



McWhirter Graduate Research Symposium

Friday, September 16, 2016
The Nittany Lion Inn

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10:00 AM	Registration				
10:30 AM	Session 1	Ballroom AB	Ballroom DE		
		<i>Fully conjugated block copolymers as model systems to understand fundamental mechanisms of charge photogeneration in organic photovoltaics</i>	Melissa Aplan	<i>Using linear viscoelasticity to probe the chain conformation, entanglement and the glass transitions of conjugated polymers</i>	Renxuan Xie
		<i>Quantitative analysis of the coverage density of polyvinylpyrrolidone on silver nanoparticle and the underlying implication on cubes formation and PVP configuration</i>	Zhifeng Chen	<i>Carleman approximation-based nonlinear model predictive control</i>	Yizhou Fang
		<i>Catalyst site selection via control over non-covalent interactions in self-assembled monolayers</i>	Gaurav Kumar	<i>Structure-function relationship of hydrophobic homogeneous and heterogeneous sulfonic acid catalysts in the presence of water</i>	William Elliott
		<i>Understanding and potentially mitigating Li-plating in Li-ion batteries</i>	Dan Marple	<i>Enhanced stability to high temperature steam by controlling crystallization of PAEKs</i>	Dustin Veazey
12:00 PM	Lunch – Ballroom C				

1:00 PM	Session 2	Ballroom AB	Ballroom DE
		<i>Adsorption of transition metal precursors on refractory and reducible metal oxide supports characterized by isothermal titration calorimetry</i>	Ahana Mukhopadhyay
		<i>Redesign of E.coli water channel protein, OmpF, using Iterative Protein Redesign and Optimization suite (IPRO)</i>	Ratul Chowdhury
		<i>Spray drying of pharmaceuticals- solubility and diffusivity in solvent-HPMCAS systems</i>	Derek Sturm
		<i>Shape-controlled synthesis of Ag nanocrystals mediated by polyvinylpyrrolidone: thermodynamics vs. kinetics</i>	Xin Qi
		<i>Kinetic modeling of metabolism in Clostridia</i>	Satyakam Dash
		<i>Hydrocarbon cracking to light olefins - from the microscale to the mesoscale for applications in endothermic fuel reactions</i>	Taslima Zaman
		<i>How to quantify and improve the performance of biomimetic membrane matrices?</i>	Tingwei Ren
		<i>Modeling regulation and metabolism in Cyanobacteria</i>	Thomas Mueller
2:30 PM	Keynote Speaker – David Latulippe – Ballroom C		
3:15 PM	Poster Session – Ballrooms AB and DE		
4:00 PM	Session 3	Ballroom AB	Ballroom DE
		<i>Predicting kinetic nanocrystal shapes through multi-scale theory and simulation: polyvinylpyrrolidone-mediated growth of Ag nanocrystals</i>	Tonnam Balankura
		<i>Insights into the effects of conformational disorder on the intra-chain electronic properties of polymer semiconductors</i>	Joel Bombile
		<i>Nonlinear control of transport reaction processes using discrete adaptive POD (DAPOD)</i>	Manda Yang
		<i>Shape-directed actuation and collective dynamics of spinners</i>	Syeda Sabrina
		<i>Nano-sized polymer electrode interlayer with a high-concentration of C-S-S-C bonds improves the columbic efficiency of lithium-sulfur batteries</i>	Michael Regula
		<i>Understanding the surface mechanochemical behavior of soda lime silica glass through ion-exchange process</i>	Jiawei Luo
5:00 PM	Reception		

Session 1

Fully conjugated block copolymers as model systems to understand fundamental mechanisms of charge photogeneration in organic photovoltaics

Presenter: Melissa Aplan

Advisor: Enrique Gomez

Power conversion efficiencies of single-junction organic photovoltaic (OPV) devices are currently at 11%; the theoretical limit of a silicon single-junction solar cell is 32%. Despite extraordinary advances in OPVs, many challenges remain. It is difficult to extract a set of design rules from successes in the field to guide the rational design of high performing systems. Fully conjugated block copolymers, consisting of an electron donor block covalently linked to an electron acceptor block, can be used as model systems to elucidate fundamental processes in OPVs. These donor-acceptor complexes can be fully dispersed and studied as isolated chains in solution. In this report, we use block copolymers to examine how the energy offset between donor and acceptor highest occupied molecular orbitals (HOMOs) influences charge transfer. We synthesized a series of block copolymers consisting of a poly-(3-hexylthiophene) (P3HT) electron donor and three different push-pull polymer electron acceptors, either poly-((9-(9-heptadecanyl)-9H-carbazole)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PCT6BT), poly-((9,9-dioctylfluorene)-2,7-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PFT6BT), or poly-((2,5-dihexylphenylene)-1,4-diyl-alt-[4,7-bis(3-hexylthiophen-5-yl)-2,1,3-benzothiadiazole]-2',2''-diyl) (PPT6BT). By altering only the electron rich unit of the acceptor, we adjust the energy difference between the donor and acceptor HOMOs by tenths of an electron volt (eV). Dynamic light scattering confirms that the synthesized block copolymers can be fully dispersed as isolated chains in solutions, enabling studies of photoluminescence quenching within individual chains. The absorption and emission spectra of the block copolymers can be deconvoluted to extract the contributions from each block, enabling us to quantify the yield of intramolecular charge transfer states. Taking the data from all copolymers together, we find a critical driving force required to generate charge transfer states that depends on the dielectric constant of the solvent.

Using linear viscoelasticity to probe the chain conformation, entanglement and the glass transitions of conjugated polymers

Presenter: Renxuan Xie

Advisor: Enrique Gomez and Ralph Colby

Conjugated polymers are promising materials that can serve as the active layer in a variety of electronic devices, such as solar cells and thin-film transistors. However, fundamental properties, including the glass transition temperature (T_g) and the entanglement molecular weight (M_e), are still in dispute for most conjugated polymers. These parameters play a central role in the microstructures, such as intercrystalline connectivity and tie chains, which are believed to ultimately influence bulk electrical charge transport. We started with a wide range of molecular weights of both regiorandom (RRa) and regioregular (RRe) Poly(3-hexylthiophene-2,5-diyl) (P3HT). Coupled with the absolute Mw from static light scattering and the molecular weight distribution from GPC, M_e was extracted by fitting the linear viscoelastic data of multiple molecular weight samples using the classic tube reptation model. Furthermore, by using low-temperature oscillatory shear test, two glass transitions (T_g s) for both RRe and RRa P3HT were clearly identified. The higher T_g , corresponds to segmental motion, follows the Flory-Fox equation well for various MWs and yields a high MW $T_{g\infty} \sim 20$ C. RRe P3HT has a significantly larger M_e than RRa P3HT, which might originate from either the difference in side chain packing evidenced by their different lower T_g values or the possible presence of nematic phase. This difference was also investigated in the context of dilute solution by the Ubbelohde viscometry in order to further understand entanglements in these semiflexible polymers. In addition, this linear viscoelasticity study was also expanded to other high performance electron donor/acceptor conjugated polymers, such PFTBT and P11-2T, to determine its molecular weight dependence of T_g and the extent of nanophase separation through side chain engineering.

