**Overview**

Throughout my time at University of Michigan as a graduate student, I worked in the Laine lab focusing primarily on **novel solid-state electrolytes (SSEs)** for lithium-ion batteries (LIBs) derived from **polymer syntheses** along with other projects, including **oxysilylation**, reactions between metal chlorides with hexamethyldisilazane (**M-HMDS**) towards metal nitride precursors, and zirconia toughened alumina (**ZTA**) ceramics.

**Motivation**

Replacing traditional combustion-based energy sources, i.e., fossil fuels, with clean and reliable energy supply is one of the most important research goals for the 21st century. Electrochemical energy storage/conversion systems, including LIBs, electrochemical capacitors (ECs), and fuel cells (FCs), have thus drawn great interest. LIBs are becoming the most important electrochemical storage system owing to their high energy densities (~250 Wh/kg), providing an escape from consumption of fossil fuels. However, current LIBs with flammable organic liquid electrolytes suffer from poor electrochemical and thermal stabilities that can lead to severe thermal runaway accidents. All-solid-state batteries (ASSBs) are regarded as a fundamental solution to address the safety issue by applying non-flammable SSEs. Therefore, the research objectives are to develop novel polymeric SSE materials through polymer synthesis methods with low-cost, scalable and environmentally friendly features, establish new chemistries for synthesizing polymer precursors towards SSEs, optimize electrochemical performance and fabricate ASSBs.

**Polymer Syntheses**

1. Oxysilylation

I started with exploring nanocomposites by oxysilylation of [HSiMe<sub>2</sub>O(SiO)<sub>1.5</sub>]<sub>8</sub> (OHS) crosslinked via ring-opening of epoxy groups. The linkages containing ether oxygens may facilitate Li<sup>+</sup> transport, while the 3-D ordered organic-inorganic hybrid structure of silsesquioxane cages (SQs, RSiO<sub>1.5</sub>) offers mechanical stability. Oxysilylations of different diepoxides with TMDS [O(SiMe<sub>2</sub>H)<sub>2</sub>], OHS, D<sub>4</sub>H and D<sub>5</sub>H [(CH<sub>3</sub>SiHO)<sub>4,5</sub>] catalyzed by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at ambient were studied. Although flexible transparent films were successfully cast, they failed to offer ionic conductivity with LiClO<sub>4</sub> impregnation due to the rigid structure. Nevertheless, a novel synthesis of self-reinforced epoxy resin nanocomposites was established.

2. Novel SSEs

LixPON and LixSiPON

I continued to investigate polymer precursor electrolytes based on lithium phosphorous oxynitride (LiPON) glasses. LiPON glasses form lithium dendrite impenetrable interfaces at electrodes offering the potential to replace liquid electrolytes. Unfortunately, to date such materials are introduced only via gas phase deposition. The design and synthesis of easily scaled, low-temperature, solution processable inorganic polymers containing LiPON/LiSiPON elements were established. OPCl3 and (Cl2P=N)3 provide starting points for elaboration using NaNH2 or (Me3Si)2NH producing OP(NH2)3-x(NH)x,OP(NH2)3-x(NHSiMe3)x and (P=N)3(NHSiMe3)6-x(NH)x. It is followed by lithiation with selected amounts of LiNH2 providing varying degrees of lithiation. We were able to produce LixPON/LixSiPON oligomers/polymers with superior electrochemical performance compared to traditional LiPON glasses, and nearly all-solid-state Li-S batteries were assembled using polymer precursors impregnated Celgard separator or solid solutions with polyethylene oxide (PEO), which provided an optimized capacity of ~1000 mAh/gsulfur (at 0.25-1 C) retaining coulombic efficiency of ~100 % over 100 cycles.

LixSiON

Another set of LixSiON (Li/Si = x = 2, 4, 6) oligomer/polymer precursors derived from agricultural waste rice hull ash (RHA) were also studied, providing a novel, low-cost, clean and green route towards ASSBs. Silica, ~90 wt. % in RHA, can be catalytically dissolved (20-40 wt.%) in hexylene glycol and distilled directly as spirosiloxane [(C6H14O2)2Si, SP] at 200 °C. SP can be lithiated using LiNH2 to produce LixSiON oligomers/polymers, and the Li content is easily controlled by LiNH2 amounts correlating with Li+ conductivity. Li6SiON exhibits the highest ambient conductivity of ~10-5 S/cm. Nearly ASSBs were assembled with Li6SiON impregnated Celgard separator, which delivered a reversible capacity of ~725 mAh/g at 0.5 C over 50 cycles.

Next steps

Based on the work on polymer precursor electrolytes, next steps going forward include but not limited to the following.

* LixSiON precursor solid solutions with PEO.
* LixSiO system derived from the LixSiON precursors.
* Use polymer precursor electrolytes as coatings on inorganic SSEs to serve as buffer layers while improving their mechanical properties and interfacial contact with electrodes.
* Sodium-based systems such as NaxPON, NaxSiPON and NaxSiON for sodium ion batteries.

3. M-HMDS

Inspired by the work on LixSiPON precursors that started with the reaction of hexamethyldisilazane [(Me3Si)2NH, HMDS] with OPCl3, where the -SiMe3 group reacts with -Cl resulting in byproduct Me3SiCl while producing OP(NH2)3-x(NHSiMe3)x as the desired product, I continued to investigate the possibility of reactions between metal chlorides with HMDS, which may be potential precursors to metal nitrides. As a result, a simple, novel, low temperature (ambient to 60 °C/N2 in solvents), scalable and general route to metal nitride precursors was established.

**Ceramic Processing**

**ZTA Ceramics**

As a separate project, I also worked on zirconia toughen alumina (ZTA), which are one of the most important engineering ceramics with high melting points, excellent mechanical strength and chemical stability, and are commonly used as wear resistant and high-temperature components, as prosthetic implants and electric circuit substrates. Methods of processing fine-grained, dense, thin, free-standing (ZrO2)x(Al2O3)1-x films (x = 0-50 mol. %, ~40 μm thick) by sintering flame made nanopowders (NPs) to optimize the *t*-ZrO2 content, sinterability and microstructures under select conditions (1120-1500 °C/5 h in O2 or 95 %N2/5 %H2) were explored. Excellent fracture toughness (24 MPa m1/2) and small AGSs of 0.7 μm were found for ~200 μm thick ZTA films. Furthermore, homogeneous ZTA thin films (<5 μm thick) can be sintered on Si3N4 substrates (thickness ≈ 300 μm) to provide physical protection against oxidation under extreme conditions (1500 °C/1 h/O2), offering additional practical utility for high-temperature ceramics and power electronic substrates.