

NMR Studies of Water in Acetylated and Unmodified Wood

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Acetylation is a safer alternative to previous wood preservation methods such as arsenic pressure treating, which can leech into communal water sources¹. Acetylated wood shows better resistance to fungal growth and greater dimensional stability upon water absorption due to minimalized shrinking and swelling as compared to untreated wood products². Though the large scale impacts of this product are clearly established, little is known about the local morphology of acetylated wood. This research uses NMR relaxation studies to gain a better understanding of the environments of water in acetylated and untreated wood samples. T_2 relaxation times were measured at varying hydration levels in an attempt to understand the local environments of water and to calculate the percentage of water in each environment. From this data, we can conclude that there are two environments of water within each wood sample. Based on findings in similar wood studies^{3,4}, we believe that the short component T_2 value corresponds to water confined within the cell walls while the longer T_2 component corresponds to more freely moving water located in the lumen of the wood. In analyzing the percentage of water in each component over varying hydration levels, both the control and acetylated wood initially showed a greater percentage of water in the long component but reached a crossover point upon drying at which a greater portion of water was contained in the shorter component. This crossover point occurred at much higher hydration levels for the control samples. This research is an important step in the process of understanding the morphology of acetylated wood and explaining why this wood exhibits such different properties than traditional untreated wood.

3D Printing of Ceramic Suspensions using Microstereolithography toward Water and Gas Filtration

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Stereolithography (SLA) is an additive manufacturing (AM) technique where a liquid photopolymer resin is cured layer by layer by ultraviolet (UV) radiation to build high resolution, geometrically complex three-dimensional structures. Ceramics have been processed into structures using AM to utilize their thermal, electrical, and chemical resistivity for numerous applications such as capacitors¹, water filtration membranes², bone implants^{3,4} and heat sinks⁵. The authors in this study investigated ceramic suspension behavior and geometric designs to process and fabricate efficient, tunable and porous cylindrical filters towards removing heavy metals from water and air. This work utilizes mask projection microstereolithography (MP μ SL) to print 60 weight percent calcium phosphate suspended in photocurable resin. Porous insulators were printed and heated to 1300°C through a sintering process to obtain fully densified ceramic structures. The photocuring and flow behavior of the calcium phosphate suspension were measured by photo-rheology and rheology respectively. The structural morphology was analyzed by high-resolution light microscopy, which revealed pores with a diameter of 100 microns. The post-sintering dimensional shrinkage of fabricated insulators was measured. Porous insulators

had shrinkage values of $31.8 \pm 3.58\%$ and $28.8 \pm 3.27\%$ for their length and diameter respectively. Thermal stability of sintered insulators was measured by thermogravimetric analysis (TGA) which exhibited mass losses of 0.02%, indicating the ceramic's excellent thermal stability. These properties can be modeled in future designs to predict the insulator's anisotropic shrinkage behaviors, porosity and heat capacity of ceramic parts. The authors believe this study can also be applied towards designing micro-scaled, geometrically complex heat capacitors used in the semiconductor, automotive, energy and aerospace industries.

Synthesis and Characterization of Post-Modified Polybenzimidazole Membranes for Gas Separation of H₂ and CO₂

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Polybenzimidazoles (PBI) are a promising membrane material for gas separations at elevated temperatures due to their excellent chemical and thermal stability and high glass transition temperature. The thermo-oxidative stability of PBIs allows them to be used at the processing temperature, around 250 °C, of pre-combustion syngas for gas separation of H₂ and CO₂, reducing both the energy required for and cost of operation. The H₂ can be utilized as a green energy source while the CO₂ can be captured and stored. However, the processability of PBIs is limited by their poor permeability and solubility, a consequence of rigid chain structuring and hydrogen bonding. Grafting long chain polymers onto a PBI backbone and then extracting the grafted chains via thermal degradation is hypothesized to increase free volume and improve gas permeability through the membrane. Previous work involved synthesizing PBI polymers with sulfonyl-containing tetraamine, which resulted in improved PBI solubility as compared to the commercial standard, Celazole®. The monomer tetraaminodiphenylsulfone (TADPS) was prepared by a three-step process. The PBI was synthesized via solution polymerization of TADPS and oxybisbenzoic acid (OBA) using Eaton's Reagent as a solvent and condensing agent. Additionally, monomethyl ether polyethylene oxide (m-PEO, M_n 350 Da) was tosylated to provide a good leaving group for the grafting reaction. All final structures were verified using ¹H-NMR. The PEO-Tos and PBI were then reacted in the presence of base to produce grafted PBI-PEO. ¹H-NMR, COSY, and SEC were employed to confirm the structure of the PBI-g-PEO and determine the percentage of grafted PEO. Preliminary results showed that 37% PEO was successfully grafted onto the PBI backbone. Future work includes casting a grafted PBI-PEO film and investigating its thermal degradation and gas transport properties.