Quantitative analysis of the coverage density of polyvinylpyrrolidone on silver nanoparticle and the underlying implication on cubes formation and PVP configuration

Presenter: Zhifeng Chen

Advisor: Robert Rioux

The role of polyvinylpyrrolidone (PVP) in the shape control synthesis of Ag nanoparticles (NPs) has been attributed to its preferential binding to Ag (100) facets compared to Ag (111) facets. Theoretical studies have been done to validate the hypothesis, however, with limit to small molecule analog of PVP. We experimentally measured the coverage density of PVP on different shaped Ag NPs and equilibrium PVP amounts in solution. Based on the linear region of Langmuir isotherm, a weak (32 M^{-1}) equilibrium adsorption constant of PVP to Ag nanocubes surface was obtained directly. With molecular weights larger than 10K, constant PVP monomer coverage densities were found and implied a similar equilibrium adsorption constant. For molecular weight of 10K, lower equilibrium adsorption constant was expected due to no detectable amount of PVP was measured and accordingly no Ag nanocubes were formed. As we changed from Ag nanocubes to octahedron, the equilibrium adsorption constants decreased half, which confirmed the existing preferential hypothesis but the difference is far less than the simulation results. Besides, we varied PVP concentration during the Ag NP synthesis to obtain the low and high boundary of the Ag nanocubes phase diagram. The low boundary implied the role of PVP as a stabilizer and the high boundary indicated the role of PVP as a reducing agent during the Ag NP synthesis.

Carleman approximation-based nonlinear model predictive control

Presenter: Yizhou Fang

Advisor: Antonios Armaou

The recent three decades witnessed wide applications of advanced process control in chemical, petroleum and pharmaceutical industries. Model Predictive Control (MPC), started gaining attention as a powerful methodology to control chemical unit operations. The basic architecture of MPC is to convert an optimal control problem to a receding-horizon optimization problem. This architecture enriches MPC with several unique advantages over traditional control strategies, including the capability of handling state, input and performance constraints, the ability to control large state-space systems with multiple variables, and the readiness to cope with disturbances and model-mismatches.

Any physical system in nature is virtually nonlinear. Nonlinearity leads to many challenges holding back the applications of MPC. The complexity in the computation gives rise to feedback delays, degradation of controller performances, and potential stability issues. As a result, it is strongly motivated to develop new MPC algorithms for nonlinear systems that decrease computational efforts.

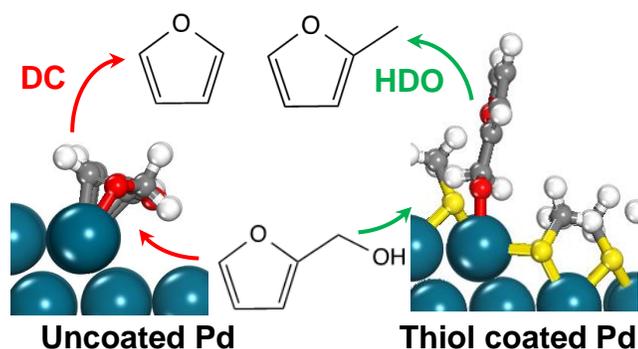
This research project aims at developing an advanced nonlinear MPC algorithm that accelerates computation in order to improve controller performances. Nonlinear systems are approximated with Carleman Approximation (also known as Carleman Linearization) and represented with bilinear expressions while carrying nonlinear dynamics information. Hence, we are able to analytically predict future system states and provide the sensitivity of the objective to the control signals as the searching gradient. In this way, the computation of optimal control signals is significantly accelerated compared with traditional nonlinear MPC. We also calculate the optimal control signals off-line and update them instantaneously with pre-calculated sensitivity matrices as the real system states are observed or estimated on-line. This makes our nonlinear MPC algorithm more adaptive when dealing with unknown disturbances or model-mismatches.

Catalyst site selection via control over non-covalent interactions in self-assembled monolayers

Presenter: Gaurav Kumar

Advisor: Michael Janik

One strategy for controlling selectivity in surface-catalyzed reactions is to precisely control the types of surface sites available for reaction. Here, we show that such control can be achieved on Pd/Al₂O₃ catalysts modified by alkanethiol self-assembled monolayers (SAMs) by changing the length of the modifier's alkyl tail. Density functional theory (DFT) calculations show that thiolates with short alkyl chains preferentially bind to under-coordinated Pd step sites but that adsorption on (111) terrace sites is more favorable at higher chain lengths due to greater stabilization by van der Waals interactions. Linear alkanethiol SAMs with chain lengths ranging from six to 18 carbon atoms were deposited on Pd/Al₂O₃ catalysts to probe this predicted effect experimentally. Infrared spectroscopy measurements conducted after CO adsorption confirmed that increases in alkyl chain length resulted in increasing specificity in poisoning of terrace sites. The catalysts were also evaluated for furfuryl alcohol hydrogenation, a structure-sensitive probe reaction. Selectivity to the desired hydrodeoxygenation to methylfuran increased from <20% to >60% as chain length increased from six to 18 carbons, consistent with increasing efficiency for thiolate blocking of Pd terrace sites. DFT models demonstrate that the presence of thiolates strongly suppressed decarbonylation reactions and that step sites surrounded by thiolates could still be active for hydrodeoxygenation. This work demonstrates that site availability, and thus catalyst selectivity, can be tuned by changing the architecture of SAM precursors.



Structure-function relationship of hydrophobic homogeneous and heterogeneous sulfonic acid catalysts in the presence of water

Presenter: William Elliott

Advisor: Robert Rioux

Acid catalysts can be used to upgrade fast pyrolysis-derived bio-oils via esterification. Esterification reduces the acidity of the bio-oil and improves stability. However, bio-oil typically contains a significant amount of water, which deactivates acid catalysts. Water tolerant acid catalysts must be developed for acid catalyzed esterification to be a viable method of upgrading for bio-oil. We have tested a series of homogeneous and heterogeneous sulfonic acid catalysts with varying degrees of hydrophobicity for their tolerance towards water.

Hydrophobic surface area improves water tolerance of catalysts.¹ We have systematically modified a series of silica-supported propylsulfonic acid catalysts with increasing hydrophobicity by grafting hydrophobic moieties to the catalyst surface. Surrounding the active site with hydrophobic surface area excludes water from the active site, preventing deactivation. Similarly, we have tested a series of homogeneous sulfonic acid catalysts, by modifying the hydrophobicity of the carbon backbone.

We aimed to determine a structure-function relationship between water tolerance and hydrophobicity. Calorimetry was used to quantify the level of hydrophobicity by measuring the heat of solution and heat of wetting of water for the homogeneous and heterogeneous catalysts, respectively. The level of hydrophobicity was compared to the performance of the catalyst under dry and wet conditions to determine the relationship between hydrophobicity and water tolerance. This investigation focused on the esterification of acetic acid with methanol in 1,4-dioxane as a model reaction to determine the effect of water on the series of sulfonic acid catalysts. Apparent activation energies were determined for the catalysts under dry and wet conditions over the range of 30-70 °C. Water tolerance of the catalysts was quantified by determining the reaction order of water over the concentration range of 0-5 M.

