INVESTIGATION OF THE INFLUENCE OF POLYMER TYPE ON THE ELECTROCHEMICAL BEHAVIOR OF IONIC LIQUID/POLYMER GEL ELECTROLYTES

Thomas E. Sutto¹²*, Paul C. Trulove³*, and Hugh C. De Long³

¹Naval Research Laboratory, Code 6170, Chemistry Division, Washington D. C., 20603
²Chemistry Department, US Naval Academy, Annapolis MD 21402
³Air Force Office of Scientific Research, 801 Randolph St., Arlington, VA 22203-1977

ABSTRACT

The electrochemical properties of polymer gel electrolytes, prepared using either polyethylene oxide (PEO) or Polyvinylidenedifluoro-hexafluoropropene (PVdF-HFP) and the ionic liquid 1,2-dimethyl-3-n-propylimidazolium tetrafluoroborate, were evaluated. The composition of all polymer gels studied was 20% polymer and 80% ionic liquid. A solvent dissolution method was used for preparation of both polymer gel types. The PEO gels were white, waxy, and somewhat fragile, while the PVdF-HFP gels were translucent and rubbery. The room-temperature ionic conductivities for both types of polymer gels were in the range of 1 to 5 mS/cm. Cyclic voltammetry was performed using graphitic paper, and good cationic intercalative behavior was observed. However, the anionic intercalative behavior was poor. The PVdF-HFP gels exhibited 80% cation charge/discharge efficiencies, with a discharge potential of -1.1 V, while the PEO gels exhibited only 50% charge-discharge efficiencies at -0.45 V. For both gel systems, the anionic charge-discharge efficiencies were below 50%.

INTRODUCTION

Molten salts that are liquid at or below room-temperature (a.k.a. ionic liquids) have been extensively studied for their unique physical and electrochemical properties (1,2). One area of long standing interest has been the application of ionic liquids to the development of electrochemical power sources. Recently, ionic liquids have been investigated for their use as both the electrolyte and the source of the intercalative guest species in Dual Intercalating Molten Electrolyte (DIME) batteries (3-6). Ionic liquids have also been recently studied for their use in forming polymer composite gel electrolytes with the polymer, PolyVinylidenediFluoro-HexaFluoroPropylene (PVdF-HFP) (7-11).

The DIME system consists of a graphitic cathode, a graphitic anode, and the ionic liquid as both the electrolyte and the anionic and cationic intercalates. Due to the much

* to whom correspondence should be directed
larger size of the current carrying species, the DIME battery system does not exhibit energy densities as high as those found in Li-ion batteries. However, the DIME system does represent the simplest form of a graphite-based battery.

With the discovery of polymers such as polyethylene oxide, PEO, and others that are ionically conductive, much effort has been spent on trying to prepare a true solid-state battery using a solid polymer electrolyte. Unfortunately, these solid polymers are poor ionic conductors at room-temperature (12). In order to overcome this drawback, polymer composite gel electrolytes have been studied. In these materials, a liquid electrolyte is added to the polymer to produce solid polymer composites with higher ionic conductivities. For much of this work, the most commonly used solvents for these systems have been organic carbonate-like derivatives (13). However, these organic carbonates pose serious safety concerns because of their volatility and high flammability (14). Ionic liquids, on the other hand, exhibit no volatility and are nonflammable (15).

Previously, polymer gel electrolytes have been prepared by combining various ionic liquids and PVdF-HFP (7-9). Although these gel electrolytes have proven to be stable and to possess reasonable ionic conductivity, the highly non-polar aspect of the polymer has led to difficulties in preparing gel electrolytes for use in lithium-type batteries (10,11). In order to address this concern, we choose to investigate the preparation and properties of polymer gel electrolytes prepared from PEO and an ionic liquid.

In the present study, polymer gel electrolytes were prepared from either PEO or PVdF-HFP, using the ionic liquid, 1,2-dimethyl-3-n-propylimidazolium tetrafluoroborate (DMPIBF₄). These polymer gel electrolytes were then studied for both their ion conducting properties, as well as their general electrochemical behavior in a DIME battery configuration.

EXPERIMENTAL

Preparation of the Initial Salt: DMPICl

The preparation of 1,2-dimethyl-3-n-propyl-imidazolium chloride (DMPICl) was accomplished by the direct reaction of 1,2-dimethylimidazole (Aldrich, 98%) and 1-chloropropane (Aldrich, 99%) in a 1:1.15 molar ratio. The 1,2-dimethylimidazole was vacuum distilled at approximately 10⁻³ torr and 135 °C prior to use. The remainder of the synthetic preparation is as previously reported (3-6).

