The University at Buffalo Department of Chemical and Biological Engineering presents

The 2018 Graduate Student Research Symposium

"Humanizing Therapeutics Discovery & Development"

Douglas A. Lauffenburger
Massachusetts Institute of Technology
Department of Biological Engineering

Friday, October 12, 2018
Center for the Arts, UB Amherst Campus

University at Buffalo
Department of Chemical and Biological Engineering
School of Engineering and Applied Sciences

The 21st Annual Graduate Student Research Symposium

Friday, October 12, 2018

1:00-3:00 p.m. Welcome and Opening Remarks
Mark Swihart, Ph.D.
UB Distinguished Professor and Department Chair
Department of Chemical and Biological Engineering
University at Buffalo

Graduate Student Lectures
Junyi Liu, Ph.D. Candidate
Highly Polar Polymers with Superior Membrane CO_2/N_2 Separation Properties for Carbon Capture

Faculty Advisor Haiqing Lin, Ph.D.
Department of Chemical and Biological Engineering
University at Buffalo

Andrew Kroetsch, Ph.D. Candidate
A Platform Engineering Approach for the Design of Recycling Therapeutic Antibodies

Faculty Advisor Sheldon Park, Ph.D.
Department of Chemical and Biological Engineering
University at Buffalo

Keynote Speaker
Douglas A. Lauffenburger, Ph.D.
Humanizing Therapeutics Discovery & Development

Ford Professor of Bioengineering and (founding) Head of the Department of Biological Engineering at Massachusetts Institute of Technology

Questions and Answers

3:00 p.m. Reception Begins

3:30 p.m. Poster Judging Competition Begins

5:00 p.m. Announcing of the Winners of the Poster Competition
Mark Swihart, Ph.D.

Abstracts for Graduate Student Speakers

Highly Polar Polymers with Superior Membrane CO_2/N_2 Separation Properties for Carbon Capture

Junyi Liu, Ph.D. Candidate

[1]Department of Chemical and Biological Engineering, University at Buffalo, The State University at New York, Buffalo, New York 14260, USA
[2]Department of Chemistry, University of California, Riverside, California 92521, USA
[3]Commonwealth Scientific and Industrial Research Organization (CSIRO) Manufacturing, Private Bag 10, Clayton, South Victoria 3169, Australia
[4]WCU Department of Energy Engineering, Hanyang University, Seoul, South Korea

Junyi Liu[1], Shaoze Zhang[2], De-en Jiang[2], Cara M. Doherty[3], Anita J. Hill[3], Chong Cheng[1], Ho Bum Park[4], Haiqing Lin[1] ⋆

Membrane technology has emerged as a potentially economically viable alternative for CO_2 captures from fossil fuel-fired powers, enabled by advanced membrane materials with high CO_2 permeability and high CO_2/N_2 selectivity. Current leading membrane materials usually contain poly(ethylene oxide) (PEO) because the ether oxygen in PEO interacts favorably with CO_2, resulting in high CO_2/N_2 selectivity. Herein we prepare a series of highly branched amorphous polymers containing poly(1,3-dioxolane), which has an O:C ratio of 0.67, higher than 0.5 in PEO. The length of the poly(1,3-dioxolane)-based branches are tuned to yield amorphous nature, and mobile ethoxyl chain end groups are introduced to provide high free volume and gas diffusivity. These ether oxygen-rich polymers exhibit more superior CO_2/N_2 separation properties than the PEO-based materials at practical conditions for flue gas processing, and above the Robeson's upper bound. This work demonstrates that harnessing the interactions between polymers and CO_2 may provide unprecedented opportunities in designing gas separation membranes with robust performance under practical conditions.

A Platform Engineering Approach for the Design of Recycling Therapeutic Antibodies

Andrew Kroetsch, Ph.D. Candidate

[1]Department of Chemical and Biological Engineering, University at Buffalo, Buffalo, New York 14260
[2]Department of Pharmaceutical Sciences, University at Buffalo, Buffalo, New York.

Andrew Kroetsch[1], Dhaval K. Shah[2], Sheldon Park[1]

A new modality in antibody engineering has emerged in which the antigen affinity is designed to be pH dependent (PHD). In particular, the combination of high affinity binding at neutral pH with low affinity binding at acidic pH leads to a novel antibody that can more effectively act on its target through a pH dependent recycling mechanism. We have studied how the in vivo pharmacokinetics of the soluble superantigen, Staphylococcal enterotoxin B (SEB), is affected by an engineered therapeutic antibody with pH dependent binding. PHD anti-SEB antibodies were made by introducing mutations into a high affinity anti-SEB antibody using rational design and directed evolution. This same two-step engineering approach was applied in another, unrelated, therapy to generate anti-tumor antibodies with pH dependent binding to a cell surface receptor. The effect of using PHD anti-tumor antibodies was an overall increase in antibody internalization and subsequent increase in killing of tumor cells. Therefore, these novel antibodies can be generated using this platform approach in a robust and efficient manner, which may be applied to a wide variety of diseases.

Abstract for Keynote Speaker

Humanizing Therapeutics Discovery & Development

Douglas A. Lauffenburger, Ph.D.

Ford Professor of Bioengineering and (founding) Head of the Department of Biological Engineering at Massachusetts Institute of Technology

The therapeutics discovery/development pipeline involves multiple stages for progress from idea to approved treatment, and has become highly expensive over the past decades mainly due to the large proportion of potential drugs that fail in costly clinical trial stages. A chief reason for failure in clinical trials following promising findings in preclinical studies is that results in preclinical animal model studies do not generally translate strongly to similar results in human patients due to the incomplete correspondence of animal biology, physiology, and pathology in comparison to that in humans. Alongside this scientific issue, there exists a level of societal concern about the most appropriate use of animal experimentation. The therapeutics discovery/development field has been attempting to address the challenge of 'humanizing' the pipeline along multiple avenues of research endeavor – prominently including efforts to construct human tissue and organ surrogates outside the body, using stem cell and 'organ-on-chip' platform technologies, and machine learning computational modeling approaches to bridge the preclinical-to-clinical divide either with human genomic data or with modeling of animal experiment data. In this presentation I will outline various approaches to addressing this therapeutics discovery/development challenge, and their current stage of prospect.

Biography:

Dr. Douglas A. Lauffenburger is Ford Professor of Bioengineering and (founding) Head of the Department of Biological Engineering at MIT. His major research interests are in cell engineering: the fusion of engineering with molecular cell biology, with central focus on systems biology approaches to complex pathophysiology in application to drug discovery and development. Lauffenburger has co-authored a monograph entitled Receptors: Models for Binding, Trafficking & Signaling, published by Oxford University Press in 1993; he also co-edited the book entitled Systems Biomedicine: Concepts and Perspectives, published by Elsevier in 2010. More than 100 doctoral students and postdoctoral associates have undertaken research education under his supervision.

Prof. Lauffenburger has served as a consultant or scientific advisory board member for numerous biotechnology and pharmaceutical companies, and his awards include the Galletti Award from AIMBE, the Coburn Award and Walker Award from AIChE, and the Distinguished Lecture Award and Shu Chien Career Achievement Award from BMES. He is a member of the National Academy of Engineering and the American Academy of Arts & Sciences, and has served as President of the Biomedical Engineering Society, Chair of the College of Fellows of American Institute for Medical & Biological Engineering, on the Advisory Council for NIGMS, and as a co-author of the 2009 NRC report on A New Biology for the 21st Century.

University at Buffalo
Department of Chemical and Biological Engineering
School of Engineering and Applied Sciences

www.cbe.buffalo.edu

Department of Chemical and Biological Engineering

- Outstanding funding from NIH, NYSTEM, NSF, USAF, AHA, DOE
- 9 NSF CAREER Awards
- 4 members of National Academy of Engineering

Bioengineering research

- **Andreadis** - Adult and induced pluripotent stem cells for cardiovascular tissue engineering, signaling pathways in cell-cell adhesion and wound healing, biomaterials for protein and gene delivery, lentiviral vectors and lentiviral microarrays for high-throughput gene expression analysis and gene discovery
- **Gunawan** - Computational methods for the extraction of mechanistic and actionable insights from biological data
- **Neelamegham** - Cell biomechanics, systems biology, thrombosis and hemostasis, glycosciences
- **Parashurama** - Stem cells, liver tissue engineering and regenerative medicine, advanced imaging modalities
- **Park** - Biotechnology, protein engineering, simulated dynamics, bioinformatics, drug discovery
- **Pfeifer** - Metabolic engineering, heterologous natural product biosynthesis, genetic vaccine design

Modeling and computational research

- **Dupuis** - Chemistry fundamentals for new energy technologies from multi-physics Multi-scale modeling
- **Errington** - Molecular simulation, statistical thermodynamics, interfacial phenomena
- **Furlani** - Multidisciplinary modeling: microfluidics, computational fluid dynamics, mass/heat transfer, multiphase systems, MEMS, nanophotonics, biomagnetics
- **Hachmann** - Computational chemistry and materials science, virtual high-throughput and Big Data, machine learning, electronic structure theory and methods, quantum effects in catalysis and materials
- **Kofke** - Statistical physics, molecular modeling and simulation, software engineering
- **Lockett** - Mass/heat transfer, distillation, separations
- **Nitsche** -Transport phenomena, dermal absorption, biological membrane and pore permeability

Students in front of new Davis Hall engineering building

Materials research

- **Alexandridis** - Self-assembly, directed assembly, complex fluids, soft materials, nanomaterials, interfacial phenomena, amphiphilic polymers, biopolymers, product design
- **Cheng** - Biodegradable functional polymers and nanostructures, new drug delivery systems, synthetic materials for tissue engineering
- **Goyal** - Clean energy technologies, high temperature superconductivity, nanomaterials for energy and the environment
- **Kyriakidou** - Rational design of catalytic and hydrocarbon trapping materials to meet automotive emissions regulations
- **Lin** - Membrane materials and processes for gas and vapor separation and water purification
- **Lund** - Heterogeneous catalysis, chemical kinetics, reaction engineering
- **Ruckenstein** - Catalysis, surface phenomena, colloids and emulsions, biocompatible surfaces and materials
- **Swihart** - Synthesis and application of nanoparticles, reactor modeling, computational chemistry, particle nucleation and growth
- **Thundat** - Nanomaterials for novel biosensors, battery-less implantable sensors, sensor network systems and electricity transmission using a single wire
- **Tsianou** - Molecularly engineered materials, self-assembly, interfacial phenomena, crystal engineering, bio-inspired materials
- **Wu** - Advanced electrocatalysts and functional materials for electrochemical energy technologies
- **Zukoski** - Suspension mechanics, protein crystallization and nanoparticle self-assembly

University at Buffalo North Campus

UB Department of Chemical and Biological Engineering ■ www.cbe.buffalo.edu ■ 716-645-2909

Acknowledgements

Welcome to the 2018 CBE Graduate Research Symposium. Over the past 21 years our research Symposium has grown to be an exciting event that showcases the high quality research that is conducted in CBE across diverse areas such as molecular engineering of novel materials, nanotechnology, bioengineering, and molecular modeling. Every year our faculty and graduate students welcome the opportunity to present their work to their peers from CBE, other UB departments, representatives from local industry, and UB alumni and friends. As the Symposium has grown in ambition and scale, the effort needed to coordinate it has grown commensurately, and we owe many thanks to those whose time and hard work have brought it together this year.

First I would like to acknowledge the leadership and tireless efforts of CBE Graduate Student Association President **Andrew Kroetsch** (2015-2018), and **Janel Abbott** (2018), whose legwork and logistics on behalf of our students is commendable. They truly care about their colleagues and friends in CBE and how they fare in both their academic and free time while here at UB. We also owe much to the dedicated assistance of the CBE staff: **Marlo Roetzer, Andrew Schultz, Todd Nibbe, Lori DuVall-Jackson,** and **Joan Wilson**.

We are also very grateful to the Graduate Student Association for their continuing support.

I also want to acknowledge the faculty members of the organizing committee, **Johannes Hachmann, Natesh Parashurama, and Elina Kyriakidou**, our **advisory board members**, and all of our friends and colleagues who have graciously agreed to join us today to serve as **poster competition judges**.

Finally I thank the speakers and other participants who highlighted this Symposium. This includes graduate students - **Andrew Kroetsch** (Park group), and **Junyi Liu** (Lin group).

I would especially like to thank our keynote speaker, **Douglas Lauffenburger, Ford Professor of Bioengineering and (founding) Head of the Department of Biological Engineering at Massachusetts Institute of Technology**, who despite his very busy schedule traveled here to join us for this occasion. Thanks are also owed to all of the CBE graduate students who have worked so hard on their research over the years, and for presenting their work through the many carefully crafted posters that fill the Center for the Arts.

