Ionic Liquid Based Polymer Gel Electrolytes for Li-Ion Batteries

Thomas E. Sutto1,2, Douglas M. Fox3, Hugh C. De Long1,4, and Paul C. Trulove1,5
1Naval Research Laboratory, Code 6170, Chemistry Division, Washington D. C., 20375 U.S.A.
2Chemistry Department, US Naval Academy, Annapolis MD 21402 U.S.A.

With the discovery of ionic liquids as potential electrolytes for Li-ion batteries, 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 Polynvinylidenedifluoro-hexafluoropropene (PVdF-HFP) and an ionic liquid as the liquid component. Ionic liquids are essentially non-volatile and non-flammable,3,6 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.4,6 Similar work in the chloroaluminate ionic liquids using electrodes composed of spinel phase LiMn$_2$O$_4$ also found that interactions between the AlCl$_4$ anion and the graphite present in the LiMn$_2$O$_4$ electrode (added to improve the conductive nature of the native spinel oxide) resulted in relatively poor electrochemical behavior.6

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-sulfonfyl-imide (TFSI); and either a di-substituted imidazolium cation, 1-butyl-3-methylimidazolium, BMI$^+$ or a tri-substituted imidazolium cation 1,2-dimethyl-3-propylimidazolium, DMI$^+$ 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. Arhenius Plots of the ionic conductivity of polymer gel composite electrolytes composed of 25 wt % PVdF-HFP and 75 wt % DMI/DMF or 0.5M Li/DMBITFSI.](image1)

![Figure 2. Charge (A) and Discharge (B) at 50 μA/cm$^2$ for a LiMn$_2$O$_4$ using Li metal anode and a polymer gel composite electrode composed of 25 wt % PVdF-HFP and 75 wt % 0.5 M Li/DMBITFSI.](image2)

References