A Study of the Electrocatalytic Activity of Metal-Organic Framework PCN-223 in the Oxygen Reduction Reaction

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Clean energy sources are needed to meet growing energy demands without producing greenhouse gases or other harmful pollutants. Fuel cells could meet these demands; however, one limitation of current technology is inefficient cathodic reaction, which requires the use of expensive and scarce Pt-based catalysts. Other non-platinum group metal catalysts

are lower in cost, but have inferior performance. Metal-organic frameworks (MOFs) have emerged as promising alternative to traditional Pt catalysts because of their highly porous nature and wide array of chemical properties, which can be optimized for specific applications. Our study focuses on investigation of the electrocatalytic properties of a MOF known as PCN-223-Fe (PCN = porous coordination network) deposited on fluorine-doped tin oxide (FTO) for the oxygen reduction reaction (ORR). This framework contains Zr-oxo nodes which are connected by Fe(III) porphyrin ligand (Fe(III)TCPP) previously shown to be catalytically active for ORR. The electrochemical behavior and stability of the PCN-223-Fe thin films was compared to that of Fe(III)TCPP using cyclic voltammetry (CV), controlled potential electrolysis (CPE), and rotating ring disk electrode experiments (RRDE) in Ar and O₂ saturated environments. Acetic and trichloroacetic acids were employed as proton sources and their effect on the redox properties of Fe(III) porphyrin was investigated. The MOF was characterized by a wide array of techniques, including powder x-ray diffraction (PXRD), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), and inductively-coupled plasma mass spectroscopy (ICP-MS). These measurements confirmed the structure of PCN-223-Fe. Soluble Fe(III)TCPP complex was found to generate higher currents than the thin film PCN-223. Trichloroacetic acid exhibited superior performance as a proton source compared to acetic acid; however, CPE stability testing demonstrated that it resulted in faster current decay and deactivation of PCN-223-Fe. RRDE experiments showed that the catalyst has good selectivity for the production of H₂O vs H₂O₂ which beneficial for fuel cell applications.

Characteristics or Culture?: Determinants of Household Energy Use Behavior in China, Germany, and the USA

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Future climate agreements will require an understanding of the factors that underlie country energy behavior disparities in order to generate multilateral agreements that are sensitive to country-specific conditions. An Oaxaca-Blinder decomposition is employed to empirically analyze differences in household energy use behavior using survey data from China, Germany and the United States. Two basic energy conservation methods, increasing energy efficiency and reducing energy use, serve as a basis for the three dependent variables of the study: purchasing energy-efficient appliances, saving energy at home, and purchasing fuel-efficient vehicles. Observed country disparities are decomposed into three components: variable mean differences, variable coefficient differences and variable mean-coefficient interaction differences. The analysis demonstrates that variable mean differences are a major contributor to observed differences in energy use behavior in Chinese households, relative to U.S. and German households. Chinese households report higher national averages for the majority of variables that are found to be positively associated with energy-efficient behavior. Conversely, variable coefficient differences explain most of the observed energy use behavior differences in German and U.S. households. Across all observed differences, several variables are significant in each component of the decomposition; most notably income, the perceived financial advantages of energy behavior, and the perceived effectiveness of energy behavior in combating climate change. Thus, income growth and perceived cost-effective energy-reducing technologies with clear environmental

contributions appear to be key components for cross-country pathways to global greenhouse gas reductions.