The Graduate Research Symposium continues to be an exciting occasion for our department. It is a showcase for the excellence that we strive for in our scholarship and graduate education. We look forward to many more years of this celebration of our research accomplishments. I hope you find this to be an enjoyable and informative event and that you will return in future years.

Cheers!

Mark Swihart, UB Distinguished Professor and Chair

Table of Contents

Biological Engineering

1. Metabolic Mechanisms Underlying NANOG-Induced Reversal of Aging

Debanik Choudhury, **Izuagie Ikhapoh**, **Na Rong**, **Aref Shahini**, **Nika Rajabian**, **Pedro Lei**, **Stelios Andreadis**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: debanikc@buffalo.edu, ikhapoh@buffalo.edu, nrong@buffalo.edu, arefshah@buffalo.edu, nikaraja@buffalo.edu, pedrolei@buffalo.edu, sandread@buffalo.edu

Recently, we discovered that ectopic expression of the pluripotent factor NANOG in senescent hair follicle-derived mesenchymal stem cells, reversed major aspects associated with cellular aging. NANOG restored ACTIN polymerization by reactivating ROCK and Transforming Growth Factor (TGFb) pathways which were otherwise impaired in senescent cells. Collectively, our data reveal that cellular senescence can be reversed and NANOG can also restore function lost to aging without reprogramming back to the pluripotent state. In continuance of this study, we propose to expand our understanding of the interface between cellular signaling and metabolic reprogramming in the context of cell senescence which drives a variety of pathological diseases. Our central hypothesis predicts that dysregulated amino acid breakdown fuels mitochondrial aging and that NANOG rejuvenates aged mitochondria by stimulating the expression of COXIV and superoxide dismutase II. Cellular senescence was characterized by loss of telomerase expression and increased SA-beta galactosidase stain. Enzyme-link immunoassays demonstrated that the senesced HF MSC increased citrate, oxaloacetate, urea, and ROS production. Furthermore, western blot analysis revealed a decrease in COXIV expression in the same cells, indicating defective electron transport chain. However, ectopic expression of NANOG in senesced cells restored telomerase expression and COXIV translation. Intriguingly, aminotransferase blockers impeded urea and ROS production and normalized citrate and oxaloacetate levels. Our results indicate that although senesced HF MSC have defective electron transport chain, the carbon skeleton from amino acid breakdown still feeds into the TCA cycle producing more ROS and urea. In conclusion, NANOG rejuvenates aged cells by reprograming amino acid metabolism. To the best of our knowledge, we are the first group to resurrect telomerase expression in aged HF MSC. Additionally, we discovered that amino acid catabolism drives aging and NANOG reverses this process.

Key words: aging, stem cells, senescence, metabolism

2. From Skin to Nervous System : Experimental and Bioinformatics Approaches Investigating Signaling in Neural Crest Stem Cells from Interfollicular Human Epidermis

Georgios Tseropoulos, **Pihu Mehrotra**, **Samaneh Moghadasi Boroujeni**, **Stelios Andreadis**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: gtseropo@buffalo.edu, pihumehr@buffalo.edu, samanehm@buffalo.edu, sandread@buffalo.edu

Neural Crest cells (NC) play a central role in forming the peripheral nervous system, the craniofacial skeleton and pigmentation of the skin during development due to their broad multilineage differentiation potential into neurons, Schwann cells, melanocytes, and mesenchymal stem cells. Recently, we identified an easily accessible source of pluripotent neural crest stem cells from human inter-follicular keratinocyte (KC) cultures. Here, we investigate the importance of two growth factor, FGF2 and IGF1 in the induction of KC to NC, with respect, to the expression of potent NC markers Sox10 and FoxD3 and proliferation potential. Our approach contains both experimental and high-throughput genomic sequencing tools in order to shed light to the gene regulatory networks and pathways that govern our system. Using chemical inhibition and shRNA knockdown strategies, we uncovered that the downstream regulatory pathways AKT/PI3K, MEK/ERK and cJun are critical in Sox10 and FoxD3 regulation in our system. In addition, 10X single cell RNA-sequencing is employed to analyze the different stages of the KC to NC induction over time. After identifying clusters with discrete genetic profiles, such as KC expressing epidermal markers or pluripotent NC (towards the later days of induction), we compare our findings with genetic profiles from human embryonic stem cell or induced pluripotent stem cell-derived NC. This high-throughput RNA-seq analysis provides insights into the genes and pathways that play a critical role in our KC-NC system. In summary, our study provides a better understanding of the role of FGF2 and IGF1 on the induction of NC from KC cultures and sheds light on the pathways through which these growth factors regulate key NC transcription factors Sox10 and FoxD3, which can prove pivotal in sustaining the pluripotent phenotype of NC, rendering them a potent stem cell source for applications in cell therapies.

Key words: Neural Crest, Keratinocytes, Epidermis, Signaling Pathways

3. Transforming human skin cells to neurons: an attractive cell source for treatment of spinal cord injury

Pihu Mehrotra, **Georgios Tseropoulos**, **Samaneh Moghadasi Boroujeni**, **Stelios Andreadis**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: pihumehr@buffalo.edu, gtseropo@buffalo.edu, samanehm@buffalo.edu, sandread@buffalo.edu

Our lab discovered that multipotent Neural Crest cells (NCs) can be derived from a culture of neonatal and adult interfollicular keratinocytes (KCs), without genetic manipulation, in a defined culture media. These KC derived NCs are multipotent and can give rise to functional melanocytes, smooth muscle cells, schwann cells (SCs), neurons of the peripheral nervous system (PNS) and cartilage. Neural crest cell identity has developmentally been established by the characteristic expression of the transcription factor SOX10. This transcription factor plays a major role in NC development and differentiation, maintenance of NC stemness and specification of NCs to a derivative cell lineage. NCs exhibit a transient phenotype and have a tendency to lose their multipotency when maintained in culture, by spontaneously differentiating to one of its derivative cell lineages. This limits their clinical potential, since NCs derived from a patient skin need to be maintained in culture and expanded significantly before use in cell therapy. With this regard, we have identified small molecules that can upregulate the key NC specific transcription factor SOX10 for more than 2 weeks in culture, thus indicating preservation of multipotency. Further, we have optimized conditions to differentiate skin-derived NCs to peripheral neurons. This differentiation is facilitated by continuous exposure of NCs to BMP2 in the presence of neurotrophic factors such as BDNF, GDNF, NGF and NT-3. Addition of the porcupine Wnt pathway inhibitor IWP-4 has been found to drastically aid cell survival in-vitro. The neurons so obtained express key neuronal markers such as Tuj-1, Nestin and Peripherin very early in the differentiation process. NC derived neurons also express the mature neuronal marker MAP2 after 15 days in culture. Since KC-NCs can serve as an abundant, autologous and multipotent stem cell source, we propose their use as a novel and patient specific tool to test clinically relevant molecules for the treatment of neurodegenerative diseases and as a potent cell source for the treatment of spinal cord injury.

Key words: Neural crest cells, keratinocytes, multipotency, neurons, spinal cord injury

4. The Role of Monocytes in the Endothelialization of Vascular Grafts

Randall Smith[1,2], **Stelios Andreadis**[1]

[1]Department of Chemical and Biological Engineering, University at Buffalo, SUNY
[2]Department of Biomedical Engineering
Email: Randalls@buffalo.edu, sandread@buffalo.edu

Introduction: Recently our group demonstrated that immobilized VEGF can capture circulating progenitor cells from the blood in-vitro. Furthermore, we have demonstrated proof of concept by implanting a-cellular tissue engineered vessels (A- TEVs) comprised of SIS immobilized with heparin and vascular endothelial growth factor (VEGF) into the arterial system of sheep which remained patent (92%, n=12) for 3mo (Fig.1). Upon analysis, the lumen of these grafts was comprised of a fully functional endothelium as early as 1mo post implantation. This study sought to identify the type of cells that are captured by VEGF on the lumen of A-TEVs in-vivo and understand how these cells turn into an endothelial (EC) monolayer that is capable of maintaining patency in-vivo. Materials and Methods: A-TEV implantations were performed as previously published. In-vivo Analysis: Fixed explants of 1wk, 1mo, 3mo, and 6mo VEGF functionalized A-TEVs are assessed via IHC for MC and EC markers. Blood borne mononuclear cells that are captured on surface immobilized VEGF are coaxed to differentiate into EC with a combination of soluble and biophysical signals. Results and Discussion: A-TEVs were implanted as interpositional grafts into the arterial circulation of an ovine animal model. As early as 1mo post-implantation, the graft lumen was fully endothelialized as shown by IHC for EC markers, CD144 and eNOS. At the same time, luminal cells co-expressed leukocyte markers CD14 and CD163 (Fig. 2). To understand these results, we performed cell capture experiments under flow using microfluidic devices. Interestingly, blood mononuclear cells expressing high levels of VEGF receptors were captured on CHV surfaces with high specificity under a range of shear stresses. Initially, these cells expressed high levels of CD14 and CD16. Under the right conditions they were coaxed to differentiate into an EC phenotype as shown by expression of CD144, VEGFR2, and eNOS (Fig. 3-4), additional IC analysis, qRT-PCR, and flow cytometry also confirmed this observation. We will also discuss the role of soluble signals and biophysical forces in transdifferentiation of blood cells into EC that maintain graft patency. Conclusions: We demonstrate the ability of VEGF functionalized surfaces to capture progenitor cells directly from the blood in-vitro and in vivo. In the presence of the right biochemical and biophysical signals these stem-like cells differentiate into EC like cells that maintain graft patency and vascular function. Our results shed light into the process of vascular tissue regeneration in situ using the bodys regenerative capacity via circulating monocytes. Furthermore, this study suggests monocytes as a possible stem cell population for vascular regeneration.

Key words: vegf, monocytes, vascular grafts, endothelial cells, stem cells

5. Neural Crest Stem Cells from Human Epidermis Skin Tissue

Samaneh Moghadasi Boroujeni, **Georgios Tseropoulos**, **Surya Rajan**, **Pihu Mehrotra**, **Pedro Lei**, **Stelios Andreadis**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: samanehm@buffalo.edu, gtseropo@buffalo.edu, suryaraj@buffalo.edu, pihumehr@buffalo.edu, pedrolei@buffalo.edu, sandread@buffalo.edu

Neural crest Stem Cells (NCs) are transient cells generated during early vertebrate development. These multipotent cells show extensive migratory as well as proliferative capacity. They are able to differentiate into the different type of the lineages from craniofacial skeletal tissues to the peripheral nervous system. However, Clinical application of these cells is hindered by the limited accessibility in the adulthood. Here we showed that NCs can be obtained from the Keratinocytes (KCs) culture of human adult skin tissues by treatment with a growth factor cocktail including FGF2 and IGF1. Adult NCs derived from KC culture from different donors expressed key NC markers including transcription factors such as SOX10, FOXD3 and intermediate filament, NES. Additionally, we demonstrated by both protein expression and functional assay that NC derived KC could be differentiated into all NC-specific lineages including neurons, Schwann cells, melanocytes, and smooth muscle cells (SMC) using appropriate differentiation media. Moreover, implanting Adult NC in chick embryo showed that these cells can migrate and differentiate into multiple NC derivatives. Comparing Neonatal NC and Adult NC from more than 80 year old donors showed these cells do not express considerable hall marks of the aging and can be passed up to 6 passages. These results suggest that skin can be a source of multipotent stem cells which can be utilized for regenerative medicine and stem cell biology.

Key words: Neural Crest Stem Cell, Keratinocytes, Human skin tissue

6. A Cellular Junction Protein Cadherin-11 Regulate Cell Growth Via AKT Pathway

Yayu Liu, **Sindhu Row**, **Pedro Lei**, **Stelios Andreadis**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: yayuliu@buffalo.edu, sindhuro@buffalo.edu, pedrolei@buffalo.edu, sandread@buffalo.edu

Introduction: Cadherin 11 (CDH11) as a typical type II cadherin plays an essential role in ranging from cellular adhesion to the maintenance of tissue integrity and homeostasis. Recent studies in our lab also revealed that engagement of cadherin 11 through homotypic binding is necessary for the differentiation process of mesenchymal stem cell (MSC) to smooth muscle cell (SMC). Deficiency of CDH11, not only compromises the MSC differential potential but also leads to reduced collagen and elastin synthesis, resulting in reduced mechanical property of tissues such as skin, bladder, and aorta2. Here we report our recent discovery, that in cooperation with platelet-derived growth factor receptor (PDGFRb), CDH11 regulate cell growth via the PDGFR?-AKT axis. Through interaction with CDH11, the sensitivity of PDGFR to its ligands is enhanced by 10-100 times, thereby promoting cell proliferation

Materials and Methods: Mouse tissues were isolated from Cdh11-/- (Cdh11-/- knockout, KO) and WT-wild type mice for cell isolation and immunostaining. Lentivirus encoded shRNA was used to knock down CDH11 in vitro. An engineered surface with and an immobilized fusion protein containing the extracellular CDH11 domain fused to the Fc domain (CDH11-Fc) was employed as a tool to study immediate downstream effects and identify the mechanism of intracellular signaling following the CDH11 engagement. Co-immunoprecipitation was used to test the partners of CDH11.

