Understanding the Importance of Interfaces in Composites of Solid Polymer and Glass Electrolytes through Modeling and Electrochemical and Mechanical Characterizations

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Solid state batteries will be safer than conventional Li ion technology, which utilizes flammable organic liquid electrolytes. Modeling has shown that solid electrolytes with sufficient mechanical properties can inhibit lithium anode roughening and dendrite formation. Dry polymer, glass, and ceramic electrolytes have been studied extensively as solid electrolytes, but they are too resistive for most applications. To overcome the poor conductivity and mechanical properties of polymer electrolytes, inert inorganic fillers are mixed into the polymer matrix. In many cases, adding these nonconductive particles enhances the effective conductivity of the composite. It has been speculated that a highly conductive region around the particle is created.

In this study, nanocomposites were fabricated where both phases were ionically conductive. Bilayer structures of inorganic and polymer electrolyte layers were studied to determine the effect of the interface on conductivity and mechanical properties. The inorganic layer was lithium phosphorous oxynitride (Lipon). Two copolymer electrolytes were characterized: poly[styrene-co-poly(ethylene oxide) methacrylate] and poly[methyl methacrylate-co-poly(ethylene glycol) methacrylate]. To characterize Li^+ conductivities, thin films of Lipon with compositions near $Li_{3.3}PO_{3.8}N_{0.24}$ were sputter deposited. Polymer electrolytes thin films were then fabricated on top of the Lipon film via spin coating. Electrochemical impedance spectroscopy revealed that the interfacial resistance was dominant in the bilayer structure.

Nanoindentation was used to characterize the elastic modulus and hardness of LiPON films ranging in thickness from 100 nm to 10 μm. The modulus of LiPON was found to be approximately 77 GPa and independent of the substrate, film thickness, and annealing. Using Sneddon's stiffness equation and assuming the modulus is 77 GPa, the hardness was found to be approximately 3.9 GPa for all but the annealed film. The hardness of the annealed film was approximately 5% higher, at 4.1 GPa.

A random resistor network method was used to model the conductivity of composite structures where nanoscale particulates are mixed into a polymer electrolyte matrix. The model system consisted of three phases: polymer matrix (σ_1), conductive particulate reinforcement (σ_2), and amorphous conductive layer surrounding particles (σ_3). The model targeted the simulation of a system consisting of a poly(ethylene oxide) $(PEO)_{10}LiClO_4$ matrix with spherical Lipon particles as filler. The simulation results revealed an initial increase in effective conductivity as a function of Lipon volume fraction, followed by rapid drop in conductivity of the composite electrolyte. The results of simulations were compared to predictions based on existing theories.

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