NDnano Summer Undergraduate Research
2017 Project Summary

1. Student name & university: Daniel Hardiman, University of Notre Dame

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

3. Project title: Dendrite growth in rechargeable lithium metal batteries

4. Briefly describe new skills you acquired during your summer research:
I learned how to make crosslinked solid polymer electrolyte films via UV photo-polymerization, and I learned how to use these films to make symmetrical lithium metal coin cells. I also learned how to use various instruments to test the properties of interest of these films. For example, I used the dielectric spectrometer to test the conductivities of the films that I made at different temperatures, I used the battery tester to test how long it took for coin cells made with each of the films to short circuit from dendrite formation over a range of current densities, and I used the potentiostat to find the lithium ion transference number of each of the films at different voltage pulses.

5. Briefly share a practical application/end use of your research:
The goal of my research is to develop a better understanding of the parameters that affect lithium dendrite growth and the effects of certain properties of the solid polymer electrolyte used in lithium metal coin cells on the timescales of dendrite growth and short-circuiting. Once this behavior is better understood and dendrite growth can be efficiently suppressed, it will be possible for batteries with lithium metal anodes to be designed and commercialized. Such batteries will be lighter and capable of storing much more energy than the most advanced lithium-ion batteries that currently exist, which will make those batteries particularly useful for large-scale applications such as electric vehicles and large-scale stationary energy storage.

6. 50- to 75-word abstract of your project:

Widespread commercialization of lithium metal battery technology has been prevented for decades by lithium dendrite growth, which is caused by uneven electrodeposition of lithium metal and can lead to short-circuiting. The goal of this project was to determine how various characteristics of the solid polymer electrolyte used in lithium metal batteries affect the timescales of dendrite growth and short-circuiting. The results so far indicate that the timescales of dendrite nucleation are affected by the chemical composition of the polymer electrolyte and not just its mechanical properties as previously thought.

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

1. Croce, F.; Settimi, L.; Scrosati, B. *Electrochemistry Communications* **2006**, *8*(2), 364–368.
2. Khurana, R.; Schaefer, J. L.; Archer, L. A.; Coates, G. W. *Journal of the American Chemical Society* **2014**, *136*(20), 7395–7402.
3. Brissot, C.; Rosso, M.; Chazalviel, J.-N.; Lascaud, S. *Journal of Power Sources* **1999**, *81-82*, 925–929.

4. Chen, L.; Connell, J. G.; Nie, A.; Huang, Z.; Zavadil, K. R.; Klavetter, K. C.; Yuan, Y.; Sharifi-Asl, S.; Shahbazian-Yassar, R.; Libera, J. A.; Mane, A. U.; Elam, J. W. *J. Mater. Chem. A* **2017**, *5*(24), 12297–12309.

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

The widespread commercialization of lithium metal batteries has been prevented for the past few decades up to this point due to lithium dendrite growth. Lithium metal has extremely high theoretical capacity (3860 mA h g^{-1}), low density (0.59 g cm^{-3}), and the lowest electrochemical potential relative to the standard hydrogen electrode (-3.040 V), which makes it an especially favorable anode material for lithium-ion batteries. However, lithium metal tends to electrodeposit unevenly on the anodes in such batteries, leading to the formation of dendrites. Dendrites can take on different morphologies, but the simplest shape in which a dendrite can form is that of a needle. This needle initially nucleates at the lithium metal anode and grows across the cell until it makes contact with the positive electrode, at which point the cell short-circuits since the electrodes are connected together (when this happens, the resistance of the cell drops to zero). This results in the catastrophic failure of the cell, which can involve fire/explosion, so it is necessary that this behavior be effectively inhibited before lithium metal batteries can be used for practical applications. The parameters affecting lithium dendrite growth are still not well understood, so the goal of this project was to examine the effects of changing certain characteristics of the solid polymer electrolyte films used in the lithium metal batteries on the timescales associated with the short-circuiting of such batteries at different current densities.