Results and Discussion: We discovered that CDH11 plays a critical role in mediating fibroblast cell growth. Specifically, engagement of CDH11 promotes fibroblast proliferation, while CDH11 deficiency decreases the proliferation rate significantly. In an agreement, the dermis of Cdh11-/- was much thinner and contained fewer cells as compared to wild-type animals. Interestingly, CDH11 engagement upregulated the expression of platelet-derived growth factor receptor beta (PDGFRb), as evidenced by shCDH11 knockdown in human fibroblasts and cdh11-/- mouse cells. Most notably, CDH11 was found to form a complex with PDGFRb and synergistically enhanced PDGFRb - AKT signalling cascade. This association with CDH11 led to an elevation of the sensitivity of PDGFRb to its ligands by 10- to 100-fold, ultimately promoting cell proliferation even under conditions of nutrient deprivation.

Conclusions: Taken together, our results demonstrate a novel role of CDH11 in regulating fibroblast growth through synergistic interaction with PDGFRb and suggest a novel mechanism that involves the physical interaction of CDH11 with a growth factor receptor and modulates its sensitivity to the ligands. Our results provide a better understanding of cell survival and proliferation even under nutrient deprivation, which may have significant implications in epithelial-to-mesenchymal transition and tumor metastasis.

Key words: cellular junction cadherin 11 growth akt

7. Structural Determination of N-Glycans Using Automated De Novo Sequencing

Gabrielle Pawlowski, **Sriram Neelamegham**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: gmpawlow@buffalo.edu, neel@buffalo.edu

Glycans are complex carbohydrate structures that are essential in biology for processes such as communication between cells, helping proteins form, and can also be used to help identify the presence of potential diseases. The identification of glycoproteins can be done by utilizing LC-MSn experiments and analyzing these results with the database-search program GlycoPAT. However, the structures of unknown glycans are not easily managed with the current version of GlycoPAT but can be inferred by the addition of a module to GlycoPAT that performs de novo sequencing. De novo sequencing of MSn spectra is able to determine components of a glycan structure by utilizing the workflow of LC-MSn experiments. The original mass-to-charge ratio (m/z) of a glycan is determined from the MS1 scan. Glycans corresponding to the m/z with the highest relative intensity in each scan are then fragmented in a second MS2 scan. Since almost all possible fragments of the glycan are present within the scan window so then, by relating the mass of possible glycan residues to the mass shifts between the peaks in the spectra and piecing together all of the glycan residues and comparing to the original mass of the glycan, the composition of the glycan can be determined. Incorporating rules for biosynthetic pathways and where in the spectrum the mass shifts are located, the original structure of the glycan can be determined. By altering the way that samples are prepared before they are put into the LC-MSn system, different information of terminal verses interior residues can be determined. The analysis of the mass spectrometry data is typically done manually but it requires an experienced researcher to analyze the spectra and is time consuming. Automating this process can lead to high-throughput analysis of glycomics mass spectrometry data. There are several existing computational tools that can perform de novo sequencing on MSn spectra to determine glycan structures but they do are not incorporated into a program that also incorporates glycoproteomics analysis.

Key words: Glycomics Mass Spectrometry De Novo Sequencing GlycoPAT

8. Automated annotation of glycoproteomics mass spectrometry spectra enabled by the integration of DrawGlycan with GlycoPAT

Kai Cheng, **Sriram Neelamegham**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: kaicheng@buffalo.edu, neel@buffalo.edu

Glycoproteomics experiments have adopted the traditional high-throughput LC-MSn proteomics workflow to analyze site-specific glycosylation. While a few computational tools are available for the analysis of such studies, they typically lack facilities for high-quality, visual annotation of MS/MS fragmentation spectra, and quantitative glycoproteomics. To address these limitations, we have added new modules for data analysis and also integrated two different, open-source glycoinformatics tools developed in our laboratory: i. DrawGlycan-SNFG, for the sketching of glycans in Symbol Nomenclature for Glycans (SNFG) format (Glycobiology. 27(3): 200-205); and ii. GlycoPAT, for the scoring of high-throughput glycoproteomics MS data (Mol Cell Proteomics. 16(11): 2032-2047). The resulting platform independent software (GlycoPAT2.0) includes a three-tabbed visual interface for i. Viewing a summary of the spectrum scoring results, including cross-correlation and probability based analysis. Annotated MSn spectrum are also presented, with all identified glycan and peptide bond fragmentations rendered using DrawGlycan-SNFG sketches. ii. Label-free quantitative glycoproteomics analysis and validation of precursor monoisotopic peak assignment based on the molecular isotopic distribution profile. iii. Comprehensive spectrum annotation with full DrawGlycan-SNFG rendering and detailed analysis of all matched peaks. Besides the enhanced visualization of results, the presentation will also cover key features of GlycoPAT2.0 that enable false discovery rate calculations, increased computational speed, parallel computing on local PCs, and efficient XML-based result storage. Examples will be presented using high throughput glycoproteomics datasets that utilize either cancer cells or human blood plasma glycoproteins. Overall, GlycoPAT is an easy to use, modular computational program for high quality analysis of shotgun glycoproteomics studies. Efforts have been made to develop an intuitive, visual, user-friendly interface and also advanced scoring algorithms.

Key words: Glycoproteomics GlycoPAT DrawGlycan-SNFG

9. Pleiotropic Effect of Glycan Perturbation on Cell Signaling

Xinheng Yu, **Theodore Groth**, **Sriram Neelamegham**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: xinhengy@buffalo.edu, tgroth@buffalo.edu, neel@buffalo.edu

Glycans decorate a majority of mammalian secreted and cell surface proteins. They regulate multiple biological processes including development, inflammation, thrombosis, tumorigenesis and cancer metastasis. While glycosylation primarily affects molecular recognition and protein folding, we report that glycan perturbations also alter seemingly unrelated pathways related to intracellular signaling. Here we characterized a panel of CRISPR-Cas9 human leukocytic HL-60 cell lines that lack the necessary enzymes for O-glycan ([O]?), N-glycan ([N]?) and glycosphingolipid/GSL ([G]?) biosynthesis. Differentiating these cells to terminal neutrophils resulted in leukocytes that efficiently rolled and adhered on stimulated vascular endothelial cells. RNA-Seq differential expression analysis revealed that 2-3% of the transcripts are differentially expressed in the knock-out cell lines compared to wild-type controls. While the specific perturbed transcripts in the different knockouts were distinct, they all affected common pathways related to innate immune response, cell stress response and cell communication. Ontology and detailed biochemical pathway analysis also suggest potential crosstalk among biosynthesis pathways that result in the formation of O-glycans, N-glycans, glycolipids and glycosaminoglycans. Consistent with this RNA-Seq analysis, we observed that the ablation of glycolipids resulted in an increase in bisecting N-glycan structures, while knocking out O-glycans reduced such glycans. Additionally, whereas the differentiated wild-type neutrophils exhibited a robust calcium flux response upon chemokine IL-8 stimulation, diminished flux was observed in the differentiated [O]? and [G]? cells and was absent in [N]?. The effect was specific to inflammatory chemokines, since the bacterial mimetic formyl peptide did not alter cell calcium flux or phagocytotic capacity. Consistent with the altered response to chemokine signaling, all glycan knockouts also displayed diminished migration capacity compared to wild-type cells. Mechanistic analysis revealed that the depressed cell function may be related to reduction in the expression of the CXCR1 and CXCR2 chemokine receptors on leukocytes. Overall, the study demonstrates for the first time that in addition to controlling molecular recognition, glycan perturbations may also control cellular cell signaling processes via their action on defined gene regulatory mechanisms.

Key words: Glycosylation, Glycan, Cell Signaling

10. Engineering a Human Pluripotent Stem Cell-Derived Pancreatic Progenitor to Create a Model of Islet Development

Mitchell Maloy, **Matthew Ferrer**, **Jonah Bennett**, **Vibhor Saoji**, **Natesh Parashurama**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: mhmaloy@buffalo.edu, maferrer@buffalo.edu, jonahben@buffalo.edu, vsaoji@buffalo.edu, nateshp@buffalo.edu

Type 1 diabetes mellitus is characterized by the autoimmune destruction of insulin-producing beta-cells within the pancreatic islets, the endocrine portion of the pancreas. Current treatment methods rely on the administration of exogenous insulin, which only mitigates the disease. Human pluripotent stem cells (hPSCs) are an intriguing option to replace the beta-cells in patients. Approaches for beta-cell replacement therapies follow either hPSC differentiation in vitro to mature, functional beta-cells, followed by in vivo transplantation, or hPSC differentiation in vitro towards pancreatic progenitors, which are transplanted for in vivo maturation. However, complete maturity of the hPSC-derived beta-cells in vitro has been difficult to achieve. We hypothesize that a series of improvements in cultivation will improve pancreatic progenitor induction and maturation. We are investigating differentiation under low oxygen (5%), which better mimics physiological oxygen levels available during progenitor development. Furthermore, we are focused on improving native epithelial markers which are lost in vitro. We have derived a pancreatic progenitor population from hPSCs that expresses high levels of pancreatic and duodenal homeobox 1 (Pdx1), the master transcription factor associated with the pancreatic lineage, as well as a 250-fold increase in neurogenin 3 (Ngn3) and an 800-fold increase in NK2 homeobox 2 (Nkx2.2) expression, signifying endocrine commitment of pancreatic progenitors. To model organ formation and model epithelial-mesenchymal interactions, our lab is also developing organoid models to mimic the environment experienced by endocrine progenitors as they aggregate to form the fetal islets. Preliminary models utilizing PANC-1 cells, a human pancreatic ductal carcinoma, have demonstrated increased gene expression of Nkx2.2 and somatostatin following cell aggregation in suspension. We are exploring these organotypic models to improve in vitro differentiation, and further investigating in vivo transplantation of pancreatic progenitors.

Key words: Diabetes, Islet, Pancreas, Stem Cells, Organoid

11. Engineering Developmentally Inspired Hepatic Microtissues from Human Pluripotent Stem Cells

Ogechi Ogoke[1,2], **Cortney Ott**[1], **Allison Kalinousky**[1], **Tala Mon**[1], **Claire Shamul**[1], **Lin Wayne**[1], **Saroja Rao**[1], **Shatoni Ross**[1], **Natesh Parashurama**[1]

[1]Department of Chemical and Biological Engineering, University at Buffalo, SUNY
[2]Clinical and Translational Research Center Buffalo, NY 14260
Email: ogechiog@buffalo.edu, cortott@buffalo.edu, akalinou@buffalo.edu, talamon@buffalo.edu, clairesh@buffalo.edu, waynelin@buffalo.edu, sarojara@buffalo.edu, shatonir@buffalo.edu, nateshp@buffalo.edu

A fundamental understanding of liver development is important for research areas in liver tissue regeneration, direct tissue replacement and alleviating chronic liver diseases. It is therefore critical to replicate human liver physiology with biological models that mimic its functions. We hypothesize that the structures and cues that initiate 3D liver formation can be mimicked with hepatic microtissues. Thus we aimed to engineer an in vitro organoid model of the liver diverticulum (LD), a key structure that: 1) arises in mouse development (E9.5) and human development (d26) and 2) forms the 3D liver. From inside the gut to outside, the LD is composed of a single layer of hepatic endoderm (HE), encased by a single layer of endothelial cells, and surrounded by the septum transversum mesenchyme (STM). 3D liver formation starts when the hepatic endoderm (HE) delaminates, joins with the endothelial cells, and migrates into the STM. We first determined the appropriate LD dimensions with an online mouse database. To investigate this phenomenon further, we utilized an in-vitro model of the developing liver. Human pluripotent stem cells (hPSCs) were differentiated into definitive endoderm and hepatic endoderm respectively using STEM Diff Kit media (Stem Cell Technologies) under low oxygen for 4 days on a coated matrigel (MG) surface. The definitive endoderm cells (DE) showed high expression of FOXA2 and SOX-17. After definitive endoderm induction, the media was switched to a serum free media (SFD) that contained BMP4 and FGF for hepatic endoderm differentiation. After three days of differentiation cells changed morphology exhibiting a more cuboidal shape suggesting epithelial phenotype. Initially we investigated the formation of hepatic endoderm microtissues. Hepatic endoderm cells were harvested using accutase and seeded at 20,000 cells per well of a 384 well round bottom plate in the presence of SFD, 20% knockout serum (KOSR), 10 (ug/mL) fibroblast growth factor (FGF) and 20 (ug/mL) bone morphogenetic protein-4 (BMP4). The microtissues expressed significantly high levels of AFP and CDX2 consistent with early hepatic fated cells in-vivo. In a subsequent experiment hepatic endoderm cells were co-cultured in a 1:1 ratio with HUVEC endothelial cells to form compact spheroids that were embedded in MG containing 20,000 MSCs. These spheroids displayed finger-like projection into the ECM mirroring a transcriptional upregulation of SNAI2, an EMT marker present in the LD. Altogether these finding suggest the feasibility of utilizing stem cell derived hepatic progenitor cells to model the LD. Further work shall encompass improved characterization of hepatic microtissues regarding rate of formation, and analysis of morphological changes associated with growth in the presence of MSCs. Thus elucidating the mechanisms that govern liver development remains of utmost importance.

