Organic/Inorganic Hybrid PEO-Based Polymers as Electrolyte: Synthesis and Characterization
Zhe Jia, Gregory L. Baker
Department of Chemistry
Michigan State University
East Lansing, MI 48824

Due to the leakage and sealing problems of liquid electrolytes used in batteries or cells, the development of solid-sate electrolytes is important. One of the approaches to solve this problem is to develop organic/inorganic hybrid nanocomposite materials, considered to have the combination of advantages of both organic and inorganic materials, these nanocomposite materials have core-shell architectures comprised of organic polymer shells and inorganic nanoscale cores. These combine the flexibility, and processability of organic polymers with the rigidity and thermal stability of the inorganic component.

We designed, synthesized and characterized several novel hybrid inorganic/organic electrolytes that consist of poly(ethylene oxide) (PEO) based polymer grafted onto silica nanoparticles. The hydroxyl groups attached to the surface of the silica particles provide a pathway to chemically bond the polymers, which can create a three-dimensional network that prevents the viscous flow of low molecular weight PEO, thus, providing the required mechanic property, while coordinating with lithium cation simultaneously to maximize the ionic conductivity.

As shown in Scheme 1, initiators were attached to 7-10 nm silica nanoparticles. Through Atom Transfer Radical Polymerization (ATRP), poly(ethylene glycol) methyl ether methacrylate (PEGMA) monomers were polymerized from the surface to generate PEO polymer brushes with controlled molar mass, architecture and functionality. A series of silica-polymer was made with different length of PEO side chains. The high polarity of ethylene glycol repeating unit in PEO chain caused an ion-dipole interaction between lithium cation and oxygen atom that facilitate cation dissociation in polymer network, resulted in a solvent-desolvation process. Electrolytes were later prepared from the functionalized particles and low-molecular weight (~500 g/mol) polyethylene glycol dimethyl ether (PEO-DME500) with the addition of Li as the iodide salt.

Figure 1. Conductivity of Hybrid Si-Polymer Electrolyte (For all electrolytes, oxygen to lithium ratio was fixed at 110:1.)

Upon the introduction of particles, the electrolyte became very viscous and gel-like. With the increase of PEO side chains, the viscosity of the electrolyte increased dramatically, to point that some, like Si-poly(PEGMA-1100), became solids. The room temperature conductivity of hybrid silica-polymer electrolytes are in the range of 6×10^-4 to 1.2×10^-2 S/cm. Si-poly(PEGMA-475) and Si-poly(PEGMA-1100), with much higher viscosity, represented better ionic conductivity. This is presumably due to the lithium cations coordinate to the long pairs of electrons in oxygen atom was via a 4-8 oxygen chelation.

Acknowledgement
We thank the National Science Foundation (NSF-0934568) for funding this research.

Scheme 1. The architecture used in this project (top) and the TFSI analogue polymer grafted nanoparticle (bottom).