Preparation of the Polymer Gel Electrolytes

It is important to note that previous work reported for the PVdF-HFP based gels used a technique involving prolonged periods of heating and stirring (7), while several different methods have been reported for PEO gels (16,17). The preparation method presented here, using a sonication horn (Sonics and Materials Vibracell) resulted in much quicker preparation times, greater reproducibility and much more stable composites with a significantly higher ionic liquid content. Some earlier work reported extreme difficulty in preparing PVdF-HFP based gels containing more than 66% ionic liquid (7).
The polymer gels were prepared in an Ar drybox (H₂O and O₂ < 1ppm). The PVdF-HFP (Kynar −2801-00 from Elf Atochem) was dissolved using 4-methyl-2-pentanone, 4M2P, (98%, Aldrich, dried with 4.2 Å molecular sieves) as the solvent. The PEO, (Aldrich, Mₐ ca. 100,000, Tₘ = -67 °C), was dissolved in dry acetonitrile (Aldrich, 99.5%, dried with 4.2 Å molecular sieves). For each sample prepared, 0.5 g of the polymer was added to 10 mL of the appropriate solvent. The solvent/polymer mixture was sonicated for 2 minutes at high power, allowed to cool, and then resonicated for 2 additional minutes. 2 g of the ionic liquid were added, and sonication was continued, with intermittent pauses to allow for sample cooling, until there was a marked drop off in the sound of cavitation produced. The resulting ionic liquid-polymer solution was removed from the sonicator and allowed to stir at 60 °C under Ar until the mixture became extremely viscous. The liquid composite material was removed from the heat, poured into a 6.35 cm diameter Al weighing boat and cured at room temperature for 24 hours in the drybox. The Al dishes were subsequently placed in a desiccator, and then moved to a vacuum oven and dried at 75 °C an additional 24 hours under an active vacuum (approximately 10⁻³ torr). For all polymer gels prepared, the thickness of the gels was typically between 1-2 mm.

It must be noted that polymer gel compositions for this study were restricted to a maximum of 20 % polymer/80 % ionic liquid. This was due to the fact that the near solvent like interaction of the ionic liquid with PEO made it impossible to increase the amount of the ionic liquid in the PEO based gels beyond 80%. On the other hand, it has been shown previously, that high quality PVdF-HFP polymer gel electrolytes can be prepared with as little as 10% polymer (10).

Electrochemical Measurements

Temperature dependent impedance measurements were made with a Solitron Si 1260 Gain Phase Analyzer at frequencies from 100 kHz to 1 Hz, using AC amplitude of 5 mV. The sample holder was a standard T-cell composed of polypropylene and fitted with stainless steel rods and swage-lock fittings (10,11). All measurements were made starting from an initial temperature of 125 °C. Temperature intervals were approximately 10° C. The cell was allowed to come to thermal equilibrium for approximately 1 hour before the measurement was taken. A vernier caliper was used to measure the gel thickness. The thickness of a gel sample was determined be the difference between the end-to-end length of the stainless steel rods with and without the polymer gel between them. The ionic conductivity was calculated from the measured resistance when the imaginary component at high frequency fell to zero.

Cyclic Voltammetry and Charge-Discharge experiments were performed using either an EG&G PAR 273A or 263A Potentiostat/Galvanostat controlled by the M270 version 4.30 software. The pure ionic liquid was characterized using two pieces of the graphitic paper as the working and counter electrodes, and a reference electrode composed of a silver wire immersed in a 0.01 M AgBF₄ solution in 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) and separated from the remainder of the cell by a wetted Vycor tip. Electrochemical data for the polymer gels was collected using a specially designed flat cell (Figure 1). This cell was designed for ease of operation inside of the drybox. A number of ½” diameter circles of graphitic paper (Toray

56 Electrochemical Society Proceedings Volume 2002-19
Industries, TGP-H-090, composed of PAN Graphite Fibers) were cut out, dried overnight in a vacuum oven (90 °C, 10^{-3} torr) and used as both the working and counter electrodes. Also, two ½" diameter discs of Pt foil were cut out and used to determine the electrochemical window of the gels. Cell assembly simply required the stacking of a graphitic disc, two discs of the polymer gel electrolyte with a 0.03 mm Pt wire inserted between them for use as a pseudo reference, and another graphitic disc on top of the sandwich. This thin solid-state cell was then placed between the two Pt current collectors and the entire cell was clamped with a spring-loaded clip to ensure good contact. All electrochemical data was collected in a drybox under Ar.