We found that in homogeneous sulfonic acid catalysts, the hydrophobicity of the backbone failed to have an impact on water tolerance. Above 3 M water, all catalysts exhibited the same reactivity, despite differing in reactivity under dry conditions. Calorimetry of the homogeneous sulfonic acids failed to adequately quantify hydrophobicity of the backbone. Calorimetry, instead, reflected the strength of the acid.

The heterogeneous study is ongoing. Early results show that modifying propylsulfonic acid silica with alkyl chains modifies catalyst activity under dry conditions. C8 modified catalysts exhibit a sharp drop off in activity relative to C1 and C3 modified catalysts suggesting that longer alkyl chains begin to crowd the active site and prevent not just water from accessing the active site, but also reactants. More results forthcoming.

References

1. Okuhara, T., *Chem. Rev.*, 2002, 102 (10), pp 3641–3666

Understanding and potentially mitigating Li-plating in Li-ion batteries

Presenter: Daniel Marple

Advisor: Chao-Yang Wang

Increases in gasoline prices and greenhouse gas emissions have spurred the growth of hybrid electric vehicles (HEV) and pure electric vehicles (EVs). Rechargeable Li-ion batteries are the leading candidate for these vehicles due to their high energy and power density relative to other battery chemistries. In order to be effective, fast charging methods are needed that can be implemented in a wide range of temperature conditions. Graphite anodes in Li-ion batteries are well known to suffer from Li depositing on the surface, which can be accelerated at high charging currents, high SOC or at low temperatures. Li plating not only causes capacity and power fade issues, but can cause several important safety issues as well. In this study, we produced $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2/\text{graphite}$ ($x:y:z = 1:1:1$ and $6:2:2$) with an n/p ratio of 0.6 to better understand Li-plating. Accelerated aging at various temperatures (5, 15 and 35 °C) found that cells cycled at 5 °C lasted less than 5 cycles (70% SOH), while cells cycled at 15 °C lasted at least 10x longer and cells at 35 °C lasting more than 20x longer. It was also seen that as aging increased, the amount of reversible plated lithium per cycle decreased. Electrochemical impedance spectroscopy was also used to determine resistance evolution for fresh and aged cells.

Enhanced stability to high temperature steam by controlling crystallization of PAEKs

Presenter: Dustin Veazey

Advisor: Enrique Gomez

The poly(aryl ether ketone) (PAEK) family of thermoplastic polymers is widely used in oil and gas applications due to their excellent chemical resistance and good mechanical properties at elevated temperatures. State-of-the-art technologies for enhanced oil and gas extraction utilize aggressive chemicals and increasingly higher temperatures and pressures. Polymeric materials used in down-hole applications must stand-up to high pressure, high temperature (HPHT) conditions, while maintaining reasonable service life. Current commercially available PAEKs struggle to meet the demands of current downhole environments, and will be obsolete for next generation oil recovery technologies.

In this study, PEEK and various PEKKs were exposed to high pressure steam at 550°F(288°C). The effect on mechanical properties was measured by dynamic mechanical analysis (DMA) in order to evaluate stability and potential for use under HPHT conditions. Crystallinity and microstructure of exposed specimens were characterized using DSC and WAXD. Exposure to high temperature steam for up to 72 hours causes an increase in crystallinity for both PEEK and PEKK. The change is significantly more pronounced in PEKK and leads to embrittlement and reduction of mechanical strength. We demonstrate the high temperature steam resistance of PEKK is improved through crosslinking the amorphous phase, thereby inhibiting crystal growth during steam exposure. The crosslinked PEKK retains mechanical properties at elevated temperatures and exhibits a stable microstructure. Such crosslinking technologies are proposed to improve the HPHT resistance of PAEKs and give them the potential to be used for current and future down-hole oil and gas applications.

Session 2

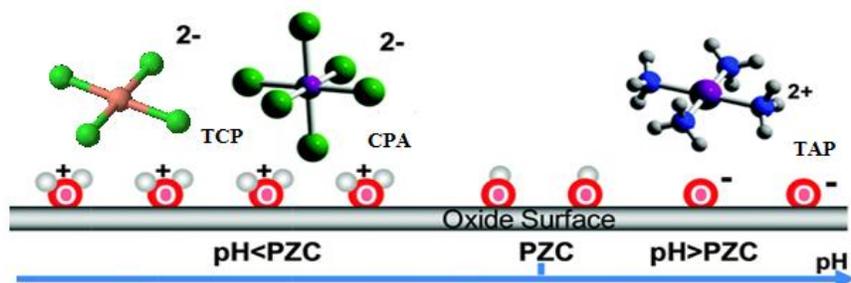
Adsorption of transition metal precursors on refractory and reducible metal oxide supports characterized by isothermal titration calorimetry

Presenter: Ahana Mukhopadhyay

Advisor: Dr. Robert M. Rioux

Widespread industrial applications of supported late transition metal catalysts demand economic and scalable synthesis of these catalysts. The proper selection of the oxide support is of great importance to ensure high dispersion, activity and selectivity of the nanoparticles. The ability of these supports to enhance the dispersion of the active metal on their surface and control their morphology and sintering kinetics is fundamentally related to the nature and strength of the metal–metal oxide interaction at the time of adsorption. Ceria is a well-known reducible oxide support for transition metal catalysts and it has been used as an additive to the three way catalyst (TWCs) to aid in CO oxidation and other automotive exhaust treatment reactions. The interesting electronic nature of ceria allows the rapid formation and elimination of surface and sub-surface oxygen vacancy defects. This high “oxygen storage capacity” has allowed ceria to successfully stabilize noble metal dispersion and delay sintering to maintain small sized nanoparticles on its surface compared to other oxide supports. The metal–ceria interface interaction remains complicated and there is lack of substantial information on the energetics of binding and their influence on particle size and growth.

In this work, we study the adsorption of Pt and Pd based precursors, chloroplatinic acid, tetraammineplatinum (II) nitrate and ammonium tetrachloropalladate (II) on ceria under strong electrostatic solution conditions by adjusting the pH of the ceria surface far from its PZC to create a driving force for precursor adsorption. Bulk uptake studies aid in quantifying the amount of Pt and Pd metal adsorbed on the support surface and equilibrium isotherms describe the uptake behavior and sheds light on the possible precursor – support surface and sub-surface interactions. The adsorption of Pt and Pd on possible defect sites on ceria may be the reason leading to increased reactivity, increased strength of binding and protection against sintering to give enhanced control over nanoparticle size. The adsorption energy for binding of Pt and Pd precursors on the ceria surface is determined through the use of isothermal titration calorimetry (ITC) to experimentally evaluate the equilibrium binding constants, binding stoichiometry, and enthalpies of adsorption. The estimated thermodynamic parameters help to quantify the type of bonding at the metal – support interface. Based on these observations, an understanding of the growth and sintering kinetics of the catalysts can lead to developing a structure–function relationship between metal–metal oxide interaction and final catalyst properties.



