

Investigations of the Effects of Lithium Ion and Polymer Type on the Electrochemical Behavior of Ionic Liquid/Polymer Gel Electrolytes

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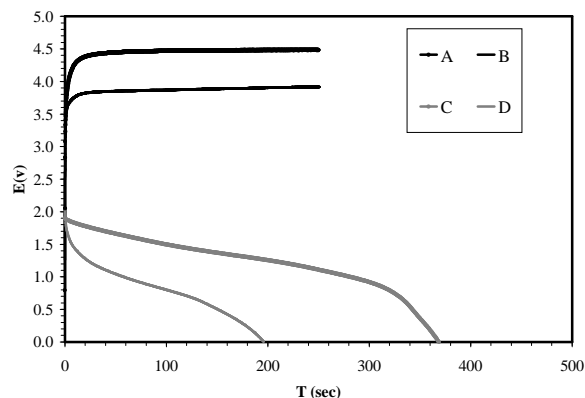
Previously, polymer gel electrolytes have been prepared by combining various ionic liquids and polyvinylidene hexafluoropropylene (PVdF-HFP). (1-3) Although these gel electrolytes have proven to be stable, the highly non-polar aspect of the polymer has led to difficulties in preparing gel electrolytes for use in lithium-type batteries. (4-5). In order to address this concern, polymer gel electrolytes were prepared from either polyethylene oxide (PEO) or PVdF-HFP, using the pure ionic liquid 1,2-dimethyl-3-n-imidazolium tetrafluoroborate (DMPIBF₄), or a solution of 0.5 M lithium tetrafluoroborate in the same ionic liquid.

In order to produce the highest ionic conductivity possible, the amount of polymer used was reduced to 20%, which allowed for the formation of extremely stable gels. All work was done in a dry box under argon. A solvent dissolution method was used, in which the PVdF-HFP was first dissolved in a minimum amount of 4-methyl-2-pentanone using sonication, and then the ionic liquid, with or without lithium was added, and the mixture was sonicated again. For the PEO, astringently dried acetonitrile was used, but a similar sonication protocol was used to prepare homogeneous solutions of the polymer gel mixtures. After extensive drying, the PEO gels were white, and non-transparent, while the PVdF-HFP gels were semi-transparent. Ionic conductivity measurements indicated ionic conductivity in the 1-5 mS/cm range at room temperature for all four gels, with Arrhenius type of behavior observed in the temperature range from 60° to 110° C.

The polymer gel electrolytes prepared with the pure ionic liquid were characterized as Dual Intercalating Molten Electrolytes (DIME) in which the imidazolium cation and the tetrafluoroborate anion act as both the electrolyte and the intercalating species of a simple battery (6). The polymer gel electrolytes were studied by cyclic voltammetry using graphitic paper as the working and counter electrodes and a strip of Pt foil as a pseudo-reference electrode. Strong cationic intercalative behavior was observed, especially for the lithium containing gels. However, the tetrafluoroborate anion behaved very poorly as the intercalating species. As a result, galvanic cell charge-discharge experiments yielded low overall efficiencies, of near 50% for DIME studies, in which the imidazolium cation and the tetrafluoroborate anion were the only intercalating species, although the PVdF-HFP gels performed about 10% better than the PEO gels.

In polymer gel electrolytes with lithium present, a significant difference was observed between the two different types of polymers studied. The PVdF-HFP polymer gel electrolytes exhibited only a 39% charge-discharge efficiency in a galvanic cell. However, as shown in figure 1, the polymer gel electrolyte, made with PEO, exhibited 70% charge-discharge efficiency. This clearly indicated that these types of polymer gel electrolytes are more suitable choices for lithium-based battery systems.

Figure 1: Galvanic cell charging behavior using two



0.5" diameter circles of graphite paper as the electrodes for (A.) 20% PEO and 80% 0.5M LiBF₄ in DMPIBF₄, (B.) 20% PVdF-HFP and 80% 0.5M LiBF₄ in DMPIBF₄ using a current density of 0.1 mA/cm²; and their discharging behavior, (C.) 20% PEO and 80% 0.5M LiBF₄ in DMPIBF₄ (D.) 20% PVdF-HFP and 80% DMPIBF₄, using a current density of 0.05 mA/cm²

References:

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