**RESULTS AND DISCUSSION**

The temperature dependent ionic conductivity data for both types of polymer gels are shown in Figure 2. Both polymer gels appear to exhibit similar behavior around room-temperature with conductivities in the mS/cm range. However, the 20% PVdF-HFP/80% DMP/IBF_{4} begins to show higher conductivity than the PEO gel around 100°C. Figure 3 shows the Arrhenius plot of the data from Figure 2. The experimental data was fit to the Arrhenius relationship to determine the activation energies (E_{a}) for ionic conduction. These data and the room-temperature ionic conductivity values are presented.
in Table 1. For the polymer gel electrolytes, little difference is observed between the two different types of polymer used, although the PEO gel did exhibit higher $E_a$'s and lower conductivities than those observed for the pure liquid, or the PVdF-HFP based gel.

**Figure 2.** Ionic conductivity in mS/cm as derived from ac-impedance measurements vs. °K for: (A) Pure DMPIBF$_4$, (B) 20% PVdF-HFP/80% DMPIBF$_4$, (C) 20% PEO/80% DMPIBF$_4$.

**Figure 3.** Arrhenious plots for: (A.) Pure DMPIBF$_4$, (B) 20% PVdF-HFP/80%DMPIBF$_4$, (C) 20% PEO/80% DMPIBF$_4$. The solid lines represent the best linear fit to the data.
Table 1. Ionic Conductivity and Thermodynamic properties of the Polymer Gel Composite Electrolytes

| Sample measured                  | Ionic Con. at 22 °C (mS/cm) | $R^2$ for Linear Least Squares Fit | Estimated $E_a$ in kJ/mol |
|---------------------------------|-------------------------------|-----------------------------------|---------------------------|
| Pure DMPIBF$_4$                | 5.22                          | .9879                             | -23.42                    |
| 20% PEO /80% DMPIBF$_4$        | 2.64                          | .9977                             | -25.59                    |
| 20% PVdF-HFP /80% DMPIBF$_4$   | 3.85                          | .9912                             | -23.82                    |

Figure 4 shows the Cyclic Voltammograms of the pure ionic liquid at both platinum (Figure 4A) and graphitic paper (Figure 4B) working electrodes. The differences in the two voltammograms are indicative of cation and anion intercalation into the graphitic electrode. The intercalative behavior for the cation is reasonably reversible. However, that for the tetrafluoroborate ion shows poor reversibility indicating significant instability of the intercalated anion with respect to the oxidized graphite. The cyclic voltammograms for the PVdF-HFP and PEO films at a graphitic paper working electrode are shown in Figure 5. The overall behavior of both these voltammograms is similar to that observed for the pure DMPIBF$_4$ ionic liquid. However, both voltammograms (Figure 5) are of poorer quality most likely due to the effects of resistance. From these cyclic voltammograms, it is clear that the DMPI$^+$ exhibits good intercalative behavior. However, as previous work has shown, the BF$_4^-$ anion is particularly prone to electrochemically-induced degradation during intercalation (4-6).

Figure 4. Cyclic voltammogram for pure DMPIBF$_4$ at, (A) platinum and (B) graphitic paper working electrodes. A scan rate of 20 mV/sec was used.
Figure 5. Cyclic voltammograms for the (A.) 20% PEO/80% DMPiBF$_4$ and (B.) 20% PVdF-HFP/80% DMPiBF$_4$ at a graphitic paper working electrode. A scan rate of 10 mV/sec was used.

Figure 6 shows the cathodic charge-discharge behavior (cation intercalation-deintercalation) for both types of gels after the 10th charge-discharge cycle. After approximately 8-10 cycles, the charge-discharge behavior of the polymer gel electrolytes exhibited nearly constant charge-discharge efficiencies. For these cathodic charge-discharge experiments, the charging current was 0.2 mA/cm$^2$, and the discharge rate was 0.1 mA/cm$^2$. The PVdF-HFP gel did exhibit a level discharge plateau at approximately -1.1 V, which trailed off as it reached the end of its discharge. The overall efficiency observed, as determined at the point where zero potential was reached, which was near 80%. The PEO gel has an anodic discharge plateau at ca. -0.4 volts, and exhibited a very poor efficiency (45%). This could be attributed to the fact that the transport of the imidazolium cation is more restricted in the PEO gel.