The first material that I used for testing was poly(ethylene oxide) (Mw = 100,000 g/mol) with lithium bis(trifluoromethylsulfonylimide) (abbreviated as LiTFSI, used in all films). This material is not cross-linked and was only meant to be used as a baseline to which to compare the results of the cross-linked films that I made and tested later. However, the fact that it wasn't cross-linked meant that it became liquid-like upon heating and deformed within the batteries that I made with that material every time that I tried to run tests with it (all short-circuit testing was carried out at 90ºC since all of the materials tested had high enough conductivities at that temperature for the batteries to be able to operate). This deformation resulted in the two lithium metal electrodes becoming fused together within the cell and short-circuiting from heating alone. It took me a couple of weeks to realize that this was happening, and in that time the test results that I was getting from using these cells were very confusing and ended up being unusable since the cells were all short-circuiting immediately. My solution to this problem was to use a Teflon O-ring spacer within the battery to force the material to hold its shape (which it did), but even then, the results of the short-circuit tests were fairly inconsistent.

The next material that I used was poly(ethylene glycol) dimethacrylate (Mw = 1000 g/mol) (PEGDMA 1000), which I used to make cross-linked films. To make these films, I dissolved the PEGDMA 1000 with a certain amount of tetra(ethylene glycol) dimethyl ether (TEGDME), a plasticizer, with a total mass of 1g in anhydrous methanol with a small amount of photo-initiator. Once dissolved completely, I placed the solution between two glass plates separated by four glass microscope cover slips and exposed it to UV light in a UV oven to initiate photo-polymerization. Once the film polymerized, I transferred it to a glass petri dish and allowed it to dry in the fume hood overnight. The next day I moved the film to the glovebox and heated it in a vacuum oven at 80ºC for 16 hours so that the next day after that it would be ready to use. I made a total of five films with the PEGDMA 1000, ranging from 80% PEGDMA 1000/20% TEGDME to 30% PEGDMA 1000/70% TEGDME, and tested each of them with the dielectric spectrometer to find their DC conductivities at temperatures ranging from 0ºC-100ºC. I didn't make any batteries to use for short-circuit testing with any of these films because I didn't have enough material for multiple cells, and I was only using the PEGDMA 1000 in the first place to become familiar with this technique for making films.

The primary material that I studied and used to make cross-linked films was poly(ethylene glycol) diacrylate (Mw = 5000 g/mol) (PEGDA 5K). I used the same procedure described above for making these films with the same plasticizer, TEGDME. However, while I found that the PEGDMA 1000 film with the highest conductivity ended up being that made with 60% TEGDME, the PEGDA 5K film with the highest

conductivity was that made with 20% TEGDME; for both materials, the conductivities dropped off at higher proportions of TEGDME. It makes sense that the optimal proportion of TEGDME for PEGDA 5K would be lower than that for PEGDMA 1000 because of the much longer average chain length of the PEGDA 5K monomers. I also conducted short-circuit tests with each of the four PEGDA 5K films that I made (100% PEGDA 5K, 80% PEGDA 5K/20% TEGDME, 70% PEGDA 5K/30% TEGDME, 60% PEGDA 5K/40% TEGDME) at a range of current densities. The trend that the short-circuit timescales followed with respect to proportion of TEGDME was similar to the trend observed with the DC conductivities: the short-circuit times increased from the 100% PEGDA 5K film to the 80% PEGDA 5K/20% TEGDME film and then decreased slightly for the other two films. This result indicates that dendrite nucleation timescales are affected by the chemical composition of the solid polymer electrolyte and not just its mechanical properties since the modulus of the films decrease with increasing proportion of plasticizer, though the decrease in modulus does seem to eventually outweigh the benefits from changing the chemical composition, as evidenced by the observed drop-offs in DC conductivity and short-circuit time.

These results certainly don't settle the question of what parameters affect lithium dendrite nucleation and growth, but they are encouraging and they do provide a good starting point for further work that I will do on this project during the fall semester. One characteristic of the solid polymer electrolyte films that I will investigate next is changing the ratio of ethylene oxide units (from the PEGDA monomers and plasticizer) to lithium ions (from the salt). Up to this point, I have used the same EO:Li ratio for all of the films that I've made (20:1) since that is supposedly the ratio at which DC conductivity is maximized. I plan to make 100% PEGDA 5K films with EO:Li ratios ranging from 12:1 to 40:1 to use for short-circuit testing in symmetrical lithium metal batteries. I expect that the DC conductivities of those films will decrease relative to the 20:1 films that I've made and tested already, but I think it will be worthwhile to see how the short-circuit timescales change by changing the EO:Li ratio. If my previous tests are any indication, the short-circuit times should decrease along with the DC conductivities, but it will be interesting to see the magnitude of those change whether they increase or decrease.