Ion Transport in Ionic-Liquid/Polymer Gel Electrolytes

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Recently, Fuller and Carlin have demonstrated that stable solid gel electrolytes and membranes can be formed by the addition of a polymer, polyvinylidene hexafluoroproplyene (PVdF-HFP), to 1,3 dialkyl imidazolium ionic liquids (1-3). These solid gel electrolytes have the potential to provide the structural and stability advantages of a polymer with the ionic conductivity approaching that of the pure molten salt. The properties of these novel electrolyte gels are strongly dependent on the type of ionic liquid, the amount of polymer, and the preparation method used.

In the present work we are investigating the effect of ionic liquid and polymer content on the transport properties of ions in the ionic liquid gels. We have employed conductivity measurements to provide information on the overall transport of charge in the gels, and we have used Pulsed-Gradient Spin-Echo NMR (PGSE) to investigate the movement of cations and anions separately (4-6).

Figure 1 shows representative temperature dependent conductivity data for the series of polymer gels prepared with 1-ethyl-3-methylimidazolium tetrafluroborate ($EMIBF_4$) and PVdF-HFP. For comparison Figure 1 also shows the data for pure $EMIBF_4$. These data clearly show the dramatic effect of polymer content on the gel conductivity. For example, the gel containing 50% polymer content has a room temperature conductivity more than three orders of magnitude less than that of the pure $EMIBF_4$, 9.8×10^{-6} S/cm versus 1.1×10^{-2} S/cm. When the polymer content is reduced to 15%, the room temperature conductivity of the gel increases to 5.5×10^{-3} S/cm; 50% of the value for the the pure $EMIBF_4$. More importantly this difference in conductivity between the 85% ionic liquid gel and the pure $EMIBF_4$ decreases with increasing temperature. At 378 K the 85% ionic liquid gel has 78% the conductivity of the pure $EMIBF_4$. The Arrhenious fits of the data in Figure 1 give activation energies of 19.2 kJ/mol, 20.5 kJ/mol, 21.0 kJ/mol, 19.1 kJ/mol, 27.1 kJ/mol, and 37.5 kJ/mol for the conductivities of 100%, 85%, 80%, 75%, 65%, and 50% $EMIBF_4$, respectively. The activation energy for conduction of $EMIBF_4$ is essentially unchanged in the polymer gel down to 75% ionic liquid. This would seem to indicate that movement of the $EMIBF_4$ in the gels is unimpeded by the polymer up to a certain threshold composition, and that the observed decrease in conductivity appears to be due to the decrease in concentration of ionic species as the polymer content of the gels increases. PGSE measurements of the self-diffusion coefficients of ions in these gels appear to confirm the conclusions made from the conductivity data.

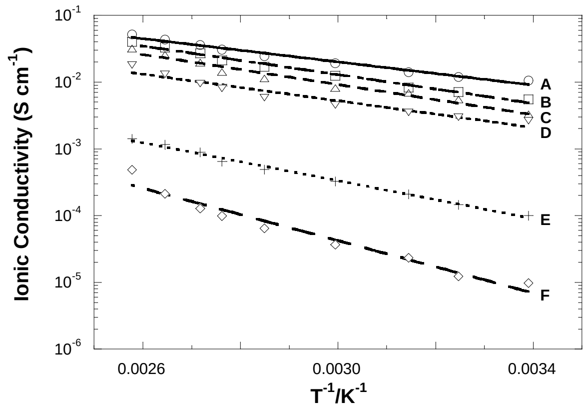

Figure 1. Effect of molten salt content on the temperature dependent conductivity of PVdF(HFP)-$EMIBF_4$ gel electrolytes: (A) neat $EMIBF_4$; (B) 85% $EMIBF_4$; (C) 80% $EMIBF_4$; (D) 75% $EMIBF_4$; (E) 65% $EMIBF_4$; (F) 50% $EMIBF_4$.

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