NDnano 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):LiClO₄ 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:LiClO₄ 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\textsuperscript{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:

Publications (papers/posters/presentations):

NDnano NURF Research Presentation
University of Notre Dame
July 22, 2015
Presentation Title: “Thermal Properties of Polyvinyl Alcohol (PVA):LiClO₄ 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):LiClO₄ Electrolytes for Room Temperature Doping of 2D Crystal Transistors”