Figure 7 shows the anodic charge-discharge behavior (anion intercalation-deintercalation) for both types of gels. The data in Figure 7 clearly illustrates the poor charge-discharge behavior of the tetrafluoroborate anion. For both the PVdF-HFP and PEO gels, the efficiencies were never higher than 50%, and no well-defined discharging plateau was observed.
CONCLUSION

In the present work, polymer gel electrolytes prepared from the PVdF-HFP polymer were superior in physical and electrochemical properties to gels prepared with the PEO polymer. The higher efficiencies in the DIME battery systems and the more clearly defined cyclic voltammograms indicate that the PVdF-HFP gels provide a less hindered medium for the transport of the charged imidazolium rings. Future work will...
further investigate the transport properties of these two polymer gel electrolytes. In addition we plan to expand these studies to include the behavior of Li-ion in these polymer gel electrolytes.

ACKNOWLEDGEMENTS

This work was sponsored by the Air Force Office of Scientific Research, and space was provided by the Naval Research Laboratory. Opinions, interpretations, conclusions and recommendations are those of the authors and are not necessarily endorsed by the United States Air Force.

REFERENCES

1. C. L. Hussey in Chemistry of Nonaqueous Solvents. A. Popov and G. Mamantov, Editors. Chap. 4, VCH Publishers, New York (1994).
2. J. S. Wilkes, L. A. Levinsky, R. A. Wilson, and C. L. Hussey, Inorg. Chem. 21, 1263 (1982).
3. R. T. Carlin, H. C. De Long, J. Fuller, and P. C. Trulove, J. Electrochem. Soc. 141, L73, (1994).
4. T. E. Sutto, P. C. Trulove, H. De Long, in Proceedings of the 12th International Conference on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, S. Deki, Editors, PV 99-41, p. 32, The Electrochemical Society, Inc., Pennington, NJ (2000).
5. T. E. Sutto, P. C. Trulove, H. De Long, in Proceedings of the 12th International Conference on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, S. Deki, Editors, PV 99-41, p. 43, The Electrochemical Society, Inc., Pennington, NJ (2000).
6. T. E. Sutto, K. D. Sienerth, H. De Long and P. C. Trulove, in Proceedings of the 12th International Conference on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, S. Deki, Editors, PV 99-41, p. 54, The Electrochemical Society, Inc., Pennington, NJ (2000).
7. J. Fuller, A. C. Breda, and R. T. Carlin, J. Electrochem. Soc. 144, L68, (1997).
8. J. Fuller, A. C. Breda, and R. T. Carlin, J. Electroanalytical Chem. 459, 29 (1998).
9. R. T. Carlin and J. Fuller, Chem. Commun., 1345 (1997).
10. T. E. Sutto, P.C. Trulove, and H. C. DeLong, Zeitschrift für Naturforschung B, submitted.
11. T. E. Sutto, H. C. DeLong, and P.C. Trulove, Zeitschrift für Naturforschung B, submitted.
12. M. Alamgir and K. M. Abraham, “Room Temperature Polymer Electrolytes”, Lithium Batteries, Ed. G. Pistoia, Industrial Chemistry Library, Vol. 5, (1994).
13. S. C. Ventura, S. C. Narang, G. Hum, P. Liu, P. Ranganathan, and L. Sun; SRI International, U. S. Patent 5,731,104, March 24, (1998).
14. S. Narang, S. Ventura, B. Dougherty, M. Zhao, S. Smedley and G. Koolpe; SRI International, U. S. Patent 5,830,600, November 3, (1998).
15. E. I. Cooper and E. J. M. O’Sullivan, in Proceedings of the Eighth International Symposium on Molten Salts, R. J. Gale, G. Blomberg, and H. Kojima, Editors, PV 92-16, p. 386 (1992).
16. Y. Aihara, S. Arai, and K. Hayamizu, Electrochem. Acta, 45, 8-9, 1321 (2000).
17. F. Lemaitre-Auger and J. Prud’homme, Electrochem. Acta, 46, 9, 1359 (2000).