Key words: liver diverticulum, hepatic endoderm, microtissues

12. Controlling and Maintaining Endodermal States through the Modulation of Pioneer Transcription Factors Foxa1 and Foxa2 with siRNA

Tala Mon, **Saber Meamardoost**, **Natesh Parashurama**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: talamon@buffalo.edu, sabermea@buffalo.edu, nateshp@buffalo.edu

Endoderm induction of human embryonic stem cells (hESC) is a transient process in directed differentiation towards a specific lineage. This transient nature leads to an inability to make pure, homogenous, and competent endodermal cells with uniform gene expression resulting in mixed populations in further differentiation. To control the endodermal states, developmental master gene regulatory circuits must be characterized and the role important regulatory transcription factors (TF) must be evaluated. Foxa1 and Foxa2 are possible candidates as the pair have been shown to have irreversible effects on induction, maintenance, and differentiation of endoderm. Using RNAi technology, we will determine the effect of negatively perturbing the expression of Foxa1 and Foxa2 during endoderm induction at varying time points in allowing the population to converge on a specific and uniform steady state while expressing endodermal TFs such as SOX17. From there, the perturbations can be maintained to produce a stable line and can be removed when needed for further directed differentiation. In differentiating an endodermal population without heterogeneity, we hypothesize improvements in the stability and yields of the cells of interest and eliminating the need to initiate differentiation from hESCs. UCSF4 hESCs were induced to become definitive endoderm using STEMdiff kit for four days. On the fourth day, 50 nM of siFoxa1 and 50 nM of siFoxa2 were used to transfect the endoderm with Fugene HD transfection reagent. Cells were collected after 48 hours of transfection for q-RT PCR. Gene silencing resulted in a knockdown of Foxa1 and Foxa2 and was accompanied by a decrease in mesoendoderm markers such as Brachyury, Gsc, and Eomes. This represents a delay in early differentiation or that mesendoderm TFs are activated by Foxa1/2. Future work will involve the optimization of the siRNA transfection protocol along with determining the ideal time point for silencing Foxa1 and Foxa2 during endoderm induction.

Key words: siRNA, endoderm, foxa1, foxa2, development, differentiation

13. Development of a second generation vaccine against Streptococcus Pneumoniae

Andrew Hill[1,2], **Marie Beitelshees**[1], **Roozbeh Nayerhoda**[1], **Blaine Pfeifer**[1]

[1]Department of Chemical and Biological Engineering, University at Buffalo, SUNY
[2]Abcombi Biosciences Inc
Email: ahill6@buffalo.edu, mariebei@buffalo.edu, roozbehn@buffalo.edu, blainepf@buffalo.edu

The initial development of the Liposomal Encapsulation of Polysaccharides (LEPS) vaccine againstStreptotoccus pneumoniaeresulted in a vaccine containing 20 encapsulated pneumococcal capsular polysaccharides (CPSs) and two surface-displayed virulence-associated proteins (GlpO and PncO). When LEPS was testedin vivothe vaccine demonstrated prophylactic potency against 70+ serotypes ofS. pneumoniae(the causative agent of pneumococcal disease) via an opsonophagocytosis activity (OPA) assay. We detail the further development of a next-generationS. pneumoniaeLEPS vaccine, with design characteristics geared towards best-in-class efficacy and an improved safety profile. As a consequence of this process, the virulence-associated GlpO protein antigen was eliminated from the final LEPS formulation due to off-target reactogenicity observed using immune-absorbance and OPA assays. Full vaccine efficacy was maintained by increasing the dose of the other LEPS vaccine protein, PncO, from 17 to 68 g per dose. Furthermore, the LEPS formulation readily facilitated an increase in CPS valency (to a total of 24) and variable protein-liposome attachment mechanisms that were evaluated in anticipation of translating the vaccine to clinical application. Furthermore, we conducted an acute toxicological assessment demonstrating that LEPS does not exhibit appreciable toxicity even when administered at ten times the effective dose. In summary, this new design offers the broadest, safest, and most-complete protection while maintaining desirable glycoconjugate-like features, positioning the LEPS vaccine platform for clinical success and global health impact.

Key words: Vaccine, Pneumococcal Disease

14. FBA Analysis of Natural Products and Antibiotic Activity of Ybt

Nicholas Moscatello, **Blaine Pfeifer**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: njmoscat@buffalo.edu, blainepf@buffalo.edu

The natural products 6-deoxyerythronolide B (6dEB), erythromycin D (EryD), yersiniabactin (Ybt), and salicylate 2-O-?-D-glucoside (SAG), chosen to a represent a range of primary and secondary metabolites generated through heterologous microbial biosynthesis, were analyzed using computational metabolic engineering for the purpose of predicting improved production. Specifically, flux balance analysis (FBA) allowed for the comprehensive screening of medium components and the determination of single gene deletions that resulted in improved product titers for the target compounds. Outcomes included the identification of amino acids and alternative carbon sources capable of culture medium supplementation for increased cellular production. Ybt has also been explored for its antimicrobial properties against a host of pathogens. This compound offers promise and could serve as an alternative to current antibiotics.

Key words: Flux Balance Analysis, Natural Product, Antibiotic

15. Engineering Heterologous Production of Salicylate Glucoside and Glycosylated Variants

Ruiquan Qi[1], **Guojian Zhang**[2], **Blaine Pfeifer**[1]

[1]Department of Chemical and Biological Engineering, University at Buffalo, SUNY
[2]Ocean University of China
Email: ruiquanq@buffalo.edu, zhangguojian@ouc.edu.cn, blainepf@buffalo.edu

Salicylate 2-O-β-D-glucoside (SAG) is a plant-derived natural product with potential utility as both an anti-inflammatory and as a plant protectant compound. Heterologous biosynthesis of SAG has been established in Escherichia coli through metabolic engineering of the shikimate pathways and introduction of a heterologous biosynthetic step to allow a more directed route to the salicylate precursor. The final SAG compound resulted from the separate introduction of an Arabidopsis thaliana glucosyltransferase enzyme. In this study, a range of heterologous engineering parameters were varied (including biosynthetic pathway construction, expression plasmid, and E. coli strain) for the improvement of SAG specific production in conjunction with a system demonstrating improved plasmid stability. In addition, the glucoside moiety of SAG was systematically varied through the introduction of the heterologous oliose and olivose deoxysugar pathways. Production of analogs was observed for each newly constructed pathway, demonstrating biosynthetic diversification potential; however, production titers were reduced relative to the original SAG compound.

Key words: alicylate, salicylate 2-O-β-D-glucoside, metabolic engineering, E. coli, analog

Molecular and Multiscale Modeling

16. Bimodal Hole Transport and Creation of Trap Regions by Extrinsic Doping in Photocatalytic $BiVO_4$: First-Principles based Mesoscale Characterization

Viswanath Pasumarthi, **Michel Dupuis**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: pasumart@buffalo.edu, mdupuis2@buffalo.edu

Bismuth vanadate $BiVO_4$ (BVO) is one of the most efficient anodic materials for photocatalysis with a favorable band gap of ~2.4 eV and good band edge position for water oxidation but it has limited carrier transport performance. Recently BVO was shown to exhibit facet-selective charge separation that enhances electron-hole separation. Controlled layered doping by Mo and W is another strategy for enhanced charge separation.

In this research, we performed a first-principle and mesoscale characterization of intrinsic electron and hole transport in BVO that revealed the existence of a bimodality in hole transport. The intra-VO_4 polyhedral hole polaron hops are the fastest but are not transport-efficient whereas the inter-VO_4 polyhedral hops are slow but are transport-efficient. This finding may explain the slow transport/high recombination characteristics of BVO. Hops through O-V-O bridges and through space have low activation barriers (~0.17 eV and ~0.25 eV) while hops through O-Bi-O bridges have higher activation barriers (~0.37 eV and higher). The hole mobility is gated by the slower transport across VO_4 tetrahedra through O-Bi-O bridges owing to the underlying BVO lattice network.

Supplementing this work, we also carried out a first-principle based mesoscale characterization of electron transport in W/Mo-doped BVO. Substitution of V sites by W/Mo results in the influx of mobile excess electrons into the lattice. This motility of the excess electrons is supported by the nature of their instable localization on dopant sites resulting in a positive relative energy in comparison with localization on bulk V site. Calculations using DFT+U theory shows relative energies of ~0.66 eV, ~0.08 eV for electron localizing on W and Mo respectively. DFT calculations on a 3x3x1 supercell further reveal a region of stability for electron localization around the dopant site extending up to at least 2 nearest neighbor shells. These features of dissimilar transport characteristics in and across the doping region reduce the electron diffusivity only minimally owing to a less significant increase in the doping region probability of electron residence. The electronic conductivity is thus observed to monotonically increase with increase in the doping level. These studies pave the way for characterizing the space-charge distribution in (W/Mo)-doped BVO homojunctions.

Key words: Kinetic Monte Carlo, $BiVO_4$, Bimodal Transport, Doping, Solar Water Splitting

17. Using Monte Carlo Simulation to Calculate Interfacial Properties of Ionic Liquids

Xiaoyu Liang, **Jeffrey R. Errington**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: xliang5@buffalo.edu, jerring@buffalo.edu

Room temperature ionic liquids (RTILs), which are salts with large organic ions and will melt down at room temperature, are promising materials in electrochemical and industrial application. Bulk and interfacial properties of ionic liquids play significant role in material synthesis and design. In our research, we have developed an interface potential based approach for determining interfacial properties, such as spreading and drying coefficients, surface tension and contact angle. Grand canonical Monte Carlo (GCMC) simulations are completed with Transition Matrix Monte Carlo (TMMC) scheme to get probability distributions, in order to calculate interface potential. A United-Atom model is applied to simulate Liquid-Solid interfacial properties of imidazoium-based Room Temperature Ionic Liquids (RTILs) over graphite surface. A simplified model, Restricted Primitive Model (RPM) is also used to study the wetting and prewetting transitions of ionic fluids over a structureless attractive hard substrate. Expanded ensemble techniques, combined with the direct simulations, are used to evaluate the interfacial properties over desired temperature range and under different strengths of substrate-fluid interaction. To determine the higher temperature end of the prewetting saturation line, which defined as prewetting critical (PWC) temperature, we use a boundary tension approach with finite-size scaling formalism. Interesting behaviors of wetting and prewetting transitions are observed among ionic liquids. Compare to non-ionic fluid, our result shows the properties of ionic liquid have different trends with temperature, and gives us unique structures of partial wetting, prewetting and complete wetting regions on surface phase diagram.

Key words: Monte Carlo Simulation, Room temperature ionic liquids, Interfacial properties

18. Molecular Simulation on Zwitterionic Material Fictionalized Polysulfone Membrane

Yiqi Chen, **Jeffrey R. Errington**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: yiqichen@buffalo.edu, jerring@buffalo.edu

Zwitterionic materials are a family of materials that have moieties possessing both cationic and anionic groups which possess a very unique antifouling property of resisting specific protein adsorption. Because of that, they can be used to solve various application problems. For example, zwitterionic materials can be coated onto polysulfone (PSF) membranes to provide a good fouling resistance ability which is essential in waste water treatment process. In this project, we used molecular simulation as a versatile tool to study the antifouling mechanism in those membranes at molecular level. Three membranes were constructed: pure PSF, poly(ethylene glycol) (PEG)-PSF and zwitterionic Sulfobetaine methacrylate(SBMA)-PSF. We investigated the structure and dynamics of water near the surface of different membranes as well as the dynamics of hydrogen bonds formed in the systems. The results showed a superior hydrophilicity in the SBMA-PSF membrane, which is very likely the main cause for its antifouling property. It was concluded that SBMA tethers disrupted the structure of water molecules near them and hindered their transitional and rotational mobility. These effects are the result of SBMAs ability to form more and stronger hydrogen bonds with water than other materials.

