

**Comparative Electrochemical Behavior of
1,2-Dimethyl-3-n-Propylimidazoium
Trifluoromethanesulfonyl-imide, 1,2-
Dimethyl-3-n-Butylimidazoium
Trifluoromethanesulfonyl-imide, and 1,2-
Dimethyl-3-n-Butylimidazoium**

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It has been reported that various 1-ethyl-3-methylimidazolium (EMI^+) and 1,2-dimethyl-3-propylimidazolium (DMPI^+) salts can function not only as electrolytes, but also as the electrochemical intercalates in a simple battery (1,2). Both the substituted imidazolium cation and the anion (AlCl_4^- , PF_6^- , BF_4^-) of these molten salts readily intercalate and de-intercalate into graphitic electrodes. These Dual Intercalating Molten Electrolytes (DIME) form the basis of a simple two-component battery comprised of the molten salt, and graphitic electrodes as the anode and cathode. Unfortunately, many of the metal halide based ionic liquids are extremely sensitive to moisture and can be used only under the most stringently dry conditions (3). The tetrafluoroborate and hexafluorophosphate anions have been shown to attack graphite upon intercalation, reducing their overall anionic charging efficiencies. Furthermore, the substituted imidazolium cations are subject to chemical reactions at the 2,4 and 5 positions, most notably the 2 position (4). As a consequence, the DMPI^+ , with its 2 position blocked by a methyl group, has proven to be superior to EMI^+ in previous DIME studies.

In the present study, three room temperature Ionic Liquids; DMPI: trifluoromethanesulfonyl-imide (TFMI), 1,2-dimethyl-3-n-butylimidazolium (DMBI):TFMI, and DMBI: NO_3 , were prepared. Conductivity measurements indicated ionic conductivity in the 1-5 mS/cm range at room temperature for all three ionic liquids. Both of the TFMI salts were extremely fluid-like, while the nitrate ionic liquid was extremely viscous and exhibited the lowest ionic conductivity. The TFMI salts exhibited Arrhenius type of behavior over the temperature range studied, from 0° to 120° C. The nitrate ionic liquid, however, showed a marked drop in ionic conductivity below 40 °C, most likely indicating a transition to a glass-like state.

Cyclic Voltammetry was performed using a 2 mm diameter Pt electrode to determine the electrochemical window for the ionic liquids. Both of the TFMI based ionic liquids exhibited a similar electrochemical window of near 4.8 V. The nitrate based ionic liquid exhibited a significantly reduced window towards the cathodic side, and had an overall electrochemical window of near 4.4 V. Cyclic Voltammetry studies, using graphitic paper, indicated strong cationic intercalative behavior for all three ionic liquids studied. The TFMI based ionic liquids also showed strong anionic intercalative behavior, while the anionic intercalative behavior observed for the nitrate anion was considerably less.

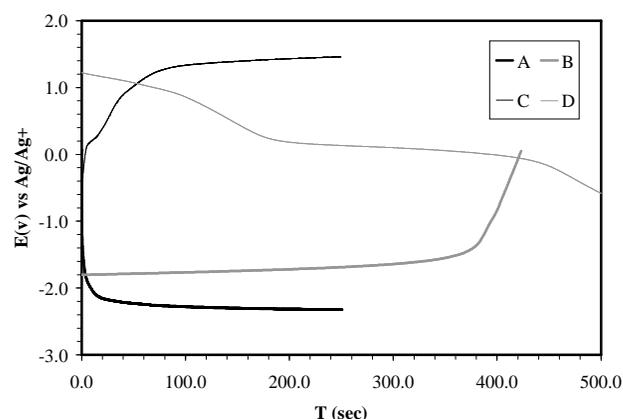


Figure 1: 5. Charge discharge behavior for the three electrode system of DMPITFSI utilizing a 0.5 cm strip of graphite paper as the working electrode and a graphitic rod as the counterelectrode. Voltage scale was determined by the reference electrode, which had a solution of 0.5 M AgBF_4 in EMIBF₄. Cationic charging (A.) was at 0.5 mA/cm², and cationic discharging (B.) was at 0.25 mA/cm². Anionic charging (C.) was performed at a current rate of 0.25 mA/cm² and anodic discharging (D.) was at 0.125 mA/cm².

Using a three electrode system, charge discharge behavior was observed for all three ionic liquids, with the following observed efficiencies: for the DMPITFMI, as shown in Figure 1., the cation exhibited approximately 85% efficiency, and the TFMI anion exhibited near 80% charge-discharge efficiencies; for the DMBITFMI, the cation exhibited approximately 75% efficiency, and the TFMI anion exhibited near 80% charge-discharge efficiencies; however, for the nitrate based ionic liquid, the cation exhibited only 45% efficiency, with no well defined discharge plateau, and the nitrate anion exhibited only 12% charge-discharge efficiencies.

References:

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