Point of zero charge of oxide surface controls charge distribution at various pH range and influences corresponding interaction with complex transition metal counter-ions in solution

Redesign of E.coli water channel protein, OmpF, using Iterative Protein Redesign and Optimization suite (IPRO)

Presenter: Ratul Chowdhury

Advisor: Costas Maranas

The water footprint for food production, processing and energy production is increasing everyday with the world population and freshwater is becoming an increasingly limited resource. Ultra-permeable membranes are rapidly emerging as a widely implemented technology to utilize and efficiently recycle marginal water sources. Existing membranes are mainly dense solution- or diffusion based or channel-based. Aquaporins (AQPs) are the most popular biological channel-based membranes due to their short pore lengths and high water permeabilities of billion molecules per second. Another particular member of the “porin” class of beta-barrel proteins is Outer Membrane Protein F (OmpF). Unlike AQPs, OmpF is exceptionally stable with the ability to survive contact with solvents such as 100% ethanol. While the stability and mutation tolerance of OmpF makes it a suitable candidate for computational design and subsequent experimental validation for performing separations at the angstrom scale, it can also be easily assembled into stable block-copolymer membrane sheets. To this end, we employed the Iterative Protein Redesign & Optimization (IPRO) suite (1) of programs to perturb the OmpF protein backbone, mutate and recursively repack the sidechains in order to obtain the selective internal structure of AQP inside the stable beta-scaffold of OmpF.

We started with the wild-type *E.coli* OmpF (elliptical pore constriction with major and minor axes of ~1.1 nm and 0.7 nm respectively). Pore sizes between 0.3 nm and 0.5 nm are key to several industrial and environmental separations such as methane/CO₂ and salt/water, which is accessible to the less stable AQPs. We first performed ensemble analysis on molecular dynamics (MD) simulations of water permeation through *E. coli* AQP1 using *k*-means clustering technique. Next, we fixed the relative coordinates of water molecules in a water-wire from each ensemble and put them inside the OmpF pore. Subsequently, we identified the OmpF pore-constricting residues and allowed them to be mutated to only hydrophobic residues to eliminate any interactions between the water-wire and the pore wall. In addition, we extended the IPRO suite with the ability to select designs based on a geometric criterion in which only designs that have both the pore-constriction axes smaller than 0.35 nm, were accepted. Interestingly, we identified three main types of mutants from our results. The first type comprises mutants where the design positions were only allowed to mutate to tryptophan (longest hydrophobic side chain). This was performed to test out the physical limit up to which the OmpF pore area can be reduced. We have identified a mutant with 25 tryptophan mutations having pore axes of 0.224 nm and 0.18 nm, respectively. The other two types of mutants comprise one with typical hour-glass shaped constriction (pore axes lengths: 0.319 nm and 0.2552 nm respectively) and another which appears as two stacks of ellipses, one arranged on top of the other with the major axes of the lower stack nearly at a right angle to that of the ellipses in the stack above, thereby making the pore very small (axes lengths: 0.236 nm and 0.194 nm respectively). We will perform subsequent experimental validation in establishing a platform for designing precisely tuned membrane transporters. These engineered membrane proteins will serve as important industrial workhorses in energy-efficient water treatment.

References

1. Pantazes RJ, Grisewood MJ, Li T, Gifford NP, Maranas CD. The Iterative Protein Redesign and Optimization (IPRO) suite of programs. *J Comput Chem.* 2015;36(4):251-63.

*Spray drying of pharmaceuticals- solubility and diffusivity
in solvent-HPMCAS systems*

Presenter: Derek Sturm

Advisor: Ronald Danner

In the pharmaceutical industry, glassy polymers are used as a matrix for trapping poorly soluble active pharmaceutical ingredients (API) in the amorphous state. One of the key players in this process is HPMCAS (hypromellose acetate succinate), a cellulose based polymer which provides improved dissolution and kinetic solubility of the API. Spray drying is one of the methods for producing amorphous dispersions. One of the most limiting factors in the removal of solvents during the spray drying process is the rate at which diffusion occurs. Unlike liquid-liquid diffusion coefficients, liquid-polymer diffusion coefficients typically change over four orders of magnitude as the dispersion is dried. An extension of the Vrentas-Duda free-volume theory (FVT) which accurately captures the change in the mutual diffusion behavior below the glass transition is presented here. Different solubility models and this new extension of FVT are compared with the solubility and diffusivity in solvent-HPMCAS systems that have been experimentally determined using three experimental techniques: inverse gas chromatography, gravimetric sorption and differential pressure decay.

Shape-controlled synthesis of Ag nanocrystals mediated by polyvinylpyrrolidone: thermodynamics vs. kinetics

Presenter: Xin Qi

Advisor: Kristen Fichthorn

Functional nanomaterials, especially metallic materials, are highly shape sensitive, which drives the development of shape-controlled nanomaterial synthesizing techniques. Structure-directing agent (SDA)-mediated solution-phase metal nanocrystal synthesis has shown its ability to produce a large variety of nanostructures, but to further increase the product homogeneity and quantity, fundamental understanding of the workings of SDAs is a priority. Computational means can serve as an excellent tool to investigate such phenomena in low length and time scales. We use classical molecular dynamic (MD) simulations to study the role of polyvinylpyrrolidone (PVP) in PVP-mediated formation of {100}-faceted Ag nanocrystals in ethylene glycol (EG) solution. Though not fully understood in previous studies, the consensus is that PVP promotes the expression of Ag(100) facets via stronger binding to Ag(100) than Ag(111). In investigating the role of PVP, we consider both thermodynamic and kinetic control. We compute the solid-liquid interfacial free energy γ_{sl} of Ag(100) and Ag(111) in contact with the PVP-EG solution using the multi-scheme thermodynamic integration (TI) method that we have developed based on the previous “cleaving wall” method. We find that the PVP-EG solution lowers $\gamma_{Ag(100)}$ slightly more than $\gamma_{Ag(111)}$ comparing to the bare surfaces (i.e., in contact with vacuum) and Ag surfaces in contact with the solvent EG only, and it does not reverse the trend that $\gamma_{Ag(111)} < \gamma_{Ag(100)}$, so that the Ag(111) facets are still more thermodynamically stable than Ag(100) when covered with PVP monolayer. For the kinetic control, we compare the facet growth rates of Ag(100) and Ag(111) by looking at the deposition fluxes to these surfaces and predict the kinetic Wulff shapes. We calculate the mean first-passage time of a free Ag atom going from the solution phase to the Ag surface from MD simulation by approximating the Smoluchowski equation, and find that the difference in growth rates is a combined effect of both the probability a PVP segment attracts a solution-phase Ag atom and the diffusion of the Ag atom inside the surface-adsorbed PVP layer. Due to stronger binding affinity to Ag(100) facets, PVP chains pack more loosely on Ag(111) and extend longer into the solution phase, which leads to a larger probability to attract a solution-phase Ag and a faster diffusion for the Ag atom inside such PVP layer. Our findings in the kinetic study are consistent with experimental observations. Combining the interfacial free energy study and the flux study, we resolve the role of PVP in Ag nanocube formation and confirm the dominance of kinetic control in such formation. Our findings can be indicative for other similar SDA-solution/metal combinations and the methods used in this work can be applied to a broader range of systems.

