**Polymer Syntheses**

The primary subject of my research focuses on polymer syntheses towards novel solid-state electrolytes (SSEs) for lithium-ion batteries (LIBs). The story starts with polymer electrolytes.

There are two major groups of polymer electrolytes (PEs), solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs). A SPE typically consists of a polymer matrix impregnated with lithium salts, and a GPE typically consists of SPE (polymer-salt system) with liquid plasticizer or solvent. Generally, SPEs provide features including safety, easy fabrication, low-cost, high energy density, good electrochemical stability, and excellent compatibility with lithium salts. However, they also exhibit poor ambient ionic conductivities of 10-8-10-4 S/cm. In contrast, the conductivities of GPEs can reach 10-3 S/cm, but poor mechanical strength and poor interfacial properties often arise due to the incorporation of a liquid phase.

Ion transport in PEs is typically achieved by breaking/forming electrostatic interaction between alkali-metal cations (M+) with ether oxygen (EO) atoms along the polymer backbone, through either intrachain or interchain hoping. Polyethers [e.g., poly(ethylene oxide) (PEO)] with strong electron-donor character are known for their ability to complex M+. Ionic conduction is generally attributed to the amorphous polymer phase and the presence of free volume above the glass transition temperature (Tg). M+ transport is facilitated by segmental motion of polymer chains along with M+ intra/inter-segmental hopping.

In some cases, ionic conductivity is also reported in the crystalline domains of the polymer electrolyte, where polymer chains fold into cylindrical tunnels that permit M+ diffusion via ion hopping, while the anions are separated from the cations located outside these tunnels. But ion transport is typically constrained in crystalline domains, and it is widely accepted that reducing crystallinity is key to increasing ionic conductivity in polymer electrolytes.

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**Polymer Matrices**

PEO is the most studied polymer matrix for PEs owing to its flexible ethylene oxide segments and ether oxygen atoms with lone electron pairs that readily interact with Li+ ions, facilitating Li+ transport. It also has advantages such as low toxicity, easy fabrication and low cost. In fundamental PEO based PEs, a lithium salt is dissolved in the PEO matrix by coordination between the Li+ ions and the ether oxygen in the polymer chains. However, PEO is a semi-crystalline polymer with Tg ≈ -65 °C and at room temperature (RT), the amorphous phase with limited interchain mobility aids ion transportation. Consequently, PEO based electrolytes typically show poor ionic conductivities of 10-8-10-4 S/cm at ambient, and only show good conductivity (up to 10-3 S/cm) above the melting point (~65 °C), in which case the PEO electrolyte becomes a gel electrolyte rather than a SSE. The PEO gel can gradually diffuse across the porous solid electrolyte interphase (SEI) layer and can lead to a continuous loss of lithium from the cathode. Therefore, suppression of PEO crystallinity is essential for PEO-based electrolytes. In addition, PEO electrolytes generally show low ionic transference numbers (*t*Li+) of 0.2-0.5, which can result in concentration overpotential, promoting uneven Li plating and dendrite formation.

There are various strategies to solve these issues, such as addition of plasticizer and/or nanofiller, polymer blends, and designing copolymers with PEO blocks/oligomers including linear, grafted, and crosslinked structures. All of which aim to strengthen the matrix structure while decreasing crystallinity.

Oxysilylation

In my approach, organic/inorganic hybrid nanocomposite silsesquioxane cage [HMe2SiOSiO1.5]8 (OHS) crosslinked by EO containing oligomers were investigated. The initial goal was to develop materials with 3-D networked structures through oxysilylation that offer excellent structural and chemical stabilities, good mechanical properties and ionic conductivities. Although the resulting products failed to facilitate ionic transport, by investigating various reactions between different diepoxides and Si-H containing compounds under different reaction conditions, a novel and simple approach to self-reinforced epoxy resin nanocomposites was established.



**Lithium Salts**

Another aspect of PEs is lithium salts, and the most important requirement for lithium salts is good solubility in the polymer matrix. Generally, the bulkier the anion, the higher the ionic conductivity, as larger anions more easily dissociate in the polymer matrix leaving free Li+ ions to interact with polar groups along the polymer backbone, facilitating ionic transport. Therefore, Li salts with delocalized anion and low basicity are preferred. Commonly used lithium salts include LiClO4, LiPF6, LiAsF6, LiBF4, LiCF3SO3 (LiTf), LiN(SO2F)2 (LiFSI), LiN(CF3SO2)2 (LiTFSI), LiN(SO2C2F5)2 (LiBETI), etc.

It is known that the addition of a Li salt reduces PEO crystallinity and significantly reduces Tg resulting in enhanced mobility of EO segments and ionic conductivity. But a major drawback for polymer-salt systems is that as cations bind to the polymer matrix, anions can move faster which increases ionic conductivity, resulting in lower *t*Li+. The migration of anions to the anode induces serious concentration polarization, which can lead to a substantial decay in conductivity. Therefore, such PEs are also called bi-ionic conductors. To minimize polarization, a common method is to develop single-ion conducting PEs by anchoring anions to the polymer backbone.

Polymer Precursors – novel SSEs/polymeric lithium salts

Recent efforts have targeted the synthesis of polymeric lithium salts as single-ion conductors. As a major part of my research, LixPON, LixSiPON and LixSiON polymeric electrolytes based on lithium superionic conductor (LISICON) type inorganic solid electrolytes were synthesized. When impregnated in/on Celgard separators, these polymer/oligomer electrolytes show conductivities approaching 10-5 S/cm at RT and with *t*Li+ of 0.7-1. When mixed with PEO (60 wt.%), these polymer electrolytes act as polymeric Li salts forming SPEs with high ambient conductivities up to ~3 × 10-3 S/cm and *t*Li+ up to 0.8.

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**M-HMDS**

Inspired by the work on LixSiPON polymeric electrolytes, as a separate project, I studied reactions of metal chlorides with hexamethyldisilazane [HMDS, (Me3Si)2NH] in THF or ACN at low temperatures (RT to 60 °C/N2), which provides a simple, novel, scalable and general route to metal nitride precursors. Such reactions have received scant attention in the literature. The work focused primarily on the Al-HMDS precursor by reaction of AlCl3 with HMDS (mole ratio = 1:3), which produces AlN when heated to 1600 °C/4 h/N2. On heating to 800-1200 °C/4 h/N2, the precursor transforms to an amorphous, oxygen-sensitive powder with very high surface areas (>200 m2/g) indicating nanosized particles. The investigation was also extended via proof of principle studies to other metal chloride systems, including Zn-, Cu-, Fe- and Bi-HMDS. The formed precursors are volatile, offering the potential utility as gas-phase deposition precursors for their corresponding metal nitrides.