ELECTROCHEMICAL INTERCALATION STUDIES
OF 1,2-DIMETHYL-3-PROPYL-IMIDAZOLIUM TETRAFLUOROBORATE AND 1-
ETHYL-3-METHYL-IMIDAZOLIUM TETRAFLUOROBORATE IN GRAPHITE
AND GRAPHITE-POLYMER COMPOSITE ELECTRODES

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ABSTRACT

A comparative electrochemical study of DMPiBF₄ and EMiBF₄ using both Graphite Rods and Graphite-PVdF-HFP Polymer was undertaken to investigate the DIME Battery System, and the relative behavior of the di and tri-substituted imidazolium cations. Both graphite Rod and Graphite-Polymer Composite Electrodes indicated that the tri-substituted imidazole DMPi⁺ exhibited much higher efficiencies than EMI⁺, 91% and 78%, respectively. In both ionic liquids, the anion charge/discharge efficiencies were significantly lower, reaching a maximum value of 71% in DMPiBF₄. Subsequent analysis on various types of graphite/polymer composite electrodes indicated that electrodes composed of approximately 85% graphite and 15% PVdF-HFP Kynar Polymer exhibited enhanced charge/discharge behavior and general stability relative to pure graphite rods.

INTRODUCTION

It has been reported that various 1-ethyl-3-methyl-imidazolium (EMI⁺) and 1,2-dimethyl-3-propyl-imidazolium (DMPI⁺) salts can function not only as electrolytes, but also as the electrochemical intercalates in a simple battery (1). Both the cation and the anion (AlCl₄⁻, PF₆⁻, BF₄⁻) of these molten salts readily intercalate and de-intercalate into graphite rods. These Dual Intercalating Molten Electrolytes (DIME) form the basis of a simple two component battery comprised of the molten salt, and graphite rods as the anode and cathode.
The initial studies of the DIME battery system pinpointed several significant concerns. First, for a substituted imidazolium, the 2,4 and 5 positions are all subject to chemical reactions, most especially the 2 position (2). In the initial studies of the DIME systems, the lack of an alkyl substituent at the 2 position of 1-ethyl-3-methyl imidazolium resulted in poor anode charge efficiencies. In fact, most of these efficiencies were below 50%, while in the case of the 1,2-dimethyl-3-n-propyl-imidazolium, the anode efficiencies were above 90% (1). The EMI⁺ cation possesses inherent instability, which makes it a questionable cation for these DIME systems. Second, both the EMI⁺ and the DMPI⁺ cation exhibited extremely strong exfoliating effects upon intercalation into graphite rods at high charge densities. Therefore, successive intercalation and deintercalation resulted in significant degradation of the electrodes and a marked decrease in the efficiencies with successive cycling (1). Finally, AlCl₄⁻, the anion of choice for much of the molten salt work, is extremely sensitive to moisture and can be used only under the most stringently dry conditions (3).

To further investigate the aspects of the DIME system, a detailed series of electrochemical experiments were undertaken to compare the charge-discharge behavior of EMIBF₄ and DMPIBF₄.

The BF₄⁻ anion was chosen for its chemical stability in air and extremely facile intercalation into graphite (4,5). The DMPI⁺ cation was chosen since it is the simplest tri-substituted imidazolium ring which forms a room temperature molten salt with the BF₄⁻ anion (6). Although initial studies are performed using graphite rods, a series of graphite-polymer composite electrodes were prepared in an attempt to limit the debilitating effects of exfoliation upon the charge-discharge efficiencies.

EXPERIMENTAL

Preparation of the initial salts: EMICl and DMPICl

1-ethyl-3-methyl-imidazolium chloride was prepared as previously reported (3). The preparation of 1,2-dimethyl-3-n-propyl-imidazolium chloride was altered from that previously reported (6) in order to produce a higher yield and a purer product. 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. 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 4 days under nitrogen pressure. Cooling the solution produced a tan-white precipitate and a yellow-red supernatant. 300 ml of ethyl acetate was 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-ethyl-3-methyl-imidazolium tetrafluoroborate and 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 salts are highly soluble in acetonitrile, and NH₄BF₄ is only marginally soluble in acetonitrile (7). However, the secondary product, NH₄Cl, is not soluble in acetonitrile, and this 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 substituted 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 then 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 a 0.45 μ filter disc (Whatman, PTFE Membrane). For the final step in the purification process, the molten salt solutions 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 salts were clear and nearly colorless, with a slight yellow tint to the EMIBF₄ and a slight tan tint to the DMPIBF₄.

