LITHIUM INTERCALATION INTO GRAPHITE FROM AMBIENT-TEMPERATURE MOLTEN SALTS

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ABSTRACT

The cycling efficiency of lithium intercalation into graphite using the AlCl$_3$:EMIC$_2$:LiCl (EMIC$_2$ = 1-ethyl-3-methylimidazolium chloride) molten salt was studied using staircase cyclic voltammetry and chronopotentiometry. The cycling efficiency of the Li-graphite electrode ranges from 80 to 90% for current densities of 0.2 to 1 mA cm$^{-2}$. At 50 mV s$^{-1}$, the oxidation process occurs at a potential approximately 1 V positive of the reduction process. However, employing slower scans (< 10 mV s$^{-1}$), the separation of the reduction and oxidation processes decreases to only ca. 0.6 V. The lithium intercalation process is essentially identical in the related room-temperature molten salt AlCl$_3$:DMPIC$_2$:LiCl (DMPIC$_2$ = 1,2-dimethyl-3-propylimidazolium chloride). In addition to lithium ion, the organic cation and AlCl$_4^-$ can also be intercalated into graphite.

INTRODUCTION

The room-temperature molten salts composed of AlCl$_3$, 1-ethyl-3-methylimidazolium chloride (EMIC$_2$), and an alkali metal chloride, particularly LiCl and NaCl, have recently been employed as electrolytes for alkali metal electrochemical investigations (1-4). These melts have several unique properties which make them promising candidates for battery electrolytes, including a wide electrochemical window, high inherent conductivity, negligible vapor pressure, high thermal stability, high alkali metal cation concentration, and low alkali metal cation solvation energies. Although it is possible to reduce and anodize elemental lithium and sodium in these melts under certain conditions, their stability is very limited due to reaction with the organic cation (1).
To avoid the problems associated with elemental lithium anodes, we have employed a graphite intercalation anode in these room-temperature molten salts. The intercalation of lithium into a graphite matrix provides a more stable and safer means for lithium utilization (5). We wish to report here the investigation of lithium electrochemistry at a graphite intercalation electrode in the imidazolium-based molten salt electrolytes. In addition, we will present results for intercalation into graphite of the other melts components, i.e., the organic cation and $\text{AlCl}_4^-$.

**EXPERIMENTAL**

Lithium chloride melts, $\text{AlCl}_3:\text{EMICl}:\text{LiCl}$ and $\text{AlCl}_3:\text{DMPICl}:\text{LiCl}$, were prepared as previously described (2). All voltammetric experiments were performed using an EG&G PARC model 273 Potentiostat/Galvanostat controlled with the EG&G PARC 270 software package. The graphite working electrode was a high purity, spectroscopic grade graphite rod with a 3 mm diameter (Union Carbide). The glassy carbon working electrode was a 3 mm disk sealed in Kel-F (Bioanalytical Systems). The graphite rod was pretreated by drying at 400 °C for several hours in air and cooling under vacuum in the dry box antechamber. The reference electrode consisted of an Al wire immersed in a 1.5:1.0 $\text{AlCl}_3:\text{EMICl}$ melt contained in a separate fritted glass tube. The counter electrode was an Al wire dipped into a portion of the analyte melt contained in a 3 mm OD, D-porosity gas dispersion tube (Ace Glass). All experiments were performed in a Vacuum Atmosphere Dry Box under He with an $\text{O}_2 + \text{H}_2\text{O}$ concentration of < 5 ppm.

**RESULTS AND DISCUSSION**

**Lithium Intercalation into Graphite.**

To make certain the electrochemical response of the graphite electrode in the presence of $\text{Li}^+$ was due to graphite reduction with concurrent $\text{Li}^+$ intercalation, a 1:1 $\text{AlCl}_3:\text{EMICl}$ melt ([L]$^+$] = 0 M) and a 1:1.0:0.1 $\text{AlCl}_3:\text{EMICl}:\text{LiCl}$ melt ([L]$^+$] = 0.45 M) were prepared. Staircase cyclic voltammograms (50 mV s$^{-1}$) obtained at a graphite rod electrode in these two melts are shown in Figs. 1a and 1b. It is clear that the redox process centered at -1.4 V in Fig. 1b is due to $\text{Li}^+$ intercalation into the reduced graphite lattice. The reduction process initiated at -1.6 V in both voltammograms is due to intercalation of $\text{EMI}^+$ into the reduced graphite lattice; the -1.6 V reduction potential is well positive of the potential for $\text{EMI}^+$ reduction at glassy carbon at ca. -2.2 V.
Integration of the cathodic and anodic currents in Fig. 1b gives a lithium cycling efficiency (anode charge/cathodic charge) of only 34%. Efficiencies up to 50% are seen for this process at higher scan rates, while lower efficiencies are obtained at slower scan rates. When the reverse scan is extended to +1.0 V, a significant second oxidation process is observed starting at -0.4 V (Fig. 2a). Chemically irreversible lithium reduction at GC is shown in Fig. 2b for comparison. Integration of the anodic current and the total cathodic current in Fig. 2a gives a lithium cycling efficiency of 80%. Slowing the scan rate to < 10 mV s\(^{-1}\), reduces the separation of the intercalation and deintercalation process to ca. 0.6 V, and the more negative oxidation process is completely absent. This lower potential separation and the presence of only the more positive oxidation process is in agreement with the chronopotentiometric experiments discussed below. Staircase cyclic voltammograms performed in 1.1:1.0:0.1 AlCl\(_3\):DMPICl:LiCl (DMPICl = 1,2-dimethyl-3-propylimidazolium chloride) show essentially identical lithium intercalation behavior as the EMICl melt. The intercalation and deintercalation of lithium ions in AlCl\(_3\):DMPICl:LiCl shown in Fig. 3 at 1 mV s\(^{-1}\) illustrates the effect slow scans have on the shape of the redox process. Integration of Fig. 3 gives a cycling efficiency of 84% for lithium in the DMPICl melt.

Battery-relevant cycling efficiencies of the Li-graphite anode were obtained by collecting charge/discharge curves at constant current (double-step chronopotentiometry). Typical charge/discharge chronopotentiograms obtained at a graphite rod electrode in a 1.1:1.0:0.1 AlCl\(_3\):EMICl:LiCl melt are shown in Figs. 4a and 4b, using a current density of 0.5 mA cm\(^{-2}\) for both charging and discharging. The cycling efficiency for the data in Fig. 4 is 82%. In addition, the cycling efficiency at 0.5 mