that a thin semi-permeable silica (SiO_2) coating on the surface of Pt electrocatalysts can prevent the contamination from cations and can increase the stability of the electrocatalyst in complex solutions with little impact on the catalytic performance. Using first-principles calculations, we have previously shown that the interaction of silica membranes with Pt surfaces is environment-dependent and changes with the pH value of the electrolyte and the electrode potential.

Here, we discuss the impact of silica membrane coatings on the mechanism of the hydrogen evolution reaction (HER) at the buried interface of SiO_2/Pt. Stable configurations of reactants and products at the buried interface during HER were determined using density-functional theory (DFT) calculations. Computational interface Pourbaix diagrams show the pH and potential dependence of intermediates and of the hydrogen coverage on the metal surface. Activation energies for different reaction mechanisms at the buried interface were obtained from nudged elastic band (NEB) simulations.

Our modeling results indicate that the HER mechanism at buried SiO_2 /Pt interfaces involves the silica membrane as a mediator. In addition to the protective quality of silica membranes, this hints at the possibility of designing synergistic membrane-coated electrocatalysts that surpass in catalytic performance (activity and/or selectivity) the bare surfaces of earth-abundant transition metals.

Advisor: Alex Urban

Akash Neal Biswas

Hybrid Catalytic Systems for Sustainable CO2 Reduction to Value-Added Oxygenates

Abstract. Measures must be taken to reduce atmospheric CO_2 concentrations and mitigate the effects of climate change. One attractive solution to closing the carbon cycle is using CO_2 as the carbon source for commodity chemical and fuel production. This provides an economic incentive to utilize CO_2, while simultaneously reducing atmospheric concentrations. In this talk, two different hybrid catalytic routes for CO_2 conversion into high-value oxygenates are discussed. First, a two-stage tandem system is introduced, where CO_2 (and water) are electrochemically reduced into ethylene and syngas, which are then directly fed to an ambient pressure thermochemical hydroformylation reactor to produce C_3 oxygenates. Catalytic CO_2 reduction and hydroformylation tests were first conducted independently, before being connected together in a tandem configuration to validate the feasibility of the proposed reaction strategy. Second, a hybrid plasma-catalysis system is outlined, where CO_2 and ethane are directly converted into oxygenates in a one-step process under ambient conditions. Non-thermal plasma was implemented as a means of supplying energy to overcome the activation barriers. In particular, the effects of plasma power, feed gas ratio, and catalyst addition on activity and selectivity were investigated in a dielectric barrier discharge flow reactor. Additionally, a combination of isotopically-labeled CO_2 experiments and chemical kinetic modeling were used to gain further insight into the reaction pathway and experimental trends.

Advisor: Jingguang Chen

Xueqi Pang

Packed Bed Membraneless Electrolyzers for Electrochemical CO_2 Conversion

Abstract. Electrochemical CO_2 reduction reaction (CO2RR) provides a promising route to convert excess CO_2 emissions into value-added fuels and chemicals using renewable electricity. Many of the CO_2 electrolyzers use membranes to facilitate ion transport between the cathode and anode and separate the gas products from O_2 produced at the anode. However, the membranes can be prone to degradation or fouling. In this work, we present a novel and potentially low-cost packed bed membraneless electrolyzer (PBME) with flow-through electrodes. The new reactors have multiple pairs of electrodes to boost the CO_2 conversion performance and they are ideally suited for maintaining favorable pH between electrodes. Basic operating principles have also been modeled to help understand the current distribution of the porous electrodes.

Advisor: Dan Esposito

Robert Tannenbaum

Understanding Gas Transport in Polymer-grafted Nanoparticle Membranes

Abstract. Polymer nanocomposites have become increasingly useful materials for a diverse set of applications, including as industrial gas transport membranes for separations processes. Difficulty controlling nanoparticle dispersion in these nanocomposites has led to the use of polymer-grafted nanoparticles in a “matrix-free” configuration, where all polymer present in the system is chemically tethered to the surface of the nanoparticles. Materials composed from these grafted particles have been shown to display a remarkable enhancement in the gas transport properties of these systems. It has been proposed that the activation energy for penetrant motion through a polymeric membrane scales as the square of penetrant kinetic diameter, and can be related to a material-dependent critical size parameter. This work investigates macroscopic manifestations of this microscopic gas transport mechanism in grafted nanoparticle systems.