Key words: Zwitterionic material, molecular dynamics, water structure, water dynamics, hydrogen bond analysis

19. Data-driven approach to predict Melting Points of Deep Eutectic Solvents

Aditya Sonpal, **Johannes Hachmann**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: adityaso@buffalo.edu, hachmann@buffalo.edu

Recently, a new class of ionic liquids called deep eutectic solvents (DES) have been identified and utilized in a few specific applications. DES are obtained by the complexation of quaternary ammonium, phophonium, or sulphonium salts with a metal salt, or a hydrogen bond donor in a specific ratio. The result is a eutectic system characterized by a depression in melting point. The interest in DES has been sparked by their highly tunable structures and some important advantages over traditional ionic liquids. Therefore, we identified 36 DES systems, with choline chloride (hydroxyethylmethylammonium chloride) as the hydrogen bond donor. We create a computational model to calculate the melting point of these systems. DFT-optimized geometries of these candidates are used to calculate molecular descriptors, which serve as the feature space for our machine learning models to predict melting points. We compare the results of feature selection using genetic algorithm and Pearson correlation coefficient. We also calculate the effect of optimized geometries on our predicted results by comparing the geometries from classical molecular dynamics, to geometries from BP86/def2-SVP and PBE0/def2-TZVP. We use the resulting subset of features to predict melting points using linear regression algorithms like elastic nets, LASSO, ridge and Bayesian ridge regression. We also use neural networks to predict our target property and conduct a cost-benefit analysis for all the above methods to finally propose a favorable protocol.

Key words: machine learning, density functional theory, deep eutectic solvents, ionic liquids

20. Computational Modelling of Liquid Organic Hydrogen Carriers (LOHCs)

Amol Mahajan, **Johannes Hachmann**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: amolraje@buffalo.edu, hachmann@buffalo.edu

The development of efficient hydrogen storage materials is one of the biggest technical challenges for the coming hydrogen economy. The liquid organic hydrogen carriers (LOHCs) with high hydrogen contents, reversibilities and moderate dehydrogenation kinetics have been considered as an alternative option supplementing the extensively investigated inorganic hydride systems. With these advantages, LOHCs hold significant promise in a whole range of technologies relying on hydrogen storage and transport. The search for an ideal LOHC is then necessarily guided by discovering those LOHCs that can be hydrogenated/dehydrogenated with a minimal energy input while requiring no or minimal amounts of noble metal. Our molecular modeling efforts primarily employed ORCA and the use of density functional theory (DFT) analysis on the dehydrogenation reactions of a few potential LOHC compounds. Cycloalkanes and N-heterocycles were found to be suitable categories since they fit most of the required criteria for an ideal LOHC. Using DFT studies, enthalpy of dehydrogenation of these compounds were predicted with an error of 3 8%. The kinetics of the dehydrogenation reaction is being studied to optimize the transition state by performing geometry scans of various bonds in candidate compounds. The results show that the computational approach has a tremendous promise to study novel LOHC candidates, in which the loading of H2 as well as the in-situ release of H2 can be done efficiently.

Key words: LOHCs, computational, DFT, dehydrogenation, geometry scan

21. Machine Learning Model Selection for Predicting Properties of High Refractive Index Polymers

Gaurav Vishwakarma, **Mojtaba Haghighatlari**, **Johannes Hachmann**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: gvishwak@buffalo.edu, mojtabah@buffalo.edu, hachmann@buffalo.edu

In the ?eld of materials science and chemistry, machine learning has emerged as a promising technique in the recent times for the accelerated discovery of novel materials. This thesis focuses on one of the major aspects of machine learning, i.e., model selection, which is an important and also time-intensive task but remains highly unexplored in the materials community. We present a framework for automated model selection for machine learning with our research groups current work in the prediction of properties of organic polymers as the primary focus. The traditional approach for hyper-parameter optimization of a given machine learning model is discussed in the beginning, followed by the need for more specialized techniques due to the shortcomings of this approach that are readily identi?ed. We analyze two algorithms for hyper-parameter selection: genetic algorithm and particle swarm optimization. The algorithms are compared based on their performance as well as the time taken for the optimization to complete. It is shown that both genetic algorithm and particle swarm optimization are able to ?nd better hyper-parameter values compared to the traditional methods used for hyper-parameter tuning, but at the cost of slightly higher computational time. An approach for reducing the computational time is also explored; feature selection using genetic algorithm. It is shown that feature selection results in a lower computational time without losing much on the prediction accuracy of the machine learning model.

Key words: Machine learning, model selection, genetic algorithm, particle swarm optimization, high refractive index polymers

22. User Interface for molecular library generator

Janhavi Dudwadkar, **Gaurav Vishwakarma**, **Johannes Hachmann**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: jdudwadk@buffalo.edu, gvishwak@buffalo.edu, hachmann@buffalo.edu

The library generator is an automated combinatorial molecular library generator built using python library. The molecules are generated in the library using fusion or linking. The graphical user interface for the library generator is necessary as the library generator requires 16 inputs for the generation of the rules for building the molecular library. The graphical user interface is built on JUPYTER notebook. The interface also helps in visualization of the SMILES input of the building blocks molecules. The interface makes it easier to create the rules file for generation and makes the program user friendly.

Key words: molecular library,interface,JUPYTER notebook

23. Computational Investigations into the Functionalization of Naphthalenetetracarboxylic Anhydride and derivatives as an anode for Li ion Battery

Krishnendu Mukherjee, **Yudhajit Paul**, **Johannes Hachmann**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: kmukherj@buffalo.edu, yudhajit@buffalo.edu, hachmann@buffalo.edu

As clean energy driven electric vehicles are progressing towards full scale commercialization there exists some impediments in the Li ion battery technology which remains to be addressed for them to become an attractive choice as compared to conventional fossil fuel based vehicles. One of the major problem is that of low charge capacity and slow charging rate of existing Li Ion batteries, both of which needs to be resolved expeditiously for the viability of EVs. In this regard Organic electrode material can play a vital role since they are cheap to produce, easy to tailor with desirable functional groups and had shown wide acceptance as electrode material in the past. In this present work we look on carbonyl based compound Naphthalenetetracarboxylic Anhydride (NTCDA) for anode material as recently it was experimentally found to have specific charge capacity of 1800 mAg/h with a steady performance over a large number of charge/discharge cycles. The methodology involved placing Li Ion and atoms on a pre optimized NTCDA geometry where the location of each Li atom is chosen in a pre-determined set of instances followed by a geometry optimization. We carried out the process for 1-24 Li Ions on the surface of NTCDA and NTCDA with derivatives: CN, CF3 and OCH3. Thereafter we did DFT calculation employing PBE0 method and def2-TZVP basis set along with dispersion correction to find the absorption energy and natural population analysis data of the most stable of instances. Afterwards we scanned the trends of binding energy and natural population data to find the most number of Li Ions and atoms which can attach to the surface. We thus predicted the capacity based on the total number of Li ions shuttling between the two electrodes. The results obtained from above DFT calculations have shown good agreement with experimental charge capacity data obtained by Dr. Wus group. In addition it has been observed that the charge capacity for Li Ion batteries remains fairly constant for organic electrodes in Li Ion battery, implying that first cycle capacity gives a good estimation of the electrode performance. Therefore, we conclude that the above methodology can be easily transferred to other organic functional groups to estimate battery performance and find potential candidates for battery electrodes.

Key words: DFT, Li Ion Battery, Charge capacity, Absorption Energy, Anode, Natural population analysis

24. High-Throughput In Silico Screening of Candidate Compounds for Deep Eutectic Solvents

Yudhajit Pal, **Johannes Hachmann**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: yudhajit@buffalo.edu, hachmann@buffalo.edu

Deep eutectic solvents (DES) are a class of generally low-cost, environmentally benign solvents that have diverse chemical applications. Similar in characteristics to ionic liquids (IL), they contain a mixture of cations and Lewis acid anions, which form the hydrogen bond acceptor (HBA) species, and Lewis or Bronsted acids, which form hydrogen bond donors (HBD). The H-bond links between the donors and the acceptors allow for melting-point depression in the eutectic mixture and hence lower melting points compared to ILs. Additionally, their easy synthesis from inexpensive starting chemicals along with low vapor pressures and flammability make them attractive systems. Our work concerns the development of novel DESs for use in supercapacitors as well as of the underlying molecular modeling techniques. Key target properties our research focuses on are wide electrochemical windows (ECWs), high ionic conductivities, and low melting points, which can be tuned at the molecular level. We are employing our automated high-throughput screening infrastructure to characterize large-scale candidate libraries. We utilize a diverse set of (multi-scale) molecular simulation techniques that include first-principles electronic structure theory, and classical molecular dynamics. We will detail our mining efforts of the resulting data sets to extract rational design principles for next-generation DES lead candidates.

Key words: deep eutectic solvents, high throughput material search, electrochemical window, supercapacitors

25. Mapped-averaging: Density Distribution Functions

Apoorva Purohit, **Andrew J. Schultz**, **Jeffrey R. Errington**, **David A. Kofke**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: apoorvap@buffalo.edu, ajs42@buffalo.edu, jerring@buffalo.edu, kofke@buffalo.edu

The accurate measurement of density distributions is valuable to investigate the wetting/drying properties, membrane separation, phase coexistence, capillary effects, coarse graining, polymorphism and stability. However, the experimental uncertainty induced by quantum counting inefficiencies, experimental imprecision or sample inhomogeneities, can lead to errors in drawing meaningful conclusions from density distribution studies. Thus, computational studies are needed. Computationally, the standard approach to sample these density distribution functions is to discretize the space into a 3D grid and monitor the filling of the histograms in the course of the simulation. However, as the bin size decreases and the resolution of measuring the density profile increases, the uncertainty in the predictions via this conventional approach also increases because the number of events contributing to each bin is proportional to the volume of the bin. Thus, the variance of the distributions diverges when the grid spacing tends to zero. Hence, there is a need of methods that significantly enhance the convergence of simulations compared to the conventional counting based method used so far in literature. Recently, we demonstrated the mapped-averaging framework that allows approximate theoretical results derived from statistical mechanics to be reintroduced into the underlying formalism, yielding reformulated ensemble averages that are uncontaminated by noise produced by behavior that has already been captured by the approximate theory. By using these reformulated ensemble averages, accurate and precise values of thermodynamic properties can be obtained while using less computational effort, in favorable cases, many orders of magnitude less. In this work, we extend the mapped-averaging technique to calculate the density distribution functions. We conclude that it leads to a much reduced variance of the results with respect to the counting based technique and achieves a finite variance even when the grid spacing tends to zero.

Key words: molecular simulation, mapped average, density, singlet, pair distribution function

26. Computational Cluster-Integral Methods for Solutions

Arpit Bansal, **Andrew J. Schultz**, **David A. Kofke**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: arpitban@buffalo.edu, ajs42@buffalo.edu, kofke@buffalo.edu

Cluster-integral ideas underlie many theoretical methods in statistical mechanics. The most widely recognized and widely used approach is in the form of the virial equation of state. This framework identifies coefficients of a density expansion of the pressure (and other properties) in terms of integrals of multi-molecular interactions in a vacuum. The pairwise-additive intermolecular potential forms frequently encountered in molecular simulations are often used in this context. A corresponding framework is available for properties of solutions. Here the expansion is (typically) for the osmotic pressure, as a series in solute concentration. The coefficients again can be given as cluster integrals, but now the interactions are among solutes as mediated by their interactions with the solvent. Typically, a pairwise-additive approximation for solute-solute interactions is not as effective in such applications. Numerical evaluation of the indicated cluster integrals is not as easily accomplished, and require methods different from those that have been developed for gas-phase virial coefficients. In this poster, we present and examine novel and very effective methods, and demonstrate them for hard sphere systems. We consider in particular the performance of the methods, the nature of the effective multibody interactions, and the effectiveness of the overall framework for describing solution properties.