Preparation of the Graphite-Polymer Composite Electrodes

Graphite Polymer Composite Electrodes were prepared from 1 micron sized synthetic graphite (99.9995% Aldrich) and poly-vinylidene-difluoride hexafluorophosphate (PVdF-HFP Kynar –2801-00 from Elf Atochem). The graphite-polymer electrodes were prepared based upon the graphite to polymer mass ratios of 1:1, 2:1, 3:1, 4:1, 5:1, and 6:1 (% Graphite for each-50%, 66%, 75%, 80%, 84%, and 85.5%; respectively). Composite electrodes made with the composition of 1:2 (33% graphite) were found to be too non-conductive to be used as electrodes, and pellets of composition

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7:1 (87.5% graphite) failed to maintain structural integrity and readily came apart in the molten salts.

The composite electrodes were prepared by mixing Graphite and the polymer in the appropriate mass ratios. For each composite, the combined mass of the dry powders was 2 g. The two dry powders were placed in a 30 ml beaker, and stirred until the material appeared a homogenous gray color. 15 ml of 4-methyl-2-pentanone (98%, Aldrich) was added to completely dissolve the polymer. The sample vial was sealed and stirred vigorously with a stir bar as the solution was slowly heated to 60 °C. After approximately 2 hours of heating, the mixture became extremely viscous. The sample was removed from the heat, and air cured at room temperature for 24 hours. Samples were placed in a vacuum oven and dried an additional 36 hours under an active vacuum (approximately 10⁻³ torr) at 60 °C.

For the 1:1 sample, the graphite-polymer composite was a well-formed solid, and was simply cut into an easily manageable strip for use as an electrode. For all other samples, the graphite-polymer composite was powdery, and subsequently had to be compressed into a pellet. A pressed pellet composite electrode was prepared by placing 1 g of composite mix into a ½” IR die and compressed at 6 tons/sq. in. for 12 hours. These pellets were annealed at 60 °C under vacuum (10⁻³ torr) for 12 hours. The resulting pellets were extremely hard and stable.

For the 1:1 graphite-polymer composite electrode, strips 0.5 cm wide, 1.5 cm long and approximately 0.2 cm thick were cut from the hardened sample. Electrical contact for these strips was made by clamping the top 0.5 cm of the strip with a flat mouthed copper alligator clamp, and only the bottom 0.7 cm of the strip was placed in contact with the ionic liquid. Electrical contact for the pellets was achieved by drilling a 0.075” hole into the side of a pellet, and inserting a 0.078” diameter platinum wire. After the Pt wire was inserted, the bottom 1” of the wire was coated with a non-conductive epoxy, as was one of the ½” diameter faces of the pellet and the cylindrical edge, leaving only one of the ½” faces open.

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 an AC amplitude of 5 mV. The sample holder for the liquids was a 2” diameter Teflon bar with a ½” hole drilled through the center for the sample. Another ⅛” diameter hole for the thermocouple was drilled 2 mm from and parallel to the ½” hole. This allowed for a very close configuration between the sample and the thermocouple. One end of the ½” diameter sample compartment was plugged with a ½” diameter Al rod, capped with a platinum disc. On top of this, approximately 1 ml of EMIBF₄ or DMPIBF₄ was deposited. To complete the experimental set up, another ½” diameter Al rod, also capped with a platinum disc, was inserted into the Teflon sample holder. Compressing the two Al rods in a microbar clamp completed the cell. Thickness of the sample could be calculated by caliper measurements of the end to end length of the Al rods. This Teflon sample holder was wrapped in Pyrex wool, Al foil, and placed into a well shaped, 500 ml heating...
capped heating mantle. The mantle was attached to a calibrated temperature controller. Temperature equilibration time for each data point was ten minutes prior to measurements. The ionic conductivity was calculated from the measured resistance when the imaginary component at high frequency fell to zero (8).

Cyclic Voltammetry was measured using either an EG&G PAR 273A or 263A Potentiostat/Galvanostat with the M270 ver.4.30 software. 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 ¼" diameter graphite rod (Aldrich, 99.9995%, hardness 50) was used as the counter electrode and, at times, as the working electrode. The surface area ratio of working to counter (also a graphite rod) was 1:5. A 15 ml glass vial fitted with a Teflon cap (three ¼" holes) was used as the cell. All data was collected in a dry box under dry nitrogen. For EMIBF₄, the scan rate was 20 mV/sec. However, due to the greater viscosity of DMPIBF₄, a scan rate of 10mV/sec was required to obtain a detailed cyclic voltammogram.

Charge-Discharge experiments were also performed on an EG&G PAR 273A or 263A Potentiostat/Galvanostat and M270 software. For all anodic charging experiments, the applied current was adjusted such that the surface current density was approximately 0.8 mA/cm². In the case of the ¼" diameter graphite rod, the surface area in solution was approximately 1.25 cm² (rod inserted 5mm into the molten salt) and the applied charging current was 1.0 mA. For the pellets, the surface area of the one exposed, ½" diameter surface was 1.25 cm², and a charging current of 1.0 mA was applied. For the 1:1 sample, where only the bottom 0.7 cm of the strip was placed in the molten salt, the surface area was approximately 1.0 cm², and a charging current of 0.8 mA was applied.

For all of the cathodic charging experiments, the charging current was adjusted such that the surface current density was approximately 0.4 mA/cm². The surface area ratio of the working to counter electrode was adjusted in all cases to a value of 1:5. Thus, for both the pellet and the graphite rod, 3 cm of the rod was inserted into the solution, while only 2.5 cm of the rod was inserted for the 1:1 graphite-polymer composite electrode.

RESULTS AND DISCUSSION

The electrochemical impedance measurements for EMIBF₄ and DMPIBF₄ molten salts at various temperatures are shown in Figure 1. At room temperature, both possess high room temperature ionic conductivity near to the value 5.94 mS/cm observed for 1 M LiPF₆ in Propylene Carbonate Poly(propylene Glycol) (9), 11.55 mS/cm for EMIBF₄ and 5.67 mS/cm for DMPIBF₄. The temperature dependent plots clearly indicate simple, logarithmic temperature dependence. Based upon this logarithmic dependence, the slope of the best-fit line was used to calculate the $E_a$ for both molten salts. The calculated values of 17.36 kJ/mol for EMIBF₄ and 19.40 kJ/mol for DMPIBF₄ correspond well to experimental observations that DMPIBF₄ is more highly viscous than EMIBF₄, thus requiring greater energy in order to ionically conduct.
Cyclic Voltammetry for EMIBF$_4$ and DMPiBF$_4$. Figure 2, indicate both oxidative and reductive intercalation. The scan rate for DMPiBF$_4$ was half that used for EMIBF$_4$, in order to obtain a more detailed cyclic voltammogram, and the current densities for DMPiBF$_4$ were 1/10 of that seen for EMIBF$_4$. In EMIBF$_4$, cation deintercalation occurs at -0.74 V, while it occurs at a higher potential, - 0.495 V for DMPi$^+$. The cathodic behavior of the molten salt was more complicated. A reductive peak at approximately 1.7 V was attributed to trace Cl$^-$ from the unreacted chloride salt of the substituted imidazolium cation. However, for both EMIBF$_4$ and DMPiBF$_4$, the BF$_4^-$ deintercalation, occurred at approximately 1.36 V. The electrochemical window for these molten salts was measured using a 2mm diameter glassy carbon electrode. The anodic endpoint (defined as the point were the I(A) vs. E(v) curve became nearly perpendicular to the x-axis) was -2.3 V for DMPi$^+$, and -2.20 V for EMI$^+$. For both molten salts, the cathodic endpoint was at 2.45 V, resulting in an electrochemical window of approximately 4.7 V for either molten salt.

Figure 3 shows the typical charge discharge behavior of the DMPi$^+$ cation, for graphite rods. Figure 4 shows the charge discharge behavior of the BF$_4^-$ anion. For the anodic charging, the difference between the charging and discharging plateaus was -2.05 V up to 1.65 V upon discharging. For the cathodic charging, the plateaus could be observed at 2.4 V down to -1.55 V. For both anodic and cathodic charge-discharge cycles, the system was considered discharged when the measured potential was equal to the median potential between the initial and final discharge potential plateaus. Typically, a total of 20 charge/discharge cycles were run for each sample. After 4 or 5 cycles, a constant value for the efficiency was observed, which is the value reported.

The current efficiency for the DMPi$^+$ cation in DMPiBF$_4$, using a graphite rod electrode, was 89% at a charging current density of 1 mA/cm$^2$. This is significantly less than the 100% efficiency previously reported for DMPi$^+$ in DMPi-AlCl$_4$ at a charging current density of 1 mA/cm$^2$ (1). Our efficiency for the EMI$^+$ cation in EMIBF$_4$ at a charging current density of 1 mA/cm$^2$ was 73%. This is a significant improvement over the previously reported value of 33% for EMIBF$_4$ at a charging current density of 6 mA/cm$^2$ (1). Our improved EMI$^+$ current efficiency may simply be due to the significantly lower charging current density. For example, in EMI-AlCl$_4$ at charging current density of 1 mA/cm$^3$ the efficiency for EMI$^+$ was 59% (1). Current efficiencies for the BF$_4^-$ anion were generally less than those for the cation in both EMIBF$_4$ and DMPiBF$_4$ molten salts. The BF$_4^-$ current efficiency was 69% and 57% at a charging current density of 1 mA/cm$^2$ in DMPiBF$_4$ and EMIBF$_4$, respectively.