Kinetic modeling of metabolism in Clostridia

Presenter: Satyakam Dash

Advisor: Costas Maranas

Clostridia have broad and flexible systems for substrate utilization such as *C. thermocellum* which metabolizes cellulose and *C. ljungdahlii* that metabolizes syngas to produce biofuels, but they remain poorly characterized with significant uncertainty in their metabolic repertoire. In this study, we develop dynamic metabolic models for the two organisms using the Ensemble Modeling (EM) paradigm which requires curated genome-scale metabolic (GSM) model of the organism as its foundation. For *C. thermocellum*, we constructed a second-generation GSM model (*iCth446*) with 446 genes, 598 metabolites and 660 reactions, along with gene-protein-reaction associations by updating cofactor dependencies, maintenance (GAM and NGAM) values and resolving elemental and charge imbalances. *iCth446* model was subsequently used to develop *k-ctherm119*, a kinetic model of *C. thermocellum*'s central metabolism containing 119 reactions and 93 metabolites with cellobiose as the carbon source under anaerobic growth condition. *k-ctherm119* encompasses the cellobiose degradation pathway, glycolysis/ gluconeogenesis, the pentose phosphate (PP) pathway, the TCA cycle, pyruvate metabolism, anaplerotic reactions, alternative carbon metabolism, nucleotide salvage pathway, along with all biomass precursors and 22 substrate level regulatory interactions extracted from BRENDA. The kinetic model parameters were estimated by simultaneously imposing the mutant library data recently measured and provided by the Lynd group. This dataset includes 22 *C. thermocellum* mutants with genetic perturbations in lactate, malate, acetate, and hydrogen production pathways and combinations thereof with measured concentrations of various fermentation products such as acetate, lactate, formate, hydrogen, pyruvate, ethanol, and cellobiose (19 measured concentrations per mutant). The kinetic model accurately predicted metabolic phenotypes in multiple mutant strains not included in the model parametrization. Examples include cytosolic concentrations for fourteen out of eighteen metabolites in the ΔIdh mutant. The kinetic model also alludes to a systemic level effect of limiting nitrogen source resulting in increased yields for lactate, pyruvate and amino acids and an increase in ammonia and sugar phosphates concentrations due to down-regulation of fermentation pathways under ethanol stress. Robustness analysis of the kinetic model revealed the presence of secondary activity of ketol-acid reductoisomerase and its regulation by valine and leucine pool levels. A similar effort is also underway for *C. ljungdahlii*. A core metabolic model composed of 77 reactions and 63 metabolites was constructed with 41 substrate level regulatory interactions from BRENDA based on other Clostridia species. The network spans glycolysis, the Wood-Ljungdahl pathway, and TCA cycle. Experimental flux data for a wild-type and mutants will be used to estimate the core model parameters using the previously discussed framework. The constructed kinetic models will be ultimately used to explore metabolic drivers that underpin the over-production of isobutanol in *C. thermocellum* and acetate in *C. ljungdahlii*.

Hydrocarbon cracking to light olefins - from the microscale to the mesoscale for applications in endothermic fuel reactions

Presenter: Taslima Zaman

Advisor: Robert Rioux

Light olefins such as ethylene and propylene are used to make “clean” fuels, which burn and do not inhibit the functioning of catalytic converters in engine exhaust¹. Light olefins are obtained as a by-product predominantly from steam cracking of naphtha, which requires high temperature operating conditions (800 - 900°C)² and therefore is very energy consuming. The implementation of catalytic cracking requires less energy (550 - 650°C)² and produce light olefins with higher selectivity. For applications in endothermic fuel reactions, product selectivity coupled with the overall net energy requirement is critical.

The highly active, highly stable USY zeolite is extensively used in FCC processes. However, the large pores and supercages are more suitable for cracking heavier hydrocarbon molecules present in crude oil. The large voids promote hydride transfer and drive undesirable side reactions producing coke precursors and causing low olefin selectivity and short catalyst lifetime. Medium pore zeolites hinder the transition states formed by the hydride transfer and forces cracking to proceed via the monomolecular mechanism and favors light olefin production. Amongst the many medium pore zeolites studied including ZSM-57, ferrite, ZSM-22 and small pore zeolites including chabazite, ZK-5 and ZSM-58, HZSM-5 stood out in terms of activity, stability and selectivity for light olefin production³.

The enthalpy of n-butane cracking over HZSM-5 has been measured using differential scanning calorimetry (See Figure 1). We have utilized n-butane as a probe reactant because it is small and symmetric enough to keep the product distribution as simple as possible while providing various reaction pathways sufficient to represent alkane cracking. Due to multiple reactions taking place simultaneously (primary and secondary) in n-butane cracking, it is difficult to accurately measure enthalpy contributions from any one reaction. Hence, the impact of side reactions will also be investigated.

The acid sites available for reaction in zeolites are often correlated with catalytic activity and hence it is important to quantify the acid site density⁴. Probe adsorbates, such as basic amines, can be used to count acid sites^{5,6}. Further studies of spatial distribution of acid sites in single-large crystals provides a fundamental understanding of their structure-function relationships and possibly enable to bridge the gap between the chemistry and kinetics that occur in sub-micron particles and in single large-body zeolite crystals.

The aluminum content of ZSM-5 with different Si/Al ratio has been measured using thermogravimetric analysis (TGA) with various amines, including isopropylamine and pyridine (See Figure 2). Both sub-micron sized samples and single large-body crystal zeolites with similar Si/Al ratios have been analyzed and compared. The measured Al content has been independent of particle size demonstrating that all acid sites within the large zeolite crystals are accessible. Electron probe microanalysis (EPMA) has also been utilized to measure the aluminum content spatially within the large single crystals of ZSM-5 since it is well-known that Al tends to zone in these particles.

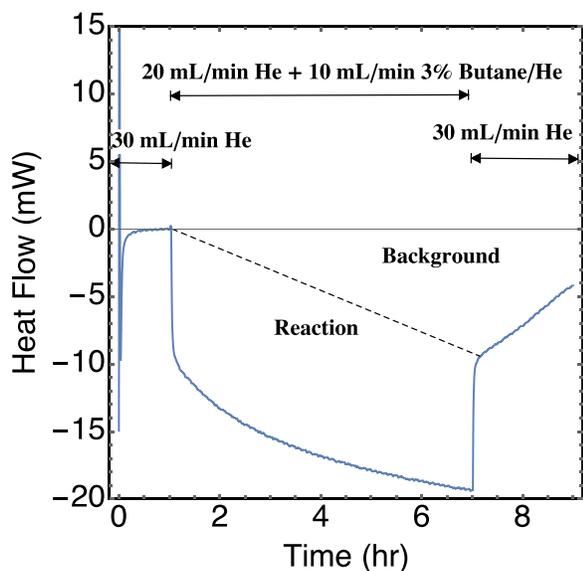


Figure 1. DSC heat flow profile for n-butane cracking at 600°C over 25mg HZSM-5 and 43% conversion.

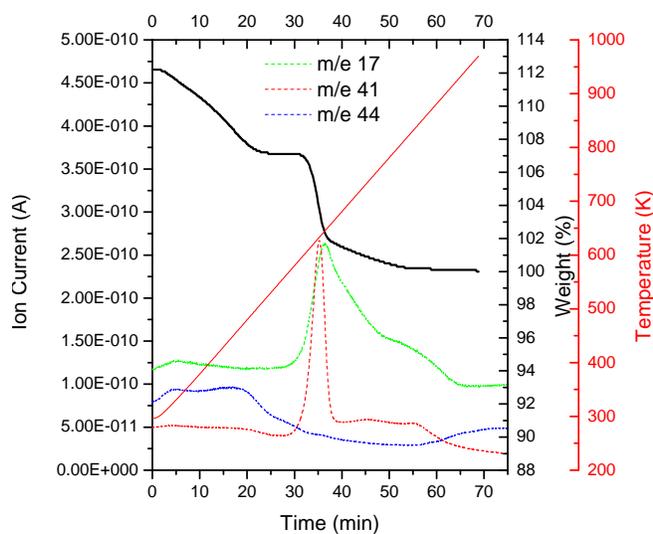


Figure 2. TGA-MS analysis of in-situ adsorption of isopropylamine to quantifying Brønsted acid sites.

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How to quantify and improve the performance of biomimetic membrane matrices?

Presenter: Tingwei Ren

Advisor: Manish Kumar

Membrane protein and membrane protein–mimic enhanced materials are rapidly gaining interest across a wide range of fields - from medicine to environmental science. Applications in these fields include drug screening¹, DNA sequencing², drug delivery³, sensors⁴, and water desalination⁵. In all these applications, performance is highly dependent on activity per protein and protein packing density. However, a clear understanding of, and accurate tools to study the activity, packing density, and insertion ability of membrane proteins and their mimics in biomimetic membranes such as lipids and amphiphilic block copolymers does not currently exist.

Here, we present methods to evaluate the compatibility of membrane proteins and their mimics with biomimetic membrane matrices. We will describe our simplified and optimized biophysical activity characterization and membrane protein density determination methods⁶. In addition, we will briefly walk the audience through the design of a novel assay for quantifying the effect of matrix hydrophobicity on protein insertion using a new optical characterization technique⁷, which for the first time provides a quantitative measure of the chemical compatibility between proteins and membranes. Water transport protein (aquaporins, AQPs), rhodopsins, and artificial water channels (specifically peptide-appended pillar[n]arene (PAP) channels) were reconstituted into a range of biomimetic membrane matrices to validate the proposed platform. We discovered that both AQPs and PAP channels preserve their single molecule water transport rates in different biomimetic membranes. We thus concluded that it is their reconstitution density difference that leads to the differences observed in membrane performance. We also provide support to a proposed hydrophobicity mismatch theory: smaller hydrophobicity mismatches between the membrane matrix and the proteins lead to higher membrane protein (or membrane protein-mimic) reconstitution densities.

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Modeling regulation and metabolism in Cyanobacteria

Presenter: Thomas Mueller

Advisor: Costas Maranas

Computational modeling of cellular processes such as regulation and metabolism serves to provide deeper insights into the factors contributing to an organism's phenotype as well as guide future experimental work. Regulatory networks can aid in the incorporation of complex processes such as nitrogen fixation that require modified control of processes across metabolism. Given that nitrogen fixation requires an anaerobic environment, diazotrophic organisms such as *Cyanothece* 51142 temporally separate photosynthesis and nitrogen fixation. To incorporate this process into the non-diazotrophic *Synechocystis* 6803, regulatory networks over a diurnal cycle were developed for both *Cyanothece* and *Synechocystis* and used to identify two transcription factors native to *Synechocystis*, LexA and Rcp1, that are promising candidates to control the *nif* gene cluster and other pertinent metabolic processes, respectively.

While regulatory networks can identify broad intervention strategies, modeling metabolism provides a more granular perspective, and enables both the identification of the metabolic repertoire of an organism and contributing factors to a desired phenotype. Genome-scale metabolic (GSM) models were developed for two closely related strains, *Synechococcus* 7942 and the *Synechococcus* 2973. Despite a 99.8% genome sequence identity between the two strains, under their respective optimal conditions *Synechococcus* 2973 grows 2.3 times faster than *Synechococcus* 7942. Incorporation of experimental data as constraints on the model gave a fold change in growth rates on the same order of magnitude as the experimental observations identifying carbon fixation rate as a contributing factor to the differing growth rates.

Session 3

Predicting kinetic nanocrystal shapes through multi-scale theory and simulation: polyvinylpyrrolidone-mediated growth of Ag nanocrystals

Presenter: Tonnam Balankura

Advisor: Kristen Fichthorn

In the shape-controlled synthesis of colloidal Ag nanocrystals, structure-directing agents, particularly polyvinylpyrrolidone (PVP), are known to be a key additive in making nanostructures with well-defined shapes. Although many Ag nanocrystals have been successfully synthesized using PVP, the mechanism by which PVP actuates shape control remains elusive. Here, we present a multi-scale theoretical framework for kinetic Wulff shape predictions that accounts for the chemical environment, in which we used to probe the kinetic influence of the adsorbed PVP film. Within this framework, we use umbrella-sampling molecular dynamics simulations to calculate the potential of mean force and diffusion coefficient profiles of Ag atom deposition onto Ag(100) and Ag(111) in ethylene glycol solution with surface-adsorbed PVP. We use these profiles to calculate the mean-first passage times and implement extensive Brownian dynamics simulations, which allows the kinetic effects to be quantitatively evaluated. Our results show that PVP films can regulate the flux of Ag atoms to be greater towards Ag(111) than Ag(100). The PVP's preferential binding towards Ag(100) over Ag(111) gives PVP its flux-regulating capabilities through the lower free-energy barrier of Ag atoms to cross the lower-density PVP film on Ag(111) and enhanced Ag trapping by the extended PVP film on Ag(111). Under kinetic control, {100}-faceted nanocrystals will be formed when the Ag flux is greater towards Ag(111). The predicted kinetic Wulff shapes are in agreement with the analogous experimental system.

*Insights into the effects of conformational disorder on the intra-chain
electronic properties of polymer semiconductors*

Presenter: Joel Bombile

Advisor: Michael Janik and Scott Milner

Polythiophenes are semiconductors with potential applications as active elements in organic electronic devices. Like other organic semiconductors, the widespread usage of these polymers is limited by a low performance relative to their inorganic counterparts. A key source of difficulties in developing high-performing polymeric semiconductors is the limited understanding of how conformational disorder affects their optoelectronic properties. A high level of conformational disorder is inherent to these soft materials. We develop a coarse-grained approach based on the tight binding approximation to model the electronic degrees of freedom of polythiophene chains, taking into account atomic coordinates changes. Particularly important are dihedral rotations and vibrational ring distortions, known to disrupt extended electronic states. The model, which coarse-grains the chains at the level of a thiophene ring, is parameterized using molecular and electronic structure calculations at the density functional theory (DFT) level of accuracy. The model predicts the formation of localized electronic states strictly due to thermal dihedral fluctuations—a disorder induced localization. We further show that this localization mechanism is for the most part responsible for the broadening of the optical absorption spectrum of poly(3-hexylthiophene) chains in solution. Our model also demonstrates the formation of self-localized carriers—polarons stabilized by the reorganization of rings in the absence of disorder. We compare the localization lengths and binding energies associated with the two charge localization mechanisms, and learn that the effects of ring distortions on the electronic transport properties of the chains are very small in comparison to dihedral disorder.

*Nonlinear control of transport reaction processes using
discrete adaptive POD (DAPOD)*

Presenter: Manda Yang

Advisor: Antonios Armaou

Control of nonlinear distributed parameter system (DPS) has been of critical importance due to the simultaneous existence of diffusion, convection and reaction phenomena in a lot of chemical processes. One approach to facilitate the controller design is to construct reduced order models (ROMs) using Galerkin's method with basis functions generated by proper orthogonal decomposition (POD). To mitigate the impact of the history observation and reduce the computational cost, adaptive proper orthogonal decomposition (APOD) was proposed. However, this method suffers from the oscillations in the dimension of the ROM. My research proposes a modified version, called discrete APOD (DAPOD) to improve the accuracy of the estimate of eigenvalues so that the oscillations in dimension can be mitigated.

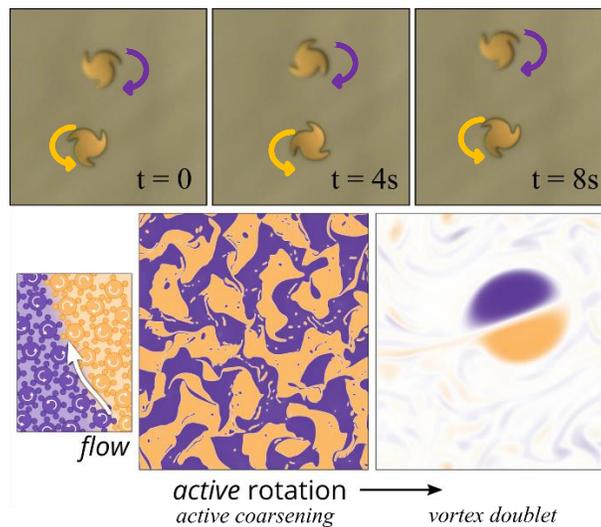
To evaluate the performance of the proposed method, APOD and DAPOD are applied to regulate a diffusion reaction process and a fluid flow system described by the Kuramoto-Sivashinsky equation. Feedback linearization and Lyapunov-based controller are designed. The system state is estimated by a dynamic observer and a static observer, respectively. The simulation result demonstrates the improvement of DAPOD in constructing ROMs.

Shape-directed actuation and collective dynamics of spinners

Presenter: Syeda Sabrina

Advisor: Kyle Bishop

Shape, symmetry and other geometric features are widely used for programming self-assembly of passive colloids. These parameters can also be used as powerful strategies for engineering motion and interactions of self-propelled particles. Unlike self-propulsion directed by anisotropic surface (*e.g.*, catalytic Janus particles), shape-directed motion of active colloids is far less explored. Shape and symmetry of particles can enable more complex forms of locomotion than simple linear motion of Janus particles. In this talk, we present shape-directed self-rotating particles (spinners) powered by ultrasound that can rotate in both clockwise (CW) and counterclockwise (CCW) directions depending on their chiral orientation (R/S). While ultrasonic propulsion in fuel-free environment can be used for biomedical applications; shape- and symmetry-directed actuation offers opportunities for designing active colloids driven by a wide range of external stimuli (*e.g.*, chemical fuel, electric field, etc.) for enhanced functionalities and applications. Our experimental efforts are also guided by numerical prediction of phase separation into “like-rotating” particles in mixtures of counter-rotating spinners. The phase separation is accompanied by steady convective flows that depend on the strength of active rotation and that of frictional interactions with the stationary surroundings. We observe new dynamical behaviors such “active coarsening” *via* self-generated convective flows as well as the emergence of self-propelled “vortex doublets”. Our results highlight further opportunities for achieving emergent collective behaviors in ensembles of spinners subject to distributed actuation enabling smart materials to shape change, adapt, sense, self-repair, and even self-replicate.



Nano-sized polymer electrode interlayer with a high-concentration of C-S-S-C bonds improves the columbic efficiency of lithium-sulfur batteries

Presenter: Michael Regula

Advisor: Donghai Wang

The advent of lithium-ion batteries at the end of the 20th century has driven the demand for both energy storage and energy itself. Despite their commercial success, state-of-the-art lithium-ion batteries have been mostly impractical for use in high energy applications, like electric vehicles, due to the relatively low specific capacity and energy density of layered metal oxide cathode structures. Alternatively, sulfur has a theoretical specific energy and energy density many times higher than layered metal oxides. Sulfur is naturally abundant as well as an unused byproduct of many industrial processes, making it an environmentally-benign, inexpensive commodity. Sulfur-based cathodes have run into three major technical issues: 1) the electrical conductivity of sulfur is low (conductivity – $5 \times 10^{-30} \text{ S cm}^{-1}$), 2) the parasitic polysulfide shuttle effect - caused by sulfur and polysulfide dissolution into the electrolyte - inactivates sulfur, and 3) the 80% volume expansion of sulfur upon lithiation interrupts electrical connections between sulfur and conductive materials. All of these issues lead to a low coulombic efficiency in each battery cycle, making lithium-sulfur batteries impractical for commercial use.

To improve the columbic efficiency of sulfur cathodes, a nano-sized polymer with a high concentration of C-S-S-C bonds was added as an insoluble interlayer between the separator and the lithium metal anode. The polymer was prepared aqueously via a substitution reaction between sodium disulfide and 1,2,3-trichloropropane in the presence of a phase-transfer catalyst. Upon discharge, the S-S bonds in the polymer are lithiated, creating a branched salt with three Li^+ ions. This salt may repel lithium polysulfides formed when lithium reacts with the sulfur electrode, slowing the polysulfide shuttle effect. The addition of the polymer interlayer exhibits a columbic efficiency of >99% over 100 cycles at a low current rate (C/10) and >97% at a higher current rate (1C). By studying this and similar polymer interlayers, lithium-sulfur batteries can fulfill their great economic potential.

Understanding the surface mechanochemical behavior of soda lime silica glass through ion-exchange process

Presenter: Jiawei Luo

Advisor: Carlo Pantano and Seong Kim

Understanding the surface mechanochemical behavior of soda lime silica (SLS) glass is of great importance because the strength of the glass is highly affected by the chemical reactions between glass and water molecules in the presence of normal and shear stress. SLS glass has been found to have very unique resistance to shear stress at high relative humidity (RH). This behavior has been correlated with the chemical structure of SLS glass in the surface region where mobile Na^+ is associated with the non-bridging oxygens (NBOs). Potassium ion-exchange process, which is replacing Na^+ with K^+ in the surface region of the aluminosilicate glass through an inter-diffusion process, has been applied as a chemical strengthening method in industry to produce highly normal stress resistant cell phone screens by creating compressive stress in its surface region. However, the ion-exchanged glass surface does not have any improvement in the wear resistance at high RH. More in-depth investigation is then required on the surface chemical structure of SLS glass before and after ion-exchange process. This talk aims to enhance the understanding of the relationship between the surface chemical structure and mechanochemical behavior of SLS glass. One way of improving the resistance to normal and shear stress at the same time for SLS glass, which maintains the chemical structure of pristine SLS glass in the near surface region and keeps the compressive stress present in its subsurface, is also proposed.

Poster Session

Electrostatic Generation and Ratcheted Transport of Aqueous Droplets

Presenter: Charles Cartier

Advisor: Kyle Bishop

Rapid droplet generation and transport within microfluidic devices enables process parallelization and applications ranging from medical diagnostics to particle synthesis. Typically high-speed droplet generation and manipulation is achieved passively *via* pressure driven flows from an external pump such as microfluidic flow focusing devices or T-junctions. Alternatively, droplets can be generated and transported through active actuation mechanisms. For example digital microfluidic systems make use of an array of electrodes to provide discrete control of droplet position (e.g. Electrowetting-on-Dielectric) however these systems are often accompanied by complex fabrication and a reduction in transport speed. Simpler active actuation mechanisms are needed to make portable droplet microfluidic systems more economically feasible. We demonstrate that a microfluidic device constructed with simple soft-lithography techniques can generate charged droplets electrostatically using only a DC voltage without bulk pressure driven flow. Once droplets are generated, rapid transport of aqueous droplets is accomplished by combining contact charge electrophoresis with ratcheted microfluidic geometries. We discuss how the voltage, pressure, channel geometry and fluid properties affect the droplet generation and transport behavior and we propose heuristics for the optimal design of this system. We believe this system could eventually act as a cheap platform for portable digital droplet PCR systems powered only by a battery.

Effects of pH and alkali cations on H^{}/OH^{*} adsorption and the hydrogen oxidation reaction*

Presenter: Ian McCrum

Advisor: Michael Janik

While traditional proton exchange membrane (PEM) fuel cells give great performance, with high efficiency and power density, their high cost has limited their use. This high cost results in part from the use of expensive platinum or platinum alloy catalysts, which are necessary to give the desired fuel cell stability/lifetime in the acidic environment of the proton conducting membrane. Anion exchange membrane (AEM) fuel cells, which conduct hydroxide anions instead of protons, may represent a significantly lower cost alternative to the PEM fuel cell, as a broader array of lower cost metal catalysts are both active and stable in an alkaline environment. However, recent research has shown that the rate of the hydrogen oxidation reaction (occurring at the anode of hydrogen fuel cells) is 2-3 orders of magnitude slower in an alkaline environment than in an acidic environment on many transition metal catalysts. This has been found to correlate with what was believed to be a strengthening of the binding of adsorbed hydrogen, a known reaction intermediate, with pH. Understanding the mechanism for this effect of pH is necessary to design high performance alkaline fuel cells.

We have used density functional theory (DFT) modeling and experimental techniques to examine the effects of pH and alkali metal cations (Li, Na, K, Cs) on the hydrogen oxidation reaction on platinum and other transition metal electrode surfaces. Our DFT results show that alkali metal cations can specifically adsorb at low potentials in high pH electrolytes to platinum surfaces. These adsorbed cations, which retain some of their charge on adsorption, interact negligibly with co-adsorbed hydrogen, but strongly with adsorbed hydroxide, weakening hydroxide adsorption in alkaline electrolytes. We have further found that hydrogen and hydroxide competitively adsorb at the same potentials on stepped or under-coordinated platinum surface sites. It is only these sites which show the experimentally measured shift in what was believed to be the hydrogen binding energy with pH. We can now show that this shift depends on both hydrogen and hydroxide binding strength and is due to the weakening of hydroxide adsorption (not the strengthening of hydrogen adsorption). This supports the involvement of adsorbed hydroxide in the hydrogen oxidation reaction, which has been proposed by others previously. We have found competitive hydrogen and hydroxide adsorption can occur on most metals that bind adsorbates more strongly than platinum, and a similar effect of a co-adsorbed cation weakening hydroxide adsorption.

Our experimental results have also shown that in an alkaline electrolyte, the identity of the cation (present in the electrolyte) has a small effect on the rate of hydrogen oxidation as well, with the order of activity following Li > Na > K > Cs. Current work is focused on using DFT to predict the rate of the individual steps of the hydrogen oxidation reaction to determine the mechanism.

The Pathway Map Calculator: A Learning Algorithm to Predict Optimal Expression Levels from Characterized Pathway Variants

Presenter: Sean Halper

Advisor: Howard Salis

Heterologous metabolic pathways are often optimized by introducing combinatorial variations of genetic parts to modulate enzyme kinetics and expression levels with the goal of finding improved pathway variants. When applied to many-enzyme pathways, such combinatorial optimization requires the construction and characterization of many pathway variants, while generating sparse, high-dimensional data-sets that remain difficult to analyze. To overcome these challenges, we developed an automated algorithm that utilizes a small number of characterized pathway variants to learn the expression-flux relationship in a high-dimensional space and to accurately predict the optimal enzyme expression levels that maximize the pathway's flux. The Pathway Map Calculator converts end-product measurements and predicted/measured enzyme expression levels into accurate expression-flux models, utilizing elementary mode analysis, kinetic metabolic modeling, model reduction, de-dimensionalization, and genetic algorithm optimization. The algorithm handles many types of genetic parts, host organisms, and measurement assays. Using experimental and *in silico* pathway examples, we rigorously tested the algorithm's ability to predict optimal enzyme expression levels, its accuracy when employing combinatorial or design-of-experiment pathway construction approaches, its scaling on many-enzyme pathways, its ability to tolerate experimental measurement noise, and its ability to quantify and rank the enzymes' kinetics. We show that only 100 characterized pathway variants are needed to optimize a typical 9-enzyme pathway. Our approach will dramatically accelerate the engineering of metabolic pathways, an has been demonstrated experimentally on multiple examples.

Novel strategies to control membrane fouling and enhance performance during ultrafiltration of plasmid DNA

Presenter: Ying Li

Advisor: Andrew Zydney

Several recent studies have demonstrated that small pore size ultrafiltration membranes can be used for purification of supercoiled plasmid DNA for therapeutic applications, but the performance of these membrane systems is severely limited by membrane fouling and low selectivity. This presentation will examine the potential of using novel strategies to control fouling and enhance performance during ultrafiltration of plasmid DNA, which is of interest in gene therapy applications and as DNA-based vaccines.

Preconditioning can be accomplished by pre-elongating the DNA by passage through a region with large pore size. Our studies have shown that pre-conditioning is able to minimize fouling while simultaneously enhancing DNA separations. Pre-conditioning was done using asymmetric hollow fiber membranes, with flow in the reverse (shell-to-lumen) orientation, and with composite membrane structures made by placing a large pore size flat sheet microfiltration membrane in series with an ultrafiltration membrane. In all cases, flow through the larger pore region leads to an increase in selectivity and a significant reduction in fouling.

The structure of plasmid DNA is known to be a strong function of solution conditions due to intramolecular electrostatic interactions between the charged phosphate groups along the DNA backbone. We have shown that the effect of ionic strength is greatest for the supercoiled plasmid compared with the linear and open-circular isoforms, providing novel opportunities for enhanced purification of this therapeutically active isoform.

Supercoiled plasmids have a unique highly “branched” structure, with the number of branches dependent on the DNA length. This difference in branching leads to a significant dependence of the transmission on the size of the supercoiled plasmid, which we were able to exploit for size-based DNA separations. Together these results provide important insights into the factors controlling plasmid DNA transmission through nanoporous membranes and exciting opportunities for enhanced DNA separations.