Key words: molecular simulation, statistical thermodynamics, cluster integral, hard sphere

27. Computing Virial Coefficients to Assess the Accuracy of Intermolecular Potentials

Navneeth Gokul, **Andrew J. Schultz**, **David A. Kofke**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: navneeth@buffalo.edu, ajs42@buffalo.edu, kofke@buffalo.edu

The most widely used molecular models are pairwise-additive and have been formulated to describe properties of condensed phases. As a result they do not describe the true interactions between molecule pairs, but rather are effective potentials that attempt to include multibody interactions and other temperature- and density-dependent effects in the pairwise form. Some models include polarization, which allows the pair interactions to be described more accurately at the expense of increased computational cost. Model parameters are typically fit to experimental data like vapor-liquid equilibria, P-V-T etc. Since Bn is a direct function of the interaction of n molecules, fitting to experimental virial coefficient data may yield a model which more accurately describes those interactions. Model virial coefficients can also be a route to inexpensively generate low-density P-V-T data from the virial equation of state (VEOS).

In this paper, we describe an efficient recursive algorithm to evaluate high-order virial coefficients along with their temperature derivatives, which allows us to describe a wider temperature range while sampling only a few temperatures. They can also be used to formulate an approximant which converges up to higher densities as compared to the VEOS. We pursue a systematic, comprehensive effort to apply these methods to TraPPE potentials for some species and their mixtures. These are collected in a database to create a publicly accessible resource of thousands of coefficients that can be used to compute all thermodynamic properties of these mixtures in the vapor and supercritical-fluid phases. In this manner the accuracy of a molecular model can be assessed and its usefulness greatly extended.

Key words: molecular simulation, statistical thermodynamics, virial coefficients, intermolecular potentials, virial equation of state, approximant

Nanoscale Materials Science and Engineering

28. Self-Assembly of Alkyl Polyethylene Glycol Ether Surfactants in Aqueous Solutions: Effect of Linker between Alkyl and Ethoxylate

Andrew M. Bodratti, **Junce Cheng**, **Marina Tsianou**, **Paschalis Alexandridis**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: bodratti@buffalo.edu, jccheng@buffalo.edu, mtsianou@buffalo.edu, palexand@buffalo.edu

We investigate non-ionic surfactants in terms of their ability to solubilize in aqueous solutions compounds that are sparingly water-soluble, including environmental contaminants and pharmaceutical actives. Fundamental information about the non-ionic surfactant self-assembly in aqueous solution can be used to assess the surfactant affinity to hydrophobic compounds, and its compatibility and potential synergism with other surfactants, polymers, and/or particles typically used in formulations. [Sarkar & Alexandridis, J. Phys. Chem. B 2010, 114 (13), 4485-4494; DOI: 10.1021/jp910939q] [Bodratti et al., Adv. Colloid Interface Sci. 2017, 244, 132-163; DOI: 10.1016/j.cis.2016.09.003] We consider here a homologous series of surfactants consisting of a C10-alcohol with varying degrees of ethoxylation, and report results on the onset of micellization (cmc), micellization thermodynamics, and micelle local environment in aqueous solutions. Structure-property relations are developed by examining the effects on self-assembly of placing propylene oxide segments between the polyoxyethylene headgroup and the alkyl tail of the surfactant, and comparing the behavior of low-molecular weight alkyl polyethylene glycol ether surfactants to that of high molecular weight polyoxyethylene-polyoxypropylene surfactants. [Kaizu & Alexandridis, J. Mol. Liq. 2015, 210, 20-28; DOI: 10.1016/j.molliq.2015.04.039] [Bodratti & Alexandridis, J. Funct. Biomater. 2018, 9 (1), 11; DOI: 10.3390/jfb9010011]

29. Cationic Poly(ϵ-caprolactone) Nanocomplexes for Gene Delivery

Amin Jafari, **Guojian Zhang**, **Mohamed Alaa Mohamed**, **Blaine Pfeifer**, **Chong Cheng**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: aminjafa@buffalo.edu, guojianz@buffalo.edu, mm446@buffalo.edu, blainepf@buffalo.edu, ccheng8@buffalo.edu

Gene transfer therapy has attracted increasing attention as a promising approach the treatment of various diseases over the past decade. Approximately 2600 gene therapy clinical trials have been performed worldwide and a few has been approved so far. Among various gene delivery approaches, non-viral vectors made of synthetic biomaterials have shown promising potentials. Due to their synthetic nature, non-viral vectors can have tunable structures and properties by using various building units. In particular, they can offer advantages over viral vectors with respect to biosafety and cytotoxicity. In this study, well-defined cationic poly(ϵ-caprolactone) (CPCL) homopolymers and CPCL-*b*-PEG diblock copolymers were synthesized. They were used to as the scaffolds for the delivery of plasmid DNAs (pDNAs), through the formation of nanocomplexes via spontaneous electrostatic interactions. The optimal complexation ratio was investigated by gel electrophoresis and dynamic light scattering studies. The nanostructures of nanocomplexes were investigated by TEM imaging. When used at optimal nanocomplexation ratio with low level of cytotoxicity, these CPCL-based polymers resulted in transfection efficiency comparable with or higher than that of Fugene-6, a commercial transfection agent. Moreover, CPCL-*b*-PEG diblock copolymers led to higher transfection efficiency than CPCL homopolymers.

Key words: non-viral gene therapy, cationic polymer, poly(ϵ-caprolactone)

30. Low Temperature Methane Combustion over Palladium Ion-exchanged Zeolites

Chih-Han Liu, **Yiran Chen**, **Eleni A. Kyriakidou**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: chihhanl@buffalo.edu, yiranche@bufffalo.edu, elenikyr@buffalo.edu

Activation of the C-H bond of methane, the main component of natural gas, is a major impediment in utilizing natural gas. Precious metal, palladium (Pd), has been reported to be the most active metal for methane combustion. Common catalysts used were Pd loaded on Al_2O_3. To achieve good performance of Pd catalysts, zeolites was introduced to be the support based on unique tunnel structure, which yields high surface area to provide chances to highly disperse metal. Commercial medium-pore zeolite ZSM-5 were studied and proved to have better performance than conventional Pd loaded on Al_2O_3. However, it was found that the activity of catalyst decreased severely when water was included in feed gas because of aggregation of active metal species. Therefore, finding a way to improve catalytic performance will be an indispensable work. Here in this work, discussion will be focused on two aspects, synthesis method and metal loading effect. It was found in our experiment that there was a better performance of catalysts prepared by ion-exchanged method than those prepared by conventional incipient wetness method. CO-pulse chemisorption results indicated that palladium species achieved through ion-exchanged method had a higher dispersion on the zeolite surface. O_2-TPD experiments also implied capacity for PdO to give away the oxygen for reaction for ion-exchanged sample was higher than incipient wetness one even the metal loading was the same, which was due to higher active surface. Metal loading effect was examined on ion-exchanged sample. Varying metal loading lead to trade-off between metal amount and agglomeration effect, since the more metals were, the higher probability for metals to collide with one another. From our result, metal amount dominated the catalytic performance.

Key words: methane combustion; zeolite; palladium; low temperature

31. Complete Methane Combustion over NiO/CexZr1-xO2 Catalysts

Junjie Chen, **Benjamin D. Carlson**, **Eleni A. Kyriakidou**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: jchen299@buffalo.edu, bdcarlso@buffalo.edu, elenikyr@buffalo.edu

As the push for alternative energy sources grows and a decline in natural gas prices have led to the wide utilization of natural gas in the power generation and transportation industries. However, the main component of natural gas, methane (CH_4), has 32 times higher global warming potential than that of CO_2. Thus, unburnt methane emissions from combustion engines or turbines have the potential to offset any positive environmental impacts gained from utilizing natural gas. Therefore, the reduction of unburnt CH_4 emissions has recently attracted significant attention. As one of the most stable hydrocarbons, methane has long presented a challenge for efficient combustion. Platinum group metals (PGMs) are widely applied regarded to have the best activity for activating C-H bond and completely oxidizing methane. However, the prohibitive cost of palladium has hindered its widespread adoption. Nickel, an earth-abundant and therefore cost-effective metal, has been shown to activate methane, as evidenced by its use in methane reforming reactions. However, non-supported nickel catalysts are easily deactivated by coking. Herein, a series of non-precious $NiO/Ce_xZr_{1-x}O_2$ (x=1, 0.83, 0.5, 0.17, 0) catalysts were synthesis by dry impregnation. The $NiO/Ce_xZr_{1-x}O_2$ catalyst shown high activity for methane combustion at a relatively low temperature (400-600 °C) without any CO formation. A promotion effect between NiO and $Ce_xZr_{1-x}O_2$ was observed. The impact of oxygen storage capacity of support and Nickel nanoparticle size were studied.

Key words: methane combustion, oxygen storage capacity, nickel, ceria-zirconia

32. Effect of Ag Loading and Oxidation State on Hydrocarbon Adsorption during Vehicle Cold-Start

Jungkuk Lee, **Eleni A. Kyriakidou**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: jungkukl@buffalo.edu, elenikyr@buffalo.edu

Stringent emission regulation led to significant attention to reduce vehicle emission during the cold-start that take place within 1-2 minutes after operation. One potential approach to regulate the cold-start emission is to utilize hydrocarbon trap. Zeolites have been emerged as a potential trap materials due to their tunable acidity, high surface area, and thermal stability. A series of Ag containing ZSM-5 zeolites with different Ag loading were prepared via ion-exchange, and characterized by CO pulse chemisorption and H_2-TPR. The hydrocarbon (HC) trapping performance of Ag/ZMS-5 was evaluated using simulated diesel exhaust containing C_2H_4, C_7H_8, NOx, CO_2, H_2O, CO, H_2. It turns out that Ag species in ZSM-5 is able to act as adsorption sites for both ethylene and toluene even in the presence of H_2O, which led to increase in adsorption capacity and desorption temperature compared to unexchanged HZSM-5. In full mixture condition, the competitive adsorption between ethylene and toluene was not observed, suggesting that ethylene and toluene adsorb on different adsorption sites in Ag/ZSM-5. With increase in Ag loading from 0.5 to 1.2 wt% led to increase in both ethylene and toluene, whereas the ethylene and toluene adsorption capacity remain similar with further Ag loading increase up to 4.6 wt%. The oxidation state of Ag species in ZSM-5 was controlled by H_2 pre-treatment at different temperatures (200 and 600 °C), and trapping performance was investigated to identify the most effective oxidation state of Ag for ethylene and toluene adsorption. The results show that ionic Ag has better adsorption efficiencies in both ethylene (69%) and toluene (90%) compared to the metallic Ag (67, 82% for ethylene and toluene) and Ag clusters (55, 72% for ethylene and toluene). Finally, it was found that Ag/ZSM-5 shows ethylene and toluene adsorption performance even after hydrothermal aging at 800 °C for 10 h under 10% O_2, 5% CO_2, and 5% H_2O.

Key words: Hydrocarbon trap, Ag ion-exchange, ZSM-5 zeolites, Ag oxidation state

33. Elucidating the Discrepancy in Gas Transport Properties of Cellulose Acetates as a Dense Film and Asymmetric Membrane

Hien Nguyen[1], **Mengyuan Wang**[2], **Yifu Ding**[2], **Haiqing Lin**[3]

[1]Department of Chemical and Biological Engineering, The University at Buffalo, SUNY
[2]Department of Mechanical Engineering, Materials Science and Engineering Program, University of Colorado at Boulder, Boulder
[3]Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: hn26@buffalo.edu, Mengyuan.Wang@colorado.edu, Yifu.Ding@colorado.edu, haiqingl@buffalo.edu

Cellulose acetates (CA) are the workhorse membrane materials for industrial CO2/CH4 separation. However, an un-resolving discrepancy exists regarding their gas transport properties as bulk polymers and asymmetric membranes. As a dense film, CA exhibits a CO2 permeability of 6 Barrers at 35 C, which corresponds to a permeance value of 30 GPU when it is made into an asymmetric membrane with a selective layer of 200-nm. By contrast, such commercial asymmetric CA membranes typically shows a CO2 permeance up to 200 GPU with a CO2/CH4 selectivity comparable to the bulk polymer. This study aims to elucidate this discrepancy by determining the effect of film thickness (ranging from 200 nm to 20 microns) on the gas transport properties of freestanding CA films. Herein, the effect of film thickness on polymer crystallinity and thermal properties are systemically studied. Prepared films were characterized by DSC, XRD, and nano-TA methods. As film thickness decreases from 20 microns to sub-micron, crystallinity is found to decrease and films of 1 micron or below are found to be completely amorphous. As such, a decrease in glass transition temperature from 202 to 193 C for CA is observed, indicating greater polymer chain flexibility in the amorphous phase. Permeability-wise, films 1 micron-thick demonstrate a CO2 permeability of 8 Barrers, while films 20-micron-thick demonstrate a CO2 permeability of 4 Barrers, representing a 100% increase. The observed increase in permeability can be partially attributed to the increase in CO2 gas sorption, where solubility in the amorphous phase of CA goes from 1.65 x 10-2 to 3.44 x 10-2 cm3 (STP)/cm3 cmHg

34. Thin Film Nanocomposite Membranes Containing Metal-Organic Frameworks for Water Desalination

Janavi Gohil, **Haiqing Lin**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: janavivi@buffalo.edu, haiqingl@buffalo.edu

Reverse osmosis (RO) has emerged as a cost- and energy-efficient technology for producing fresh water from sea and brackish water. However, current RO membranes comprise highly cross-linked polyamides and have comparatively low water flux, which limits their wider adoption. The goal of this study is to develop a novel thin film nanocomposite (TFN) membrane containing porous metal-organic frameworks (MOFs) to increase water permeance and retain the salt rejection. Specifically, ZIF-8 particles (< 35nm) were prepared and incorporated in the polyamide layer of the RO membranes. The effect of the particle loading and preparation conditions on the desalination performance of the membranes is evaluated.