Membrane Capacitive Deionization Using Electrospun Carbon Nanofibrous Electrodes

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Over 70 percent of the world is covered in water, yet only a small fraction of that water is freshwater.¹ The world's population is continuing to increase, highlighting the need for more efficient and cost-effective desalination techniques. Membrane capacitive deionization (MCDI) has the potential to be a competitive alternative to traditional desalination methods.² In order to investigate this alternative method, a cation-exchange membrane and a porous carbon electrode, two major components of the MCDI cell, were developed and incorporated into a MCDI apparatus. The cation-exchange membrane was fabricated by homogeneously sulfonating poly(ether ether ketone) (PEEK) at various degrees of sulfonation by controlling the reaction time and concentration of sulfonating reagent. These membranes were characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), water uptake, tensile testing, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and electrochemical impedance spectroscopy (EIS). With increasing degree of sulfonation, a decrease in crystallinity was observed due to an increased number of chain defects along the polymer backbone. Furthermore, an increase in water uptake and an increase in conductivity were observed due to increased ion content. To fabricate the electrodes, a 12 wt% solution of polyacrylonitrile (PAN) in dimethyl formamide (DMF) was electrospun, oxidized, then carbonized. The resulting electrodes were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and porosity measurements. A MCDI cell was assembled using the nanofibrous carbon electrodes along with commercial ion-exchange membranes, graphite current collectors, and a fabric spacer to test the performance of the electrodes. Future research will include adding the sulfonated PEEK membranes to the MCDI cell as the cation-exchange membrane, constructing a stack of N=8 cells, and optimizing the operational parameters of the MCDI apparatus in order to achieve efficient desalination.

Trace Element Analysis of Gas Shales by Laser Ablation ICP-MS: Implications for Mobility

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Trace elements contained in pyrite-bearing shale have the potential to be mobilized when the shale is exposed to oxygen. Although this occurs naturally, hydraulic fracturing processes may enhance pyrite oxidation, and trace element release, from the shale to water. First, the introduction of oxygenated fracturing fluid to the shale source rock may oxidize the pyrite *in situ*, allowing trace elements to be released into flowback water. Flowback water is typically stored in retention basins, which can leak, allowing these toxic trace elements to enter water supplies. Second, shale rock cuttings from drilling are also exposed to oxygen at the surface, producing acid drainage and allowing trace element release. In this study, pyrites and the

shale matrix of gas-producing shales were evaluated for trace element content and spatial heterogeneity. Two thin sections from two different cores in the Marcellus Formation, the most expansive shale-gas play in the U.S., were analyzed by laser ablation inductively-coupled mass spectrometry (LA ICP-MS). NIST 612 glass was used as the external standard, and the USGS MASS-1 and BIR-1G were used as check standards. Although LA ICP-MS has previously been used to evaluate trace elements in pyrites, there is little knowledge about how these data can be used to predict trace element leaching as a result of natural gas extraction. Results show elevated concentrations of some trace elements, including As, Se, Pb, Ag, Cd, and Sb, in pyrites compared to the shale matrix. In contrast, results indicate that U, V, Cr, Mn, Mo, and Ba are more abundant in the shale matrix than in the pyrite. Many of these trace elements are toxic and are regulated by the U.S. EPA; therefore, examining the mineral sources and potential mobilization mechanisms is important for protecting water supplies in areas impacted by hydraulic fracturing. Future research will include analyzing additional shales, and examining the trace element content of organic and carbonate material in addition to pyrite.

Alkyl Modification of Block Copolymers as a Means to Tailor Controlled Release

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H₂S is an endogenous signaling gas with significant therapeutic potential. The effectiveness of alkyl modification of H₂S releasing thiooxime bearing polymer as a method of controlling its thermal and kinetic properties of the polymer were evaluated. To this end, a methacrylate polymer bearing pendant aldehyde functionality was produced by reversible addition-fragmentation chain transfer (RAFT) polymerization of 2-(4-formylbenzoyloxy)ethyl methacrylate (FBEMA). Post-polymerization modification of the poly(FBEMA) was performed to replace aldehyde functionality with S-arylothiooxime (SATO) and alkyl functionality in varying composition. S-arylothiooximes decompose to release H₂S in response the presence of cysteine. The ratio of SATO to alkyl functionality allows for unprecedented control over the thermal properties and H₂S release kinetics of the polymer. Differential Scanning Calorimeter (DSC) was used to quantify the effect of polymer composition on glass transition temperature and H₂S release half-life. Additionally, amphiphilic block copolymers were produced by joining a polyethylene glycol (PEG) polymer with the poly(FBEMA). These polymers were then modified to have pendant SATO and alkyl functionality of varying composition, and the self-assembly properties of the amphiphilic polymer were characterized via Nile Red assay. TEM imaging confirmed the successful formation of self-assembled micelle structures across the range of SATO-alkyl compositions. The effect of poly(FBEMA) block composition on the size and structure of the self-assembly was characterized. The formation of micelles significantly improves the potential longevity of the polymer in biological systems, which will allow for longer treatment cycles. This work represents an expansion in the degree of control over H₂S release kinetics and H₂S releasing polymer properties.

