IONIC LIQUID, GRAPHITE AND GEL POLYMER ELECTROLYTES AND ELECTRODES USING 1,2-DIMETHYL-3-PROPYL-IMIDAZOLIUM TETRAFLUOROBORATE

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ABSTRACT

An electrochemical study of composite gel electrodes and half-cells, of DMPiBF$_4$, PVdF-HFP Kynar polymer, and graphite was undertaken. Four different graphite-to-DMPiBF$_4$ ratios were combined with six different graphite-DMPiBF$_4$-to-polymer ratios. These 24 solid, black rubber-like gels were studied initially as simple electrodes and as half-cells in solid battery systems. Initial electrode studies indicated peak charge/discharge efficiencies of over 70% for several combinations. These optimized half cells were used in a solid state battery set-up to test their charge-discharge behavior in the absence of an external, supporting electrolyte. From these solid systems, the highest cation charging efficiency of 77% with an anion charging efficiency of 65% were observed for the sample of composition 55.58:27.75:16.67, graphite:DMPiBF$_4$:polymer.

INTRODUCTION

In the field of molten salts, one of the most interesting developments has been with the combining of various molten salts and polymers to form gel-like, polymer-molten salt composites (1). These gels can exhibit many of the same properties as the pure molten salt. Also, they can be manipulated into a multitude of semi-rigid states, without the need for any type of container. In addition to this work, recent experiments have shown that by combining graphite rod electrodes and molten salts, simple batteries can be assembled. In these Dual Intercalating Molten Electrolyte (DIME) Systems (2), the molten salt serves as both the electrolyte, and the source of the intercalating ions. Thus, by combining both of these new developments, it should be possible mix graphite,
molten salt, and polymer into gels usable as semi-rigid half-cells. These half-cells would only need a simple membrane as a separator in order to form complete battery cell systems. Previous work reported briefly on the overall effectiveness of forming the straight polymer-gel composites using the polymer poly(vinylidenefluoride)-hexafluoropropylene copolymer (PVD) and EMITrif, EMIBF₄, EMIPF₆, and TEABF₄ (1). Unfortunately, as has been shown, 1-ethyl-3-methylimidazolium cation, EMI⁺ is a fairly unstable in terms of its charge/discharge behavior (2,3). Therefore, an extended series of gels have been prepared using DMPIBF₄, graphite, and polymer.

A complete series of graphite:molten-salt:polymer composites were prepared. Since the previous work has demonstrated that the ideal stoichiometry for DMPI⁺ intercalated into graphite results in a graphite-to-molten-salt mass ratio of nearly 2:1, this was chosen as the starting point for the ratio of molten salt to graphite. Four different graphite-to-DMPIBF₄ ratios were chosen, 2:1, 1:1, 1:2, and 3:1. Each of these were treated as a single component, and subsequently combined with the PVD polymer to form gels of composition 1:2, 1:1, 2:1, 3:1, 4:1, and 5:1, yielding a total of 24 gels. Initial studies of these gels consisted of cutting them into strips and then evaluating their electrochemical properties using them as the working electrode in a molten salt cell. After the optimum combinations of graphite:molten-salt:polymer were identified, the best semi-rigid gels were used in a solid state cell, without free flowing molten salt electrolyte, to determine their overall effectiveness as solid state batteries.

EXPERIMENTAL

Preparation of the initial salt DMPICl

The preparation of 1,2-dimethyl-3-n-propyl-imidazolium chloride was altered from that previously reported in order to produce a higher yield and a purer product (4). The starting materials, 1,2-dimethyl-imidazole (98%) and 1-chloropropane (98%), were purchased from Aldrich, as was the acetonitrile (99.5% anhydrous). The 1,2-dimethyl-imidazole (m.p. 38 °C) was melted at 50 °C under flowing nitrogen in a drying oven. Typically, 500 g of 1,2-dimethyl-imidazole, a 25% molar excess of 1-chloropropane, and 50 ml of acetonitrile were placed in a thick-walled, single neck, 2-liter round bottom flask fitted with a reflux condenser. The excess 1-chloropropane was added to limit the amount of unreacted 1,2-dimethyl-imidazole in the final product. The solution was degassed several times with dry nitrogen, gradually heated to 75 °C, and allowed to reflux for four days under nitrogen pressure. Cooling the solution produced a tan-white precipitate and a yellow-red supernatant. 300 ml of ethyl acetate were added to the round bottom flask to precipitate all of the 1,2-dimethyl-3-n-propyl-imidazolium chloride, and the material was filtered and washed with five 100 ml washings of ethyl acetate in order to remove all of the unreacted 1,2-dimethyl-imidazole. The solid material was dissolved in a minimum amount of hot acetonitrile and recrystallized twice by adding a large excess of ethyl acetate. This removed nearly all of the unreacted 1,2-dimethyl-imidazole. For the final recrystallization, the solid product was again dissolved in a minimum amount of boiling acetonitrile and allowed to slowly crystallize out as the solution cooled over 24 hours. The solid material from each recrystallization was washed with ethyl acetate. The
final product was a white crystalline material, which exhibited a very slight tan tint. Finally, the 1,2-dimethyl-3-n-propyl-imidazolium chloride was heated to 155 °C under an active vacuum (10⁻³ torr) for 2 days to remove the volatile contaminants.

Preparation of the BF₄ salts

The preparation of 1,2-dimethyl-3-n-propyl-imidazolium tetrafluoroborate was done by direct reaction of the respective chloride salt with NH₄BF₄ (Aldrich, 99.98%) in acetonitrile. In this solvent, the substituted imidazolium chloride salt is highly soluble in acetonitrile, while the NH₄BF₄ is only marginally soluble in acetonitrile (5). However, the secondary product, NH₄Cl, is not soluble in acetonitrile, and this fact provides the driving force for the reaction. This reaction step was performed in a dry box, under dry nitrogen, in order to limit the possible inclusion of water into the final product. For a typical reaction, one mole of the 1,2-dimethyl-3-n-propyl-imidazolium chloride salt was placed in a 1-liter reaction flask fitted with a threaded Teflon plug and dissolved in a minimum amount of acetonitrile. To this solution, a 10% molar excess of NH₄BF₄ was added. The flask was sealed and allowed to stir at room temperature for 4 days. Upon completion of the anion exchange, the solid material (NH₄Cl and unreacted NH₄BF₄) was removed by vacuum filtration using a glass frit of medium pore size. Subsequently, to the remaining molten salt/acetonitrile solution, 30 g of decolorizing carbon and 30 g of basic alumina were added and the solution was allowed to stir at room temperature in the sealed reaction flask for two days. The carbon black and alumina were removed by successive filtration; through a medium pore size glass frit, a 1 μ filter disc (Whatman, PTFE Membrane) and, finally, a 0.45 micron filter disc (Whatman, PTFE Membrane). For the final step in the purification process, the molten salts were heated to 65 °C under an active vacuum (10⁻³ torr) for 2 days to remove any trace water or acetonitrile. The final molten salt was clear and nearly colorless, a slight tan tint.

Preparation of the Graphite-Molten Salt-Polymer Composites

Graphite:molten-salt:polymer composites were prepared from 1 μ sized synthetic graphite (99.9995% Aldrich), poly-vinylidene-difluoride hexafluorophosphate (PVdF-HFP Kynar –2801-00 from Elf Atochem), and DMPIBF₄. The graphite-molten salt ratios prepared were based upon the graphite to molten salt weight ratios of 2:1, 1:1, 1:2, 1:3. These two components were considered to be one constituent when the polymer was added. These two components, the graphite-molten salt, and the polymer were combined according the mass ratios of 1:2, 1:1, 2:1, 3:1, 4:1, and 5:1. Composites made with the graphite-molten salt to polymer ratio of 1:3 (75% polymer) were found to be too non-conductive to be used as electrodes, and samples with a graphite-molten salt to polymer ratio of 6:1 (14.3% polymer) failed to form solid gels.

The mass of the graphite and polymer were determined within a 30 ml vial. The resulting mixture was stirred until a homogeneous gray color was observed. The correct mass of molten salt was added using a 20 ml gas tight syringe. The total mass of graphite and molten salt was typically 6 g. 15 ml of 4-methyl-2-pentanone (98%, Aldrich) was
added to dissolve the polymer. The vial was sealed with a Teflon lined screw cap and stirred vigorously with a stir bar as the solution was slowly heated up to 60 °C. After approximately 2 hours of heating, the mixture became extremely viscous. The sample was removed from the heat, poured into a 2.5" diameter Al weighing boat and air cured at room temperature for 24 hours. Samples were placed in a vacuum oven and dried an additional 60 hours under an active vacuum (approximately 10^-3 torr) at 50 °C. The graphite-molten salt-polymer composites formed extremely stable, black rubber discs (approximately 2-3 mm thick) which could be readily cut into a variety of shapes. For initial measurements, strips 0.5 cm wide, 1.5 cm long and approximately 0.2 cm thick were cut from the structurally stable sample. Electrical contact was made with these gel strips by clamping the upper 0.5 cm of the strip with a flat copper alligator clip.