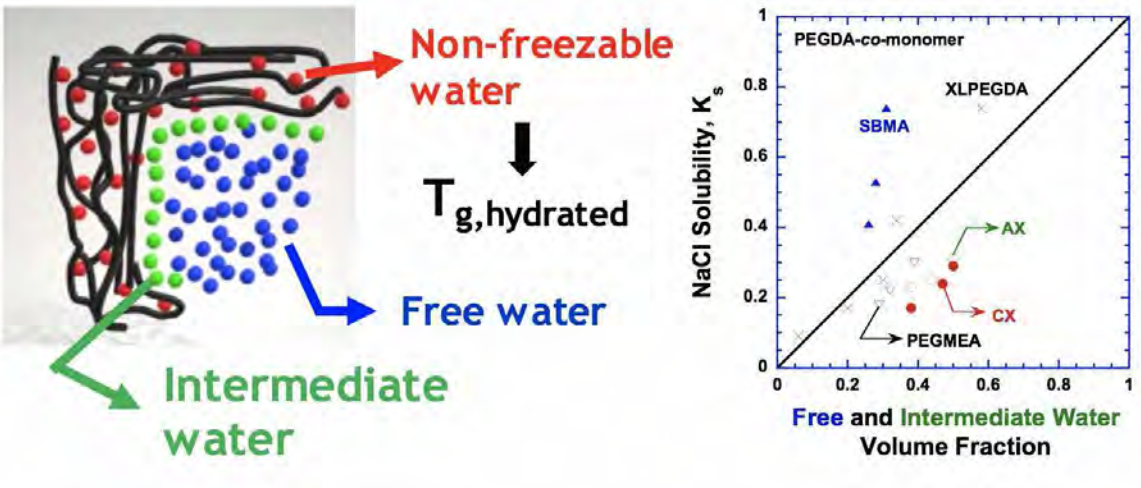
35. Elucidating the Relationship between the State of Water and Transport Properties of Ions in Hydrated Polymer Networks

Thien Tran, **Chen Lin**, **Shabdiki Chaurasia**, **Haiqing Lin**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: ttran7@buffalo.edu, clin28@buffalo.edu, shabdiki@buffalo.edu, haiqingl@buffalo.edu

Ions transport properties in hydrated polymers is usually correlated with the amount of water assuming that all water contributes equally. Herein, we demonstrate that water in polymers exists in three states (non-freezable, intermediate, and free water), and the different states of water exert different impacts on polymer properties including glass transition temperature and ion sorption and diffusion. We synthesized four systematic series of polymer networks including neutral, zwitterionic, cation exchange, and anion exchange polymers. The amounts of water in different states in the hydrated polymers were determined using Differential Scanning Calorimetry (DSC), and their dependence on the polymer composition is investigated. The glass transition temperature of the hydrated polymers is satisfactorily correlated with the non-freezable water using the Gordon-Taylor equation. The salt solubility is correlated with the combined free and intermediate water, and the salt diffusivity is satisfactorily correlated with the total water using the modified Yasuda model.

Key words: polymer, water states, transport properties, ions, PEG



36. Solution Phase Templated Synthesis of Dendritic Fibrous NanoSilica (DFNS)

Anirudh Ravi Raghavan, **Naveshkaanth Alexander**, **Mohammad Moein Mohammadi**, **Abhishek Kumar**, **Mark T. Swihart**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: araghava@buffalo.edu, naveshka@buffalo.edu, mm458@buffalo.edu, akumar37@buffalo.edu, swihart@buffalo.edu

Although mesoporous forms of silica have found broad use as catalyst supports and in other applications, they have some limitations that have lead to the search for different forms of nanostructured silica. One such promising morphology is the dendritic fibrous three dimensional structure, which can have advantages such as improved accessibility to the internal surface area and higher stability. Due to the fibrous morphology, these nanospheres are accessible from all sides and hence can have increased loading of accessible active sites. The pore size distribution is also different from conventional silica, with radially oriented pores that increase in diameter from the center of the particle to the surface. Here, we explore the synthesis of these DFNS particles using cetyl trimethyl ammonium bromide (CTAB) as a templating agent and tetraethylorthosilicate (TEOS) as the silica precursor. We have begun to explore the effects of varying the synthesis parameters and comparing against the other mesoporous silica materials. These particles have potential applications in fields including catalysis, drug delivery, gene therapy and carbon dioxide adsorption.

Key words: Dendritic structures, Silica

37. Laser Pyrolysis Synthesis of Novel Nanoparticles Using Spray-Based Precursor Delivery

Mohammad Malekzadeh, **Parham Rohani**, **Mayuresh Keskar**, **Mohammad Moein Mohammadi**, **Mark T. Swihart**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: mmalekza@buffalo.edu, parhamro@buffalo.edu, mkeskar@buffalo.edu, mm458@buffalo.edu, swihart@buffalo.edu

Nanoparticle synthesis, the production of particles from 1 to 100 nm in characteristic size, is a key component of nanotechnology. Vapor-phase nanoparticle synthesis has advantages including high throughput continuous operation, scalability, and product purity that have given it a dominant role in the commercial production of nanomaterials. Laser pyrolysis is one of the important vapor phase nanoparticle synthesis methods. In laser pyrolysis, a laser beam is used to selectively heat a gas stream containing nanoparticle precursors, such that they decompose, inducing nucleation of nanoparticles. One of the most important advantages of laser pyrolysis is its flexibility to synthesize nanoparticles of diverse materials using appropriate precursors. A key advantage of laser pyrolysis compared to furnace-based methods is that only the gas, which has small heat capacity, is heated and, moreover, only that part of the gas that absorbs the laser energy is heated. As a result, the gas benefits from very rapid heating and rapid cooling by mixing of the heated gas with unheated gas. Gaseous, liquid, or solid precursors can be used in this method. Although gaseous precursors have most often been used in laser pyrolysis synthesis, solid or liquid precursors would be preferable in many cases, due to issues of safety and precursor cost and availability. These precursors can be delivered to the reaction zone as small droplets that rapidly evaporate upon laser heating. Precursors with sufficiently high vapor pressure could also be delivered as vapors from a bubbler. However, for some metals, no sufficiently volatile precursor is available. Accordingly, spray-based precursor delivery is the most general approach to delivering precursors for the synthesis of nanoparticles by laser pyrolysis. This poster will describe our recent progress in using ultrasonic spray delivery of precursors to our laser pyrolysis reactor to prepare nanoparticles from nonvolatile precursors.

Key words: Nano-synthesis, Laser Pyrolysis, Spray-Based Precursor Delivery

38. Synthesis of Cobalt Oxide-based Nanostructures with Controlled Morphology

Zheng Fu, **Saranya Rajendra Pillai**, **Zhengxi Xuan**, **Mark T. Swihart**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: zhengfu@buffalo.edu, spillai3@buffalo.edu, zhengxix@buffalo.edu, swihart@buffalo.edu

Transition metal oxides (TMOs) have been interesting active materials for energy storage and electrochemical catalysts due to their high electrical conductivity, chemical stability and promising catalytic activity as noble metals. Here, we synthesized a type of magnetic three-dimensional (3D) hierarchical dendritic cobalt oxide (CoO) with a convenient one-pot solution phase synthesis method. Moreover, this stable CoO can serve as a flower-shaped template, based on which we also synthesized iron cobalt oxide (Fe-Co-O), manganese cobalt oxide (Mn-Co-O) and nickel cobalt oxide (Ni-Co-O) nanostructures with similar morphology and varied magnetic behavior. Shapes and sizes of these samples are controlled by tuning parameters such as ligands, additives, temperature, heating rate, and reaction time. Based upon our observations, we propose a mechanism for the nucleation and growth of these structures. In addition, an atlas of CoO and derived alloys is presented to illustrate the possibilities of their controlled shape and size evolution. These samples can potentially be applied in lithium ion batteries (LIB). $LiCoO_2$ (LCO) remains the best cathode material for use in the portable electronic domain due to its high energy density and high initial Coulombic efficiency. Also, due to the high specific surface area and promising catalytic activity of TMOs, CoO and derived alloys could have important applications in electrocatalysis. The controlled magnetic properties can allow easy recovery of dispersed catalyst particles, and could be the basis for developing other magnetic applications.

Key words: cobalt oxide, alloy, morphology control, solution phase synthesis, electrocatalysis

39. Insights into the Crystallization and Transformation of Calcium Carbonate

Mokshita Bhan, **Subhendu Banerjee**, **Rajarshi Roy**, **Marina Tsianou**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: mokshita@buffalo.edu, sbanerje@buffalo.edu, rroy7@buffalo.edu, mtsianou@buffalo.edu

Calcium carbonate (CaCO3) is one of the most abundant minerals and of great importance in many areas including global CO2 exchange, energy storage, industrial scaling, and the formation of shells and skeletons. Commercially, calcium carbonate is used in the production of cement, paints, plastics, ceramics, as well as being a key material in the pharmaceutical and cosmetics industries. Anionic polyelectrolytes are widely used in industry to control the size distribution and polymorph of calcium carbonate. However, the mechanism of action, especially in the regime of lower supersaturation still remains unclear. In this work, we have employed an anionic polyelectrolyte, poly (sodium 4-styrene sulfonate), (PSS), to investigate its role in the crystallization kinetics of calcium carbonate. We have used conductivity and calcium ion selective electrode measurements to assess the induction time and the growth rate of calcium carbonate. PSS was found to delay the induction time and decrease the maximum growth rate. Moreover, PSS addition favors the formation of metastable vaterite. Through these studies, we hope to better understand how anionic polyelectrolytes affect nucleation, growth, and polymorph selectivity, and also identify the optimal conditions for the use of polyelectrolytes as additives in scale control and inhibition and in the particle size control in various industries.

Key words: Calcium Carbonate, Biomineral, Nucleation, Growth, Crystallization kinetics

40. Utilizing the Constant Composition Method to Investigate Calcium Biomineral Crystal Nucleation and Growth

Rajarshi Roy, **Arkita Chakrabarti**, **Marina Tsianou**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: rroy7@buffalo.edu, arkitach@buffalo.edu, mtsianou@buffalo.edu

The formation of stones in the kidney, urinary bladder or urinary tract, commonly occurs as a result of increased supersaturation of minerals in the kidney. The disease affects almost half a million people every year and it is extremely painful, leading to a decreased quality of life. Kidney stones are typically composed of calcium oxalate, calcium phosphate, cystine, struvite, or uric acid among which calcium oxalate is the most predominantly present. This work aims to investigate the inhibitory effects of anionic polyelectrolytes on the nucleation and growth of calcium oxalate in aqueous media, using a constant composition potentiostatic technique. In the constant composition method, the ions that are consumed in crystallization are constantly replenished in order to maintain a constant supersaturation in the crystallization media. We evaluate the role of supersaturation and additives on the crystallization kinetics of calcium oxalate in both seeded and unseeded experiments. Moreover, we investigate the effects of polymer molecular weight and charge density and compare our findings to sodium citrate, the current standard pharmacological treatment for stone disease. These studies offer a better understanding of the calcium oxalate crystallization kinetics and may provide information on the viability of synthetic polymers as potential calcium oxalate stone therapies.