3D Printed Biosensor for Food and Water Safety

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Each year, millions of people around the world die from water-related diseases. Populations in underdeveloped regions are especially in need of robust sensing technology to monitor water quality. Advanced biomanufacturing techniques can be employed to create such a biosensor that is capable of analyzing small-volume samples without bulky supporting components. In particular, 3D printing can be used exclusively to print an electrochemical system that includes a platinum counter electrode, silver/silver chloride reference electrode, and working electrode. Additionally, this biosensor incorporates a piezoelectric acoustic transducer for heightened precision and sensitivity, which is particularly beneficial for the detection of species at low concentrations. Materials selection for the working electrode – the sensing component – was first optimized by investigating several conductive polymers and metals. The effect of protein binding on the biosensor was also explored. The system was characterized using standard electrochemical measurements, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Future research will determine the limits of detection for this system, and a calibration curve will be created based on varying concentrations of a pathogen, like *E. coli*. The ability to rapidly and efficiently detect water-borne pathogens is critical for ensuring water quality, and the electrochemical biosensor could have a profound impact in this field due to its enhanced sensitivity.

Synthesis of Biosourced, Isocyanate-free Polyureas as Controlled-Release Fertilizers

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Traditional nitrogen fertilizers, such as urea, are inefficient and harmful to the environment due to runoff, nitrate leaching, ammonia volatilization, and nitrous oxide emissions. Current controlled-release nitrogen fertilizers that utilize polymer-coated urea granules (PCUs) demonstrate excellent controlled-release properties, increasing fertilizer efficiency. However, the high cost and poor biodegradability of PCUs limits their commercialization. Introducing hydrogen bonding moieties (e.g. urea) results in high mechanical strength, while promoting biodegradability.¹ Melt polymerization of polyureas, without the use of isocyanates, is economical and affords high molecular weight polymers that are semi-crystalline and optically clear. Incorporation of biosourced monomers into polyureas increases bio-compatibility and reduces costs associated with the coating process without compromising on mechanical properties. Various analytical techniques including TGA, DMA, and DSC identify these polyureas as tough thermoplastics with melt processability, which is critical for large scale production. Finally, the use of biosourced polyureas as fertilizers capitalizes on natural soil enzymes which readily hydrolyze polyureas to yield a feedstock of nitrogen.

Novel Photocurable Molecules for Stereolithography with Electrochemical and Biomedical Applications

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Stereolithography (SLA) is an additive manufacturing (3D printing) technique that enables fabrication of high resolution parts from acrylate and epoxy-based photopolymer resins. This severely limits the applications for which SLA may be used, and thus new resins are of great interest. In this research, two novel photocurable molecules were explored: a phosphonium-based ionic liquid, 4-vinylbenzyl trioctyl phosphonium bis(trifluoromethanesulfonate)imide (TOPTf₂N), and poly(tri(ethylene glycol) adipate) dimethacrylate (PTEGA). The interlayer ionic interactions afforded by the ionic liquid were hypothesized to improve adhesion between layers and allow for the fabrication of more isotropic parts. In addition, 3D printed ionic liquid parts could have electrochemical applications in filtration and soft actuators. To assess the effect of ionic liquid content on interlayer adhesion, mechanical testing was performed on parts printed with 5, 10, 25, and 40 mol% TOPTf₂N across three layer orientations. An actuator was printed and evaluated to determine performance for electrochemical applications. PTEGA is a biocompatible, biodegradable photopolymer that is being investigated for use as a novel material for tissue engineering applications. PTEGA was found to have an achievable print resolution of 30 μm and a porous scaffold with features on the order of 400 μm was printed with high dimensional accuracy and repeatability. These scaffolds were also submerged in solutions of minimum essential media and hydrochloric acid (pH = 4.0) for time periods ranging from 4 hours to 5 days in order to evaluate scaffold degradation. After 5 days in solution, scaffolds in both conditions had lost approximately 10% of their mass while retaining the majority of their structural integrity, which indicates a moderate rate of degradation that would allow cells to attach to and grow on the scaffold before complete dissolution. Dynamic mechanical analysis showed a glass transition temperature of 3.6°C, indicating that scaffolds would be soft at biologically-relevant temperatures (37°C) making them suitable for soft tissue replacement.

