Ionic Liquid Battery Electrolytes as Sources for Reversible Graphite Intercalation Anodes for Battery Applications

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An examination of the intercalation of various cations (1,2-dimethyl-3-propylimidazolium (DMPI), 1-ethyl-3-methylimidazolium (EMI), or 1-ethyl-2,3-dimethylimidazolium (EDMI)) into graphite electrodes, in room temperature AlCl₃ molten salts, was undertaken. The reduction process involves making the graphite anionic, which allows for the above cations to incorporate into the graphite matrix. By using the cations of the electrolyte itself, this eliminates the need for separate intercalation compounds. A cell employing a (DMPI)(AlCl₄) electrolyte and two graphite rod electrodes achieved an open-circuit voltage of 3.5 V and a cycling efficiency of 85%.

Introduction

The determination of the behavior of materials in room temperature molten salts is an important step in assessing their suitability for use as electrodes in follow-on battery development. Lithium's use as an intercalation compound in graphite electrodes is known throughout the world.¹ The many improvements (reliability, safety, environmental, and economic) offered by the rocking chair battery over other rechargeable batteries comes primarily from the use of a carbon or graphite anode. The cathodes in these batteries still utilize transition metal oxides of manganese, nickel, or cobalt which are more expensive, less desirable environmentally, and more synthetically demanding than the carbon anode. In addition, the liquid electrolytes in these batteries consist of lithium salts dissolved in a mixture of organic carbonates or ethers, which require rigorous purification. Therefore, the rocking chair battery requires the synthesis, purification, and assembling of multiple active components.
What makes this work unique is that no additional compound is used for intercalation in the graphite except the electrolyte itself. The systems discussed in this paper utilize room-temperature or low-melting molten salts composed of a substituted imidazolium cation and an inorganic anion. The molten salt serves in a multifunctional capacity leading to a battery configuration requiring only two active materials - the molten salt and graphite. This would greatly simplify the construction of a battery cell. Therefore, we wish to report here the initial investigation of reversible ionic electrolyte cation insertion into graphite electrodes as a part of what we term is a Dual Intercalating Molten Electrolyte (DIME) batteries.

**Experimental**

Purification of melt components has been previously described\(^2,3\). The room-temperature 1:1 chloroaluminate molten salts were prepared by combining equal molar quantities of sublimed AlCl\(_3\) with the appropriate organic chloride inside a Vacuum Atmosphere dry box under He with an O\(_2\) + H\(_2\)O concentration of < 5 ppm. Polycrystalline platinum metal and glassy carbon electrodes were purchased from Bioanalytical Systems. Polishing was accomplished using a Struers DAP-V grinder-polisher producing a highly polished disk electrode. The geometric areas of the platinum electrode were 2.011x10\(^{-2}\)cm\(^2\) and the glassy carbon electrode was 7.068x10\(^{-2}\)cm\(^2\). The pretreated, high purity, spectroscopic grade graphite working electrode (Union Carbide) has a geometric area of 1.2cm\(^2\).

All experiments were performed in a UHP helium atmosphere using a Vacuum Atmospheres dry box at room temperature. The counter electrode was an aluminum wire immersed into a portion of the analyte melt contained in a 3 mm OD, E-porosity gas dispersion tube (Ace Glass). The reference electrode consisted of an Al wire immersed in \(N=0.60\) with either a AlCl\(_3\)-DMPI, AlCl\(_3\)-EMI, or AlCl\(_3\)-EDMI melt contained in separate fritted glass or asbestos fiber compartments. Cyclic voltammetry was performed on an EG&G PAR model 273 potentiostat/galvanostat using the M270 version 4 software environment with a Tangent 486DX/33MHz computer.

Protonic impurities in the melts were removed by vacuum treatment at 1x10\(^{-5}\) Torr for several days. Neutral melts of the three cationic species (DMPI, EMI, DMEI) were prepared slightly basic (extra organic salt) to make sure no aluminum would be plating out.
Results and Discussion

DMPI

Staircase cyclic voltammograms for the reductive and oxidative intercalation of graphite in the room-temperature molten salt (DMPI)(AlCl₄) are shown in Fig. 1. The graphite electrochemical intercalation processes occur well within the electrochemical limits of the melt which, at GC, are found at -2.2 V and +2.5 V and correspond to DMPI⁺ reduction and AlCl₄⁻ oxidation, respectively. The electrochemical process at -1.5 V in Fig. 1a involves the intercalation (forward scan) and de-intercalation (reverse scan) of DMPI⁺ into the graphite lattice. The electrochemical window of the melt is large (>4 volts). Using Cyclic Staircase Voltammetry (CSV) gives a reduction process (see Fig. 1) initiating at -1.6 V, which results in intercalation of the cationic species. This intercalation is reversible with 80 to 90 % efficiency for DMPI. Scan rate studies indicate an increasing charge density with decreasing scan rate. This is due to loading more of the cation into the graphite. The electrochemical process at +1.8 probably involves the intercalation and de-intercalation of AlCl₄⁻ into the graphite lattice. Although it has been proposed that graphite oxidation in this melt involves intercalation of Cl₂, the potential of the oxidative intercalation (0.6 V negative of AlCl₄⁻ oxidation to Cl₂) and the lack of known stable chlorine intercalates points towards the formation of an AlCl₄⁻ intercalation compound instead. Numerous chloroaluminate and other metal halide intercalation compounds are known. Therefore, the proposed electrochemical processes in Fig. 1 can be written

\[
\begin{align*}
DMPI^+ + x C + e^- &\rightleftharpoons (DMPI)_{C_x} \quad (1) \\
AlCl_4^- + y C &\rightleftharpoons C_y(AlCl_4) + e^- \quad (2)
\end{align*}
\]

Chronopotentiometric charging and discharging curves for graphite in (DMPI)(AlCl₄) are shown in Figs. 2a and 2b, respectively. The de-intercalation process for DMPI⁺ has a high efficiency, 94%, and a flat potential profile. The charging was done at 1.0 mA and discharge was done at 0.25 mA. Table I shows data for charging at 1.0mA and discharging 1.0-0.25mA to demonstrate the effect of varying the discharge rate at a different constant currents. The data indicates that reducing the discharge current and running at longer times increases the cycling efficiency. From the discharge potentials for the two couples, it should be possible to construct a battery with a voltage of approximately 3 V utilizing only two graphite electrodes. Such a cell was constructed by inserting two 3 mm graphite rod electrodes into the melt. Using the potentiostat in a two-electrode configuration, charge and discharge curves for this cell were collected. The resulting curves are shown in Fig. 2c, and the cell performance parameter are summarized in Table II. The small spikes on the discharge curve are current interrupts used to measure the open-circuit potential at various times during discharge. The net cell
reaction can be written

\[
\text{DMPI}^+ + \text{AlCl}_4^- + (x+y)\text{C} \rightleftharpoons (\text{DMPI})\text{C}_x + \text{C}_y(\text{AlCl}_4)
\]  

(3)

**EMI**

The intercalation processes of (EMI)(AlCl₄) substituted into reactions 1 and 2 were also studied using chronopotentiometry, and results for the (EMI)(AlCl₄) melt are presented as the second set of entries in Table I. Average charge (intercalation) and discharge (de-intercalation) potentials at various current densities are also provided. The cycling efficiencies, defined as \( \% \) efficiency = discharge coulombs/charge coulombs \( \times 100 \), are only approximately 60% for both graphite intercalation processes in this melt. In fact, the EMI⁺ intercalate is unstable and decomposes in a few minutes upon standing at open-circuit. The decomposition may involve reaction of the relatively acidic C-2 proton with the negatively charged graphite lattice. This is supported by the high cycling efficiencies observed for the reductive intercalation of the DMPI⁺ cation (second set of entries in Table I) in which the C-2 proton has been replaced by a methyl group.

A similar cell configuration was tested for the (EMI)(AlCl₄) melt, and these results are also presented in Table II. Both cells exhibit similar potential behavior including an open-circuit potential of 3.5 V immediately after charging; however, the (EMI)(AlCl₄) cycling efficiency is much lower due to the instability of the EMI⁺ intercalate. In reaction 3, the cations and anions for both electrochemical intercalation reactions are provided by the molten salt electrolyte, i.e., the cell operates as a DIME battery.

**EDMI**

Finally, the intercalation process using (EDMIXAICI₄) was studied with chronopotentiometry (see Table I). The data was collected at 100°C using an aluminum block heater. (EDMIXAICI₄) is a solid at room temperature and melts at 70-72°C. The charge and discharge data were better for the EDMI⁺ ion, than for EMI⁺ ion, but the anion charge and discharge were unobtainable due to its instability in this melt. Using a different anion which is more stable at these temperatures or one that lowers the temperature of the resulting EDMI⁺ melt are being researched.

We are also currently investigating the reversibility, capacity, and structure of the graphite intercalates formed in these molten salts as a function of several parameters. In particular, it is well known that the type of graphite or carbon used plays a significant role in the formation of the intercalation compound. The rate and capacity of the intercalation processes will be dependent on numerous parameters including carbon...
structure, temperature, and electrode history.

