Ionic Liquid Based Polymer Gel Electrolytes for Li-Ion Batteries

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With the discovery of ionically conductive polymers such as polyethylene oxide, much effort has been spent attempting to prepare a true solid-state battery using a solid polymer electrolyte. Unfortunately, these solid polymers are very poor ionic conductors at room temperature.[1] In order to overcome this rather significant drawback, investigators have developed polymer gel composite electrolytes, in which a liquid electrolyte is added to the polymer in order to improve the ionic conductivity while maintaining the ease of working with a solid.[2] These polymer composite gel electrolytes have been extensively studied, using a variety of polymers, as well as a multitude of electrolytes, the most common of which are the organic carbonates.[3] Unfortunately, these liquid components suffer from several electrochemical and safety concerns, the most significant of which are their volatility and flammability.[4,5] In an attempt to overcome these shortfalls, polymer gel composite electrolytes have been prepared using the polymer Polyvinylidenedifluoro-hexafluoropropene (PVdF-HFP) and an ionic liquid as the liquid component. Ionic liquids are essentially non-volatile and non-flammabile,[6,7] and should result in the formation of much safer Li-ion batteries.

Research into the Li-ion battery applications of ionic liquids has been somewhat limited. Attempts to intercalate Li into graphite in the chloroaluminate ionic liquids resulted in the formation of a Li-Al alloy on the surface of graphite, with no true intercalation.[8] Similar work in the chloroaluminate ionic liquids using electrodes composed of spinel phase $LiMn_2O_4$ also found that interactions between the $AlCl_4$ anion and the graphite present in the $LiMn_2O_4$ electrode (added to improve the conductive nature of the native spinel oxide) resulted in relatively poor electrochemical behavior.[9]

More recently, our work in the non-chloroaluminate ionic liquids has shown that lithium ion can be reversibly intercalated into a variety of electrode materials in a manner similar to the carbonate electrolytes.[10] Also, work out of our group has shown that ionic liquid polymer gel composites can be prepared with conductivities on the order to 1-5 mS/cm at room temperature (Figure 1).[11] The ionic liquids have one of three air stable anions, tetrafluoroborate, hexafluorophosphate, and bis-trifluoromethane-sulfonylimide (TFSI); and either a di-substituted imidazolium cation, 1-butyl-3-methylimidazolium, BMI^+, or a tri-substituted imidazolium cation 1,2-dimethyl-3-n-propylimidazolium, $DMPI^+$ and 1,2-dimethyl-3-n-butylimidazolium, $DMBI^+$. Results indicate high stability and efficiencies for the tri-substituted imidazolium based ionic liquids, especially the TFSI compounds (Figure 2), while poor electrochemical stability was observed for the di-substituted cation based ionic liquid.

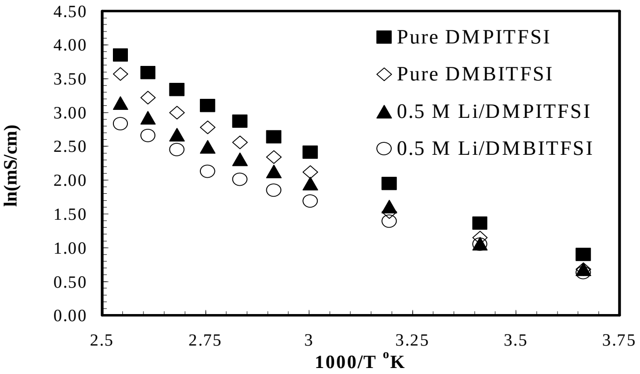

Figure 1. Arrhenius Plots of the ionic conductivity of polymer gel composite electrolytes composed of 25 wt % PVdF-HFP and 75 wt % DMRITFSI or 0.5M Li/DMRITFSI.

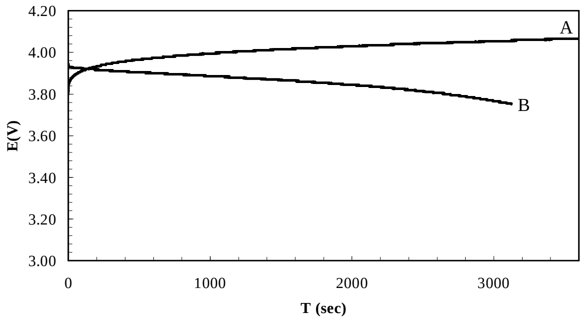

Figure 2. Charge (A) and Discharge (B) at 50 μA/cm^2 for a $LiMn_2O_4$ using Li metal anode and a polymer gel composite electrode composed of 25 wt % PVdF-HFP and 75 wt % 0.5 M Li/DMBITFSI.

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