In order to determine the overall stability of each charged intercalate, a series of time-delay experiments were performed. For both the cation and anion, using both graphite rods, and the best graphite-polymer composite electrode, discharging of the anode was delayed from 5 minutes up to 540 minute (9 hours). Figure 5 indicates the results for the 6:1 graphite pellet in EMIBF$_4$ and DMPiBF$_4$. It is clear that DMPi$^+$ exhibits a greater initial efficiency, 91% for the 6:1 graphite polymer composite electrode as opposed to 81% for EMI$^+$, and that it maintains its total charging capacity far longer than the EMI$^+$. Time delay studies of the BF$_4^-$ anion exhibited a significant drop in its discharging efficiencies over time. After 6 hours, the anion discharge efficiency for DMPiBF$_4$ lost half it’s original value, while the EMIBF$_4$ had no discharge efficiency observed.
The interaction between charged, or neutral fluorides, with graphite are characterized by numerous secondary reactions. For instance, intercalation of graphite by AsF₅ results in the oxidation of the graphite layers and formation of two different arsenic fluorides, according to the equation [1] (10):

\[ 3\text{AsF}_3 + \text{Gr}^0 \rightarrow 2\text{AsF}_6^- + \text{AsF}_3 + \text{Gr}^{2+} \]  

Interestingly, BF₃ itself cannot readily intercalate into graphite without the presence of F₂, and it is present between the layers of graphite as a mixture of BF₄⁻ and BF₃ (11). Therefore, under electrochemically driven intercalation reactions, it is possible that some of the BF₄⁻ is causing irreversible oxidation of the graphite layers by generating F, according to the equation [2]:

\[ \text{BF}_4^- + \text{Gr}^0 \rightarrow \text{BF}_3 + \text{Gr}^+ - F^- \]  

This would result in the significantly lower efficiencies observed for cathodic charging of the molten salts (12).

Figure 6 illustrates the cathodic and anodic discharge efficiencies, in both molten salts, for the complete series of graphite-polymer composite electrodes. Optimum efficiencies were observed for composite electrodes with an approximate composition of 85% graphite, 15% polymer (The percent composition of the 6:1 pellet was 85.5% graphite to 14.5% PVD). Less amounts of graphite resulted in a loss of efficiency due to capacitance effects from internal resistance, and higher amounts of graphite were not able to resist exfoliating into the molten salt upon charging, thus exhibiting lower efficiencies. It is interesting to note that the marked increase in efficiency from the 1:1, which was not compressed in the IR die, to the 2:1 pellet could be attributed to the use of pressure to improve graphite particle interactions in the polymer matrix.

**CONCLUSION**

Ultimately, it is clear, that the DMPI⁺ cation is significantly more stable than the EMI⁺ cation. Thus, the tri-substituted imidazolium ring is far more stable towards charge/discharge behavior, and results in efficiencies that are 15 to 20 % greater. Also, the use of graphite:polymer electrodes greatly enhances the efficiencies, yielding systems that will be much more suitable towards eventual, real-life application of these materials as batteries.

Future studies will address the possible use of other air stable anions, such as PF₆⁻ or mixed anion molten salts to improve the cathodic charging efficiencies. Also, two other methods of increasing the overall efficiencies of these materials is to attempt graphite:polymer:molten salt composite electrodes, or to use other layered materials as the operating electrodes.
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Figure 1. Temperature dependent impedance measurements of DMPIBM$_4$ and EMIBM$_4$, with a scanning frequency of 1 Hz to 100 kHz, and an AC amplitude of 5 V.
Figure 2. (a) Scanning Cyclic Voltammogram (SCV) of DMPIBF$_4$ using graphite rod electrodes, a scanning rate of 10 mV/sec; scanned in the cathodic direction initially. (b) SCV of EMIBF$_4$ using graphite rod electrodes, a scanning rate of 20mV/sec; scanned in the cathodic direction initially.
Figure 3. Charge/discharge behavior of DMPI⁺ in DMPIBF₄ at a graphite rod electrode. Charging at 1.0 mA/cm², and discharging at 0.5 mA/cm².

Figure 4. Charge/discharge behavior of BF₄⁻ in DMPIBF₄ at a graphite rod electrode. Charging at 0.8 mA/cm², discharging at 0.4 mA/cm².
Figure 5. Effect of time delay between charge and discharge on cation and anion current efficiencies. Cation charging at 1.0 mA/cm², discharging at 0.5 mA/cm². Anion charging at 0.80 mA/cm², discharging at 0.4 mA/cm².

Figure 6. Relative cation and anion discharge efficiencies for Graphite Polymer Composites vs. % Graphite in composite. (100% composition set as Graphite Rods.)