Synthesis of Phthalonitrile-Containing Siloxane Polymers for Semiconductor Power Modules

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Originally developed by the Naval Research Lab, phthalonitrile materials are promising candidates for high-temperature polymer applications. These materials possess good thermal and oxidative stability, excellent processability, and are of interest for various applications operating above 200 °C. The use of high-temperature polymer composites instead of metals may lighten the weight of the cooler sections of turbine engines. Phthalonitrile materials are also of interest for next generation wide-band gap semiconductor power modules, which require high-temperature polymers as encapsulation compounds. Recent research has focused on incorporating thermally stable, flexible linkages

into the backbone of the polymer. This lowers the softening point of the monomer and improves solubility without sacrificing the properties of the cured material. Recently, there has been interest in incorporating silicon-based linkages. Siloxane polymers are both thermally stable and flexible. This study investigates synthesis routes for a 1,3-Bis(p-hydroxyphenyl) disiloxane-linked phthalonitrile polymer via condensation of (benzyloxy)benzene silanol prepared by the reaction of (4-benzyloxy)benzene magnesium bromide with dichlorodiphenylsilane. Polycondensation of the of the disiloxane will then be carried out by the addition of dimethylformamide (DMF) under basic conditions with potassium carbonate. Initial results show limited reactivity of the Grignard reagent with the dichlorodiphenylsilane, and future synthesis techniques will employ halogen-lithium exchange using butyllithium to create (benzyloxy)benzene silanol.

Ion-containing Polycaprolactone-based Copolymers for 3D Printing Biodegradable Devices for Agriculture

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The research field of 3D-printing to customize many aspects of our world has increased in recent years and necessitates the generation of new materials for new applications. Besides mechanical applications of 3D-printed objects made of common materials, it is also possible to print objects made of biodegradable polymers, which can be used for drug-delivery or tissue scaffolds. The topic of this research is the generation and analysis of an ion-containing, polycaprolactone-based copolymer, which is to print 3D tissue scaffolds. Polycaprolactone (PCL) is the polyester of ϵ -caprolactone, which is highly biodegradable and biocompatible. This application is of special interest to rebuild destroyed bones, joints, or other parts of the body of humans or animals or for controlled release fertilizer. While PCL has successfully been printed and integrated into the human body, the need for enhanced interlayer adhesion to improve mechanical properties, as well as printability of lower molecular weight PCL to facilitate biodegradability, is great. PCL is copolymerized with a charged monomer to enhance the mentioned properties. Before the copolymers are printed and integrated into their host system, their mechanical and physical properties need characterization, using Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analyzation (DMA) and Rheological Analysis, which all will be done in my research. In addition, the synthesized and characterized copolymers will be tried to get 3D printed via extrusion.

Fabrication and Understanding of a Polymer Electrolyte for Battery Applications

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Two problems currently facing the battery industry are risk of fire and limited storage capacity. Commercial rechargeable batteries contain liquid electrolytes, but polymer electrolytes may decrease safety risks and be compatible with higher density electrodes. The Madsen group created a new polymer gel electrolyte material that has high ion conductivity while also maintaining thermal stability and mechanical integrity. We previously fabricated ion gels from a sulfonated aramid polyanion, poly(2,2'-disulfonyl-4,4'-benzidine

terephthalamide) (PBDT) and an ionic liquid (IL) containing the cation 1-ethyl-3-methyl imidazolium (C2mim)⁺ and the anion triflate. Current work examines gels made using an IL with a different anion, BF₄⁻. These gels form through ion exchange mechanism between the PBDT solution and the IL. We varied the PBDT concentration from 1 wt% to 4 wt% PBDT in the seed solution and found that the isotropic gels can be reliably and consistently formed, while PBDT solutions below 1 wt% form gels that are brittle and unusable. By measuring gel formation over time, we determined that gels made with higher PBDT concentrations and with larger volumes of IL require a longer time to form. We used NMR measurements to determine mole ratios of water to IL and diffusion coefficients for both the gels and their resultant supernatants. The relative amount of water to IL in both the gel and supernatant decreases with increasing PBDT content and with increasing volume ratios of IL used. The diffusion coefficients also decrease with increasing PBDT content and with increasing volume ratios of IL. These results lead to a better understanding of the gel formation and its tunable properties, including modulus and ion mobility, in order to create better polymer electrolytes for battery applications.