NDnano
Center for Nano Science and Technology

NDnano Summer Undergraduate Research
2018 Project Summary

1. Student name & home university:
Jacob Thilman
University of Notre Dame

2. ND faculty name & department:
Jennifer Schaefer
Chemical and Biomolecular Engineering

3. Summer project title:
Polymer Electrolytes for Advanced Rechargeable Batteries

4. Briefly describe new skills you acquired during your summer research:
In order to make polymer electrolyte films, I learned the use of various synthetic and purification methods such as column purification, thin layer chromatography, and NMR spectroscopy. I then learned how to make the films via UV photo-polymerization as well as the ion-exchange procedure in order to develop the films such that they could be used in a lithium or magnesium battery. From there I learned the methods used to test these films. I specifically took conductivity measurements of the films using a dielectric spectrometer.

5. Briefly share a practical application/end use of your research:
The demand for low cost, environmentally sustainable batteries has never been greater. As the world continues to transition to more energy generation via renewable resources, there will be a need to store the energy so it can be distributed at a later time to meet peak energy demand. Magnesium-sulfur batteries are of great interest due to the favorable properties of these batteries. They have high capacity and can theoretically provide one of the highest energy densities across all battery chemistries. Further, both magnesium and sulfur are relatively abundant which makes their use practical for large scale battery production. The polysulfide shuttle effect, a natural phenomenon by which magnesium sulfur batteries degrade, needs to be addressed. One proposed way to minimize the polysulfide shuttle effect is to introduce polymer electrolyte films to increase the lifespan of the battery such that it is commercially viable.

6. 50- to 75-word abstract of your project:
Current magnesium-sulfur batteries are not currently commercially viable due to their short lifespan from the polysulfide shuttle effect. One approach to preventing the polysulfide shuttle is coating the cathode with a functional polymer. In this project, a variety of monomers and film compositions are characterized to discover films which are conductive, permeable to the electrolyte, but reject polysulfides.

7. References for papers, posters, or presentations of your research:
N/A

One-page project summary that describes problem, project goal and your activities / results:

As energy diversification efforts continue globally, the use of renewable resources for energy generation is slowly being adopted. Renewable resources are environmentally responsible sources of energy but the collection of this energy presents its own sets of problems. Energy derived from wind, solar, geothermal, and hydropower sources is collected intermittently. That is, on cloudy days or days without strong wind it may be impossible to collect any energy; similarly, there may be time periods where it is extremely windy or sunny outside and the energy collected exceeds the amount of energy being drawn by consumers at the time. This phenomenon presents a need for a way to store and redistribute the energy according to demand.

For high energy storage, perhaps one of the best battery chemistries is a magnesium anode in combination with a sulfur cathode. With a high energy density of 1722 Wh/kg and a voltage of 1.7 V, magnesium-sulfur batteries have the electrochemical characteristics of a good solution to this energy storage problem. For similar reasons, lithium-sulfur batteries are also being researched. The drawback to using sulfur as a cathode is the polysulfide shuttle effect. This phenomenon occurs when polysulfides shuttle between the anode and cathode in a cycle of being reduced and oxidized without charging the battery. To create a commercially viable sulfur battery, the polysulfide shuttle effect will need to be addressed. In this project, we characterize polymer electrolyte films to work towards determining a suitable film composition for addressing the shuttle effect.

Over the course of this project, I attempted to characterize 5 different polymers. The first film I tested was Poly(ethylene glycol) diacrylate (abbreviated PEGDA). I characterized two different molecular weights of the PEGDA: 700 g/mol and 1000 g/mol. These polymer electrolyte films also contain a tethered anion, the ones to be tested here are Styrene-4-sulfonic acid salt (abbreviated SS) and bis(trifluoromethylsulfonylimide) (abbreviated TFSI). These anions can be ion exchanged such that their respective cations are lithium or magnesium. By varying the amount of SS and TFSI in the film, you can change the charge density of the film and thus change its electrochemical properties. An entire PEGDA film set had been previously synthesized by another member of the research group. This film set contained both molecular weights of the PEGDA, each with either SS or TFSI as the tethered anion, and each anion set had three unique charge densities. The first test I conducted on this film set is the swelling test. We were able to test each film's affinity for absorbing the 1M lithium TFSI in a 1:1 ratio of dimethoxyethane and dioxolane as well as the salt that it retained after the solvent is evaporated. This 1M lithium TFSI in 1:1 ratio of dimethoxyethane and dioxolane is being used here to model an actual battery system as it is a relevant lithium battery electrolyte. Then we conducted a swelled conductivity test wherein the films swelled in the same 1M lithium TFSI and placed in a dielectric spectrometer to test their conductivity as a higher conductivity is desired for a film to be used in a functioning battery. To determine their polysulfide rejection ability, we then swelled the PEGDA in polysulfide solutions that contained varying chain lengths of polysulfides and lithium TFSI salt.

The second polymer I attempted to characterize is Poly(tetrahydrofuran) diacrylate (abbreviated PTHFDA). Unfortunately, this compound is not available commercially; poly(tetrahydrofuran) (abbreviated PTHF) is sold and must be acrylated in the lab before it can be polymerized. Using both the 650 g/mol and 2000 g/mol variant of the PTHF, we were able to successfully perform the acrylation reaction. With the 2000 g/mol PTHFDA, we were able to make a single film with no tethered anion. Attempts to make films with the tethered anion were unsuccessful. Upon analyzing the NMR of our PTHFDA, it was clear that the product was not acceptably pure. In an effort to increase the purity of the product, we attempted both liquid-liquid extraction and column purification with minimal success. The liquid-liquid extraction method did not purify the product successfully. The column purification purified our product well but the yield was extremely low and getting all of the product off of the column so that the average molecular weight was consistent with the starting material became an issue. Given the fact that we were only able to make a single film, I believe it to be possible to synthesize a full film set given a

sufficient purity, but we were unable to reach that point and so no characterization could be done on the PTHFDA during my project.

The next polymer we attempted to characterize was perfluoropolyether (abbreviated PFPE). This monomer is similar to the PEGDA but it has been fluorinated, replacing the hydrogens along the repeat alkyl unit with fluorine atoms. Using a similar procedure to that of the PEGDA film synthesis, I was able to make a PFPE film set that spanned the same charge density range as the PEGDA film. In this case, the only tethered anion used was SS but I made both magnesium and lithium versions of each film to test the difference between cations. I then conducted a dry conductivity test with these polymers to test their conductivity without the electrolyte solution. From -20ºC to 90ºC PFPE is non-conductive. At elevated temperatures, from 90ºC to 180ºC, all of the films other than the highest charge density film begin to conduct. One of the low charge density film has a conductivity an order of magnitude higher than the other three films that were conductive. There is a charge density at which the conductivity peaks. I then tested the PFPE with the same polysulfide test as the PEGDA underwent and the results seem to indicate that the PEGDA and PFPE are similar in their polysulfide uptake but the PFPE films do not retain as much of the polysulfide color. Given the brittleness and non-conductivity of the PFPE at reasonable temperatures, this material seems unlikely to be practical in actual usage as a bulk separator. It may have promise as a thin film coating but I was unable to test such a system in this project.

To test the effect of the fluorination in the PFPEDA while still maintaining the desirable conductivity properties of the PEGDA 1000, I combined the two materials to make our fourth polymer. I made a set of PEGDA:PFPE combination films with varying mass ratios while still maintaining a constant charge density across all films. The PEGDA seems to plasticize the PFPE which makes all of the combination PEGDA:PFPE films far easier to work with and much less brittle. The entire composition space from 90% PEGDA to 10% PEGDA underwent a polysulfide test and the absorption across all mass fractions is fairly constant which indicates that the extent fluorination has little effect on the polysulfide rejection when PFPE is combined with PEGDA. Further tests must be conducted on this film set to determine its practicality.

The final polymer I attempted to characterize was Poly(propylene glycol) dimethacrylate (abbreviated PPGDA). In attempting to synthesize a full film set of PPGDA, we were only able to successfully polymerize the middle to lower charge density compositions. With this limited film set we first ran a polysulfide test. We discovered that the PPGDA films uptake significantly more polysulfide solution than the other films we had previously conducted a polysulfide test on. To address the issue of whether these films swell greatly due to the electrolyte solution or the polysulfides themselves, we ran a swell test like the one previously conducted on the PEGDA film set. In comparing the PEGDA and PPGDA swelling data, the PPGDA does not appear to swell significantly more in the pure electrolyte without polysulfides than the PEGDA did. This leads us to the conclusion that PPGDA inherently uptakes polysulfides more than other film compositions, making it unsuitable for minimizing the polysulfide shuttle effect.

This project does not settle the issue of precisely what film composition is best to minimize the polysulfide shuttle effect, but at the very least I have added insight into the properties of many monomers and their composition spaces so that future work can continue to work towards an ideal polymer electrolyte film for sulfur batteries.