Electrochemical Measurements.

Electrochemical experiments are divided into two different groups. The first series of experiments focused on determining the optimum combination of graphite to molten salt to polymer, and were performed in a typical liquid type cell. These initial experiments were performed for all 24 films, and they used a simple three-probe cell where a strip of the composite gel acted as the working electrode. The reference electrode was Ag/AgBF4 using a reference solution of 0.01M AgBF4 in the respective molten salt. The reference electrode was separated from the cell by a wetted Vycor tip (Bioanalytical Non-Aqueous Reference Electrode). A ½ “ diameter graphite rod (Aldrich, 99.9995%, hardness 50) was used as the counter electrode. The surface area ratio of working to counter (a graphite rod) was 1:5. A 25 ml glass vial fitted with a Teflon cap (three ½” holes) and filled with 15 ml of DMPIBF4 was used as the cell.

The second series of experiments were performed without any freestanding electrolyte. Instead, a simple solid state cell was constructed. As shown in Figure 1, two, ½” diameter discs of the composite gels were cut using a cork borer. The cell was built by first wetting two medium pore filter paper discs in DMPIBF4 (excess molten salt was simply wiped off using a tissue) and sandwiching a flattened Pt wire between them to be used as a pseudo-reference. On either side of this sandwich, a ½” disc of the composite was placed to be used as the working and counter electrodes. By compressing these components between two Pt capped Al rods, a simple solid state battery or cell was completed. For both series, Cyclic Voltammetry was measured using either an EG&G PAR 273A or 263A Potentiostat/Galvanostat with the PAR Echem Software.

Charge-Discharge experiments were also performed on an EG&G PAR 273A or 263A Potentiostat/Galvanostat. For all charging experiments, the applied current was adjusted such that the surface current density was approximately 0.8 mA/cm². For initial experiments, where only the bottom 0.7 cm of the strip was placed in the molten salt, the surface area was approximately 1.0 cm², so a charging current of 0.8 mA was applied. For charge/discharge experiments in the solid state, the ½” diameter of the flat disc yields a surface area of 1.25 cm², so a charging current of 1 mA was applied. For both types of charge/discharge experiments, the discharge current was ½ of the charging current.
RESULTS AND DISCUSSION

Figure 2 shows the typical cyclic voltammetry observed for the gel strips. Significant charging effects obscure any details of the cathodic or anodic intercalations. However, as shown in figures 3 and 4, charge/discharge behavior could be observed. Of the multitude of ways of comparing the results for these 24 strips, figures 5 and 6 show the cation and anion efficiencies vs. the % graphite in each composite. The data sets are grouped into series where the graphite-molten salt-to-polymer ratios are the same, which results in six lines. The four data points in each line correspond to the four different graphite-to-molten salt ratios studied. The results for the cation seem to indicate that more than 30% graphite is required to obtain good charge/discharge behavior. Figure 5, the anion efficiencies, clearly shows that increasing graphite increases the discharge efficiencies.

Figure 7 shows how both the cation and anion charge/discharge efficiencies depend upon the amount of molten salt present. For these comparisons, the samples are grouped into series, where the graphite-to-molten-salt ratios are the same. Samples that had a graphite-to-molten-salt ratio of 1:3, exhibited no charge/discharge efficiencies, and are excluded from this figure. Therefore, three data sets for the cation and three data sets for the anion behavior are plotted. The six data points in each line correspond to the six different graphite:molten-salt to polymer ratios studied. As can be seen, efficiencies first rose, and then fell as the amount of molten salt increased. This can be attributed to the fact that a significant amount of molten salt was required to intercalate and de-intercalate, but an excess of the molten salt significantly lowered the efficiencies due to its inability to allow electrical conduction between graphite particles.

For measurements made in the solid state, figure 8 shows that much better cyclic voltammograms are possible. This can be attributed to the fact that the composite gel in the solid cell had much more intimate contact to the Al rod, as opposed to the alligator clip. This also results in a much sharper charge/discharge behavior as shown in figures 9 and 10. Finally, in table 1 below, the best charge/discharge efficiencies for these solid-state measurements are shown.

| Graphite:DMPIBF4:Pvd (%) | Cation Efficiency | Anion Efficiency |
|-------------------------|------------------|-----------------|
| 55.58::27.75::16.67    | 77%              | 65%             |
| 53.33::26.67::20.00    | 75%              | 61%             |
| 40.00::40.00::20.00    | 62%              | 44%             |
| 41.70::41.70::16.60    | 70%              | 44%             |

TABLE 1

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CONCLUSIONS

Results indicate that the molten salt and polymer act to a significant degree as insulating material, and large amounts of either resulted in efficiencies below 20%. In fact, efficiencies of 0% were observed for most samples from the series where the graphite to molten salt ratio was 1:3. Peak efficiencies were observed for samples where the graphite to molten salt ratio was 2:1 and 1:1, and of these, the gels of composition 4:1 and 5:1 exhibited cation efficiencies over 70%, and anion efficiencies near 50%.