Key words: Calcium Oxalate, Biomineral, Nucleation, Growth, Crystallization kinetics

41. Biosurfactant Solution Self-Assembly and Surface Adsorption Properties

Yi Zhang, **Ruksana Jahan**, **Paschalis Alexandridis**, **Marina Tsianou**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: yzhang67@buffalo.edu, ruksanaj@buffalo.edu, palexand@buffalo.edu, mtsianou@buffalo.edu

Biosurfactants are naturally occurring amphiphiles that reduce surface and interfacial tension in aqueous solutions and water-oil mixtures. On the basis of their ability to mobilize and disperse hydrocarbons, biosurfactants are involved in the bioremediation of oil spills, and are being actively pursued as alternatives to synthetic surfactants in cleaning, personal care and cosmetic products. Rhamnolipids are low molecular weight glycolipid biosurfactants that are synthesized from microbes, especially Pseudomonas bacteria. We examine here the micellization of mono-rhamnolipids and di-rhamnolipids in aqueous solutions and their adsorption on model surfaces; and compare the rhamnolipid behavior to that of synthetic surfactants. A better understanding of biosurfactant self-assembly and adsorption properties is important for their utilization in environmental and consumer products applications.

Key words: biosurfactant, rhamnolipid, bioremediation, oil spill

42. Atomically Dispersed Iron Cathode Catalysts for Proton-Exchange Membrane Fuel Cells

Hanguang Zhang, **Mengjie Chen**, **Gang Wu**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: hanguang@buffalo.edu, mengjiec@buffalo.edu, gangwu@buffalo.edu

One of the bottlenecks hindering the wide implementation of proton-exchange membrane fuel cells (PEMFCs) is the high cost and massive use of platinum (Pt) catalysts for boosting oxygen reduction reaction (ORR) kinetics at the cathode in PEMFCs. Fe-N-C catalysts, derived from pyrolysis of nitrogen, iron and carbon precursors together, have been the most promising candidates to replace Pt because of the abundance and low cost of such elements as well as the highly intrinsic ORR activity of Fe-N-C sites forming during the pyrolysis. However, the major challenge for such Fe-N-C catalysts is to obtain sufficient Fe-N-C active sites catalysts to achieve high ORR activity, since undesired metallic species (i.e. Fe/Fe_3C) are easily produced during high-temperature pyrolysis due to the improper design of synthesis and the poor chemistry control in the preparation of catalysts, lowering the actual Fe-N-C active sites density of catalysts. To address this issue, we have developed a facile approach to prepare Fe-N-C catalysts with exclusively atomically dispersed Fe in Fe-N-C single-sites instead of containing metallic Fe particles by using well-defined Fe-doped metal-organic framework (MOF) precursors. The morphology of MOF precursors can be directly transferred into Fe-N-C catalysts with the retained shape after pyrolysis. Such controlled synthesis of precursors and resulting homogeneous catalysts allow us to precisely control and tune the composition and morphology of Fe-N-C catalysts such as the particle size and Fe loading in catalysts to understand how the structure and composition change of catalysts impact their ORR activity.

Key words: oxygen reduction reaction, electrocatalysis, metal-organic framework, Fe-N-C, fuel cell

43. MOF-based Electrocatalysts for CO2 Conversion to H2 and CO

Hao Zhang, **Hanguang Zhang**, **Gang Wu**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: hzhang46@buffalo.edu, hanguang@buffalo.edu, gangwu@buffalo.edu

Excessive CO2 emission caused by a large amount of fossil fuel utilization has become a widespread concern, which induces both environment and energy issues. Electrocatalytic reduction of CO2 to produce value-added chemicals such as H2 and CO have gained immense attention. Metal-organic frameworks (MOFs) and their derived materials with tunable chemical and physical properties exhibit promising performance for CO2 reduction reaction. Recently, we reported the comprehensive investigation of the structure-activity relationships over single atom M-N4 catalysts (M = Fe, Co) for electrochemical CO2 reduction. We developed the electrocatalysts with atomically dispersed Fe or Co sites into carbons containing bulk and edge hosted M-N4 structure using ZIF-8 as the precursor. The single atom Fe catalysts exhibit higher performance than the Co-based catalysts for CO2 electrochemical conversion to CO, with a FE of 93 % at -0.6 V vs. RHE. Combined the XAFS results and the atomic resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) results, we confirms the formation of single atom Fe and Co sites. DFT calculations further elucidated that the edge hosted M-N2+2-C8 moieties served as the active sites for electrochemical CO2 reduction. The dissociation of *COOH species occurs on the M-N2+2-C8 sites, and the single Fe or Co atoms are the active sites for the adsorption of *CO species.

References F. P. Pan, H. G. Zhang, K. X. Liu, D. Cullen, K. More, M. Y. Wang, Z. X. Feng, G. F. Wang, G. Wu and Y. Li, ACS Catalysis 2018, 8, 3116-3122 H. Zhang, J.Z. Li, Q. Tan, L.L. Lu, Z.B. Wang and G. Wu, Chemistry-A European Journal 2018, doi: 10.1002/chem.201803083

Key words: CO2 reduction; Electrocatalysis; MOFs; MOF derivatives

44. Hetero-atom doped MOF catalysts for Water Splitting Technology

Janel Abbott, **Qiang Tan**, **Gang Wu**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: janelabb@buffalo.edu, qiangtan@xjtu.edu.cn, gangwu@buffalo.edu

Water splitting technology is a renewable energy technology that could have considerable benefits to the society. The products obtained from the water-splitting process are hydrogen and oxygen. With renewable technology such as hydrogen fuel cells, hydrogen has emerged as an alternative carbon-free fuel. The water-splitting process requires the energy of 474.3 kJ mol-1 for a complete transformation of 1 mole of water into 2 moles of hydrogen and a mole of oxygen. The activation energy of the process can be lowered with the help of catalysts. The main reaction that determine the performance of the water -spitting technology is Oxygen Evolution Reaction (OER). Presently, the challenge for water electrolysis is the discovery and development of suitable catalysts for OER.

Various precious metal catalysts have been studied for OER. However, there are limitations in employing precious metal catalysts. Ideally, non-precious metals have the most effective means of providing sufficient surface active sites for OER and are cost effective. Within an electrochemical system, the catalysts must be stable and active in an electrolyte media. Metal-organic frameworks are a feasible catalyst that shows the greatest potential to break down water into hydrogen and oxygen gas. The main media for water splitting technology are acid and base media. Acid media shows greater enhancement for OER because it can handle higher current densities and supply the system with an abundance of protons and electrons. Specifically, heteroatom-metal doping ZIF-8 and stabilizing it on a carbon network shows an improvement in its activity and stability in acidic media. This shows the potential to replace precious metal catalysts and provide a means of new energy storage systems.

Key words: OER in acid; Water splitting technology; hetero-atom metal doping

45. Pt alloy nanoparticles decorated on large-size nitrogen-doped graphene tubes for highly stable oxygen-reduction catalysts

Mengjie Chen, **Kate Chen**, **Yanghua He**, **Shreya Mukherjee**, **Gang Wu**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: mengjiec@buffalo.edu, katechen@buffalo.edu, yanghuah@buffalo.edu, mukherje@buffalo.edu, gangwu@buffalo.edu

Pt alloy nanoparticles supported on Vulcan XC-72 (Pt/C) are the most effective catalysts for kinetically sluggish oxygen reduction reaction (ORR) in proton exchange membrane fuel cells. However, significant performance degradation has been observed with the Pt/C catalysts due to agglomeration and Ostwald ripening of Pt nanoparticles largely resulting from the corrosion of carbon supports. Here, we developed a Pt alloy catalyst through annealing Pt nanoparticles deposited on nitrogen/metal co-doped large-size graphene tubes (NGTs). The in-situ formation of PtM (M: Co and Ni) alloy during the annealing process contributes to the improvement of the catalytic activity and stability. During the accelerated stress tests(AST), after 20 000 potential cycles (0.61.0 V vs. RHE), the retained electrochemical surface area (ECSA) of the PtM/NGT catalyst is more than 2 times larger than that of the Pt/C catalyst. As for the AST tests of carbon corrosion, after 30 000 potential cycles (1.01.5 V vs. RHE) at room temperature, the NGT morphologies are well maintained and no ECSA loss of this PtM catalyst is observed, indicating excellent corrosion-resistance. Even at harsher 60 C, the PtM/NGT catalyst exhibits only insignificant loss (6 mV) of E1/2 while the Pt/C catalyst shows significant degradation (47 mV loss in E1/2). The improved stability of PtM/NGT catalyst is attributed to the highly graphitized NGTs and possible synergistic effects between the NGT carbon support and the PtM alloy nanoparticles.

Key words: ORR, fuel cell, Pt alloy, graphene tube

46. Ammonia Production from Water and Nitrogen using MOF derived Carbon

Shreya Mukherjee, **Hao Zhang**, **Gang Wu**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: mukherje@buffalo.edu, hzhang46@buffalo.edu, gangwu@buffalo.edu

Sustainable synthesis of Ammonia (NH3) is gaining great attention not only for its application as an alternative renewable energy fuel but also to substitute production of ammonia through the conventional Haber Bosh process. The conventional Haber-Bosh uses fossil fuels in deriving hydrogen from steam reforming of natural gas, is energy intensive and also leads to significant CO2 emission. Alternatively, electrochemical synthesis of ammonia (ESA) using renewable energy through the nitrogen reduction reaction (NRR) in alkaline medium saves the use of hydrogen as a reactant as the aqueous electrolyte forms the source of proton. However, the standard reduction potential of nitrogen and protons in the elctrolyte fall in the same domain. Thus, hydrogen evolution reaction is so dominant at the applied potential that selectivity of nitrogen reduction is a major challenge in the budding field. Recently, we have reported a metal-organic framework-derived nitrogen-doped metal free nanoporous carbon electrocatalyst with a Faradaic efficiency (FE) of 10 % at -0.3 V vs RHE under ambient conditions for the NRR. It exhibits a remarkable production rate of NH3 up to 3.410-6 mol cm-2 h-1 using aqueous 0.1 M KOH electrolyte. The performance has been compared with other N doped carbon derived from commercial polyaniline and nitrogen free KJ black and N doped CNT. The stability of the nitrogen-doped electrocatalyst was demonstrated during an 18-hour continuous test with constant production rates. This work provides a new insight into the rational design and synthesis of nitrogen-doped and defect-rich carbon NRR catalysts for NH3 synthesis at ambient conditions.

Key words: Electro catalysis; NH3 synthesis; MOF; N-doped carbon; DFT calculation

47. Size-Controlled Carbon Catalysts Derived from Metal-Organic Frameworks for Non-Aqueous Li-Air Battery

Yanghua He, **Hanguang Zhang**, **Yingjie Chen**, **Jingyun Wang**, **Gang Wu**

Department of Chemical and Biological Engineering, University at Buffalo, SUNY
Email: yanghuah@buffalo.edu, hanguang@buffalo.edu, ychen282@buffalo.edu, jingyunw@buffalo.edu, gangwu@buffalo.edu

The excessive use of fossil fuels has led to increasing concerns about global climate change and national energy storage. It is urgent to develop some clean, efficient, and reliable technologies to harvest and store the clean energy generated from solar and wind. Electrochemical energy technology such as batteries and fuel cells can serve as an ideal medium to store and release electricity. Among various electrochemical systems, Li-air battery has attracted wide attention to be a promising next-generation energy storage device due to its high theoretical capacity (11,000 Wh/kg). Thus, one of the most important topics is to develop an efficient, economical and safe Li-air battery. Here, we develop a series of Co-doped metal-organic frameworks derived carbon catalysts (Co-MOFs) of different sizes, which can be employed as the high-performance bifunctional cathode catalysts for Li-air battery. Controlled by anion type and the amount of 1-methyl imidazole, Co-MOFs catalysts can be obtained with various sizes, ranging from 50 nm to 5 m. Further optimization of the Co content and thermal activation procedure can produce a highly active Co-N-C catalyst, showing a half-wave potential of 0.818 V vs. RHE in aqueous solution and high selectivity for four-electron reduction, mainly due to the influence of the final morphology and structure including surface area, pore structure and nitrogen doping. Co-N-C catalyst also exhibits a higher performance in terms of onset potential, half-wave potential and current density in non-aqueous solution when compared with non-metal-MOFs derived catalysts. The high oxygen reduction reaction (ORR) activity of this catalyst could be attributed to the Co-Nx active sites embedded in the porous carbon matrix. In the battery, the cathode consisting of Co-MOFs catalysts shows a high discharged capacity of 13,000 mAh/g and a relative stable cycling performance up to 50 cycles, which implies that Co-MOFs catalysts could be a promising candidate as the replacement of platinum group metal catalysts for Li-air battery applications.

Key words: Cobalt, MOF, Li-air battery