Conclusion

A single room-temperature or low-temperature molten salt electrolyte can be used to provide the intercalating ions for a rechargeable electrochemical cell utilizing a graphite anode and cathode. This Dual Intercalating Molten Electrolyte (DIME) battery has many practical advantages including (1) inexpensive graphite electrodes are used, (2) only a single molten salt needs to be synthesized and purified, (3) no organic solvents are required, (4) the battery can be assembled in the discharged state, and (5) all components have low toxicity. DMPI ended up having the best overall performance of the cations studied in this report. It demonstrated much higher cycling efficiencies than either of the other cations. This should demonstrate the utility of using the electrolyte itself as the intercalation compound for use in graphite intercalation electrodes.

Acknowledgments

This work was supported by the Air Force Office of Scientific Research.

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Table I. Anion and cation intercalation into graphite using molten salt electrolytes. Charging time is 30 min. unless stated otherwise.

| Molten Salt Electrolyte | Intercalate Ion | T (°C) | $I_{charge}$ (mA cm$^{-2}$) | $E_{charge}$ (V) | $I_{discharge}$ (mA cm$^{-2}$) | $E_{discharge}$ (V) | Cycle Eff % |
|-------------------------|-----------------|--------|-----------------------------|------------------|-------------------------------|---------------------|------------|
| (DMPI)(AlCl$_4$)        | DMPI$^-$       | 30     | 1                           | -1.70            | 1                             | -1.25               | 60         |
|                         | DMPI$^+$       | 30     | 1                           | -1.70            | 0.5                           | -1.36               | 100        |
|                         | DMPI$^+$       | 30     | 1                           | -1.70            | 0.25                          | -1.35               | 94         |
|                         | AlCl$_4^-$     | 30     | 1                           | +2.15            | 1                             | +1.50               | 64         |
|                         | AlCl$_4^-$     | 30     | 1                           | +2.15            | 0.5                           | +1.60               | 86         |
| (EMI)(AlCl$_4$)         | EMI$^-$        | 24     | 1                           | -1.64            | 1                             | -1.47               | 59         |
|                         | EMI$^{a}$      | 24     | 2                           | -1.69            | 2                             | -1.50               | 65         |
|                         | AlCl$_4^-$     | 24     | 1                           | +1.93            | 1                             | +1.6                | 41         |
|                         | AlCl$_4^-$     | 24     | 2                           | +2.01            | 2                             | +1.6                | 64         |
| (EDMI)(AlCl$_4$)$^{b}$  | EDMI$^-$       | 100    | 1                           | -1.63            | 0.25                          | -1.50               | 62         |
|                         | AlCl$_4^-$     | 100    | 1                           | +2.25            | 1                             | -----$^c$           | -----$^c$ |

$^a$Charging time = 60 min.; $^b$Solid at room temperature; $^c$AlCl$_4^-$ is unstable in graphite at this temperature.

Table II. Performance parameters for Dual Intercalating Molten Electrolyte (DIME) cells.

| Molten Salt Electrolyte | T (°C) | $E_{open}$ (V) | $t_{charge}$ (min.) | $I_{charge}$ (mA cm$^{-2}$) | $E_{charge}$ (V) | $I_{discharge}$ (mA cm$^{-2}$) | $E_{discharge}$ (V) | Cycle Eff % |
|-------------------------|--------|-----------------|----------------------|-----------------------------|------------------|-------------------------------|---------------------|------------|
| (DMPI)(AlCl$_4$)        | 30     | 3.52            | 60                   | 1                           | 3.72             | 1                             | 2.92                | 85         |
| (EMI)(AlCl$_4$)         | 24     | 3.54            | 20                   | 1                           | 3.67             | 0.5                           | 3.22                | 44         |
Fig. 1. Staircase cyclic voltammograms at graphite in (DMPI)(AlCl₄) showing (a) reductive intercalation of DMPI⁺ and (b) oxidative intercalation of AlCl₄⁻; scan rate = 50 mV s⁻¹.
Fig. 2. Chronopotentiometric curves at graphite in (DMPI)(AlCl₄) showing (a) DMPI⁺ intercalation (1 mA cm⁻²) and de-intercalation (0.25 mA cm⁻²), (b) AlCl₄⁻ intercalation (1 mA cm⁻²) and de-intercalation (0.25 mA cm⁻²), and (c) cell charging and discharging (both 1 mA cm⁻²).