The effect of the molten salt in these gels can be seen when considered along with the results observed for the graphite-polymer composite electrodes (3). For these composites, peak charge/discharge behavior was observed for samples with approximately 85% graphite. In these tri-component gels, peak efficiencies were observed when there was only 40%-60% graphite. Clearly, the presence of molten salt in the composite greatly enhances the charge/discharge behavior. This can most likely be attributed to two reasons. First, the presence of the molten salt in the gel reduces the problems caused by swelling of the graphite and its subsequent exfoliation as the ions intercalate and de-intercalate. Secondly, the intimate mixture greatly reduces the diffusion effects upon the charging and discharging of the gel.

Finally, it is important to note that the most significant aspect of these composite gels is that a simple, solid-state battery can be prepared. The solid cell tests clearly show that these thin rubber discs can be compressed together, with a simple separator between them to form a complete, air stable, rechargeable battery. Further examination of other types of polymers, possibly even the somewhat conductive poly-acrylimide gels used in electrophoresis might yield gels that exhibit charge/discharge efficiencies superior to that observed for graphite rods, or even the graphite-polymer composites.

REFERENCES

1. J. Fuller, R. T. Carlin and R. A. Osteryoung, J. Electrochem. Soc., 144, 3881, November (1997).
2. R. T. Carlin, H. C. De Long, J. Fuller, and P. C. Trulove, J. Electrochem. Soc., 141, L73, (1994).
3. T. E. Sutto, C. Sienerth, P. Trulove, and H. De Long, these proceedings.
4. P. R. Gifford and J. B. Palimisano, J. Electrochem. Soc., 134, 610, (1987).
5. J. Fuller, R. T. Carlin, and R. A. Osteryoung, J. Electrochem. Soc., 144, 3881, (1997).
Solid State Test Cell

Pt Wire, Pseudo-Reference

Al Rod

Pt Disc

Filter Paper/Separator

Pt Disc

Al Rod

Drilled Bronze Lead—W. E.

Graphite:DMPIBF(4); Molten Salt Composite Half Cell

Drilled Bronze Lead—C. E.

Figure 1. Schematic of solid-state test cell

Figure 2. Cyclic voltammogram of graphite:DMPIBF$_4$:PVd composite electrode (40%:40%:20%) in DMPIBF$_4$, scan rate 10 mV/s, initial scan direction is cathodic.
Figure 3. Charge discharge behavior for DMPI with a graphite:DMPIBF4: PVD composite electrode (40%:40%:20%). Charging at 1.0 mA/cm², discharging at 0.8 mA/cm².

Figure 4. Charge discharge behavior of BF4 for a graphite:DMPIBF4:PVD (40%:40%:20%) composite electrode. Charging at 1.0 mA/cm², discharging at 0.5 mA/cm².
Figure 5. DMPI⁺ charge discharge behavior vs graphite composition (%) for graphite :DMPIBF₄:PVD composite electrodes.

Figure 6. BF₄⁻ charge discharge behavior vs. graphite composition (%) for graphite :DMPIBF₄:PVD composite electrodes.
Figure 7. DMPI⁺ and BF₄⁻ charge discharge efficiencies vs. DMPIBF₄ composition (%) in graphite:DMPIBF₄:PVD composite electrodes.

Figure 8. Cyclic voltammogram of graphite:DMPIBF₄:PVD composite (42.5%:42.5%:15%) scan rate 20 mV/s, initial scan direction cathodic.
Figure 9. DMPI⁺ charge discharge in the solid state test cell at a graphite:DMPIBF₄: PVD composite electrode (40%:40%:20%). Charging at 1.0 mA/cm². discharging at 0.5 mA/cm².

Figure 10. BF₄⁻ charge discharge in the solid state test cell at a graphite:DMPIBF₄:PVD composite electrode (40%:40%:20%). Charging at 1.0 mA/cm². discharging at 0.5 mA/cm².