Advisor: Sanat Kumar

Nikhil Rampal

Effects of Extended Solvation Sphere on Reactivity in Aqueous Solutions: Origin of Concentration-dependent Behavior

Abstract. To understand both equilibrium and dynamic properties in geochemical systems, it is critically important to understand the extend of ion association in aqueous salt solutions. However, the molecular structure of the associated ions, and their propensity to form, is unclear even for ‘simple’ salt solutions. In addition, existing estimates of the equilibrium constants for ion association found in thermodynamic speciation databases are often fit parameters from activity-concentration relationship models which can be incoherent with literature data. We have investigated ZnCl2(aq) solutions at various concentrations because of their propensity to form ion pairs and uncertain ion pair formation, respectively. These are explored using Classical Molecular Dynamics (CMD) simulations modeled on previously taken Neutron Diffraction with Isotope Substitution (NDIS) data. A force field for the CMD is corrected for ion hydration structures by deconvoluting the experimental pair distribution function of the solutions. This leads to a clear picture of, and capacity to simulate, chloride ion-pair formation and solvation structures in the studied system. The tuned force field is used to study the concentration-dependent reaction dynamics. We find that both water solvent and counter-cations control local specific bonding interactions and the free energy barriers for the interconversions from one stable coordination state to another increase at higher concentration. This suggests hindered reaction dynamics with ions assuming locally-favored structures, which in turn steer the solution structure and alter the reaction dynamics in highly concentrated solutions. These findings have implications on various kinds of reactions found in earth systems and several industrial applications, such as nucleation of crystalline and amorphous phases.

Advisor: Andrew Stack (ORNL) & Sanat Kumar

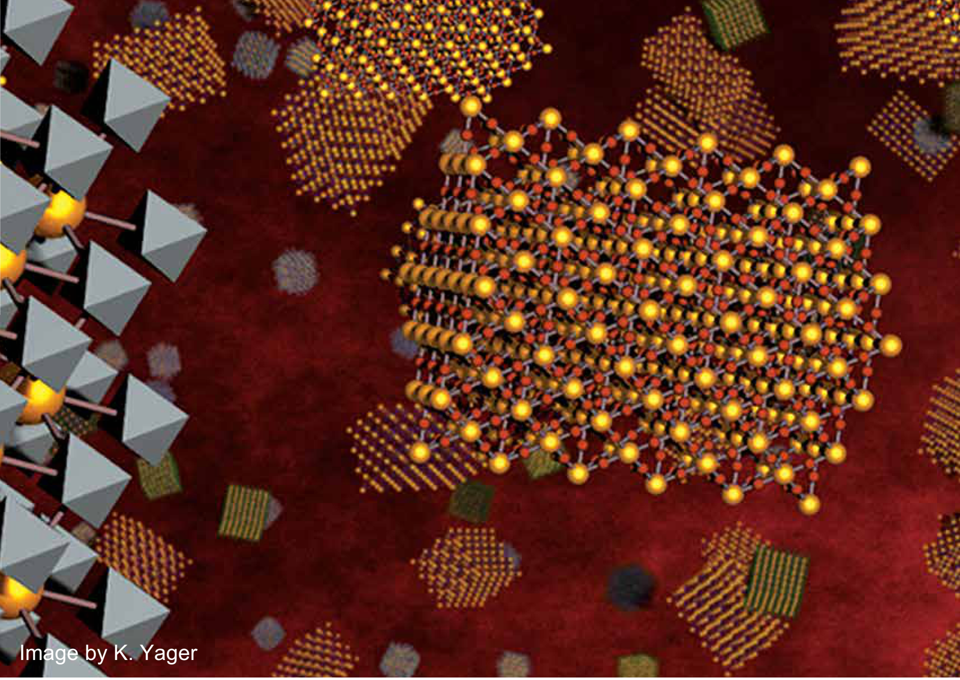

Image by K. Yager

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