UNIVERSITY OF NOTRE DAME
NDnano
CENTER FOR NANO SCIENCE AND TECHNOLOGY

ND*nano* Undergraduate Research Fellowship (NURF)
2015 Project Summary

1. Student name: Ashley Fuller

2. Faculty mentor name: Susan Fullerton

3. Project title: Thermal properties of polyvinyl alcohol (PVA):$LiClO_4$ electrolytes for room temperature doping of 2D crystal transistors

4. Briefly describe any new skills you acquired during your summer research:

During my summer research, I learned the theory behind differential scanning calorimetry (DSC), how to take measurements on a DSC instrument, and how to analyze DSC data. In analyzing the DSC data, I improved my MATLAB programming skills for creating high-resolution plots. I also learned how to use a glove box to prepare DSC samples, including bringing objects into and out of the glove box.

5. Briefly share a practical application/end use of your research:

The thermal properties of PVA:$LiClO_4$ control the temperature and rate at which 2D crystal transistors can be doped with this material. The data measured this summer will be used to inform the choice of temperature and lithium salt concentration used for gating 2D crystal transistors in the LEAST center. One particularly important result of my summer research was showing that, once the electrolyte is heated above its melting point, it does not recrystallize for at least 10 days.

Project Summary:

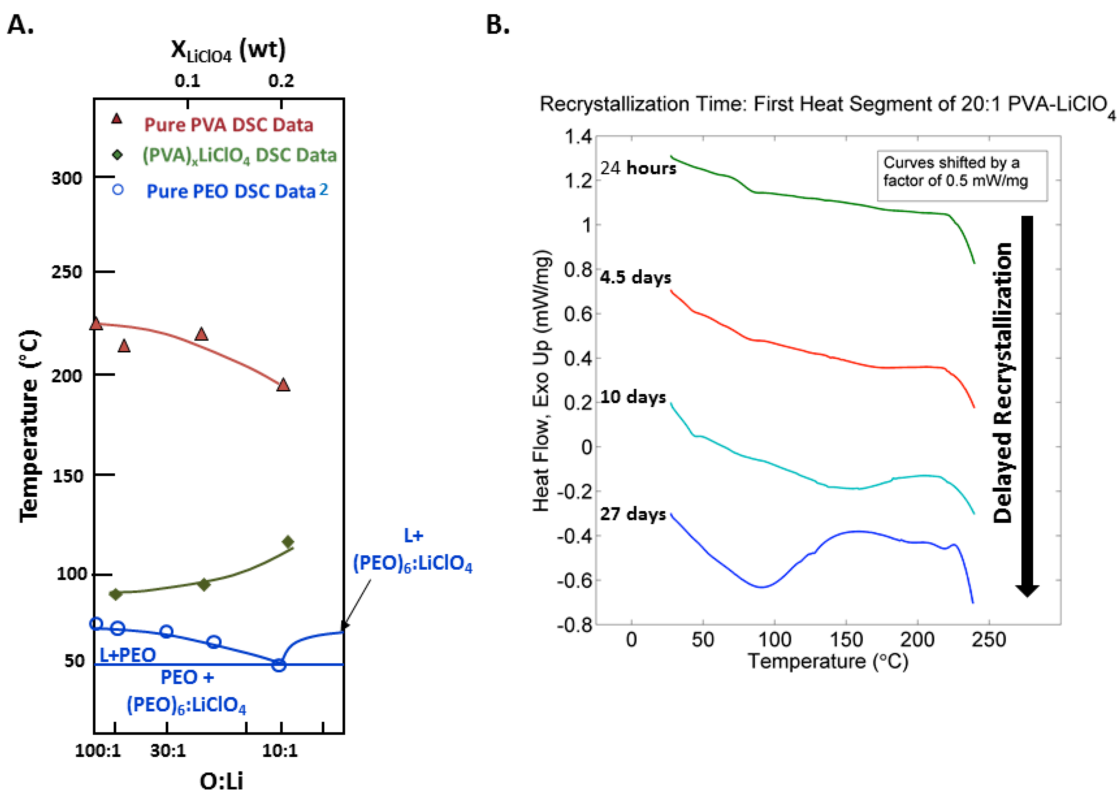
Solid polymer electrolytes have been used to electrostatically gate transistors based on two-dimensional crystals for next generation electronics. However, the temperature of the electrolyte must be lowered below the glass transition temperature (T_g) of the electrolyte. This becomes a problem when the T_g of the electrolyte is very low. An example of such an electrolyte is polyethylene oxide $(PEO)_{20}$:$LiClO_4$, which has a T_g of -30°C. To lock the ions into place in this polymer electrolyte, the temperature must be lowered to below -30°C. This is not practical, especially for use in electronic applications. The polymer polyvinyl alcohol (PVA) has a T_g of 85°C[1]. PVA-based polymer electrolytes would allow this “locking” process to be carried out at room temperature.

Three thermal properties of PVA and PVA:$LiClO_4$ — glass transition (T_g), melting (T_m), and crystallization (T_c) temperatures—were of interest. These three properties were measured using differential scanning calorimetry (DSC). Five different samples were measured using DSC, one pure PVA sample and four PVA:$LiClO_4$ electrolyte samples at molar ratios of 8:1, 10:1, 20:1, and 100:1. The T_g of the samples remained within 4°C of the T_g of pure PVA (~80°C), suggesting that polymer mobility is not strongly affected by $LiClO_4$ concentration. Because the T_g of the electrolytes remained well above room temperature, the "locking" procedure could be carried out at room temperature regardless of salt concentration. However, unlike T_g, the addition of $LiClO_4$ to PVA had a strong effect on the T_m and the crystal fraction. Specifically, the T_m of pure PVA decreased with increasing $LiClO_4$ concentration and a new crystal feature arose, which is attributed to a $(PVA)_x$: $LiClO_4$ crystalline complex. As shown in the phase diagram in Figure A, the T_m of PVA:$LiClO_4$ exhibits a similar dependence on $LiClO_4$ concentration as polyethylene oxide (PEO):$LiClO_4$ (commonly used to electrostatically gate transistors); however, the transitions occur at temperatures more than three times greater than (PEO):$LiClO_4$.

The addition of $LiClO_4$ also slows the rate of recrystallization as seen in Figure B. For a concentration of 20:1, the sample recrystallizes on a timescale of weeks. This result has important consequences for device performance because the time constant associated with "locking" the ions into position in a transistor is likely correlated to the crystal fraction.

References:

1. Poly(vinyl alcohol). *Polymer Data Handbook.* Oxford University Press: New York, 1999. pp 890-909.



[2]Fullerton-Shirey and Maranas J. Phys. Chem. C 2010, 114, 9196

Publications (papers/posters/presentations):

NDnano NURF Research Presentation
University of Notre Dame
July 22, 2015
Presentation Title: "Thermal Properties of Polyvinyl Alcohol (PVA):$LiClO_4$ Electrolytes for Room Temperature Doping of 2D Crystal Transistors"

Undergraduate Research Symposium Poster Session
University of Notre Dame
July 31, 2015
Poster Title: "Thermal Properties of Polyvinyl Alcohol (PVA):$LiClO_4$ Electrolytes for Room Temperature Doping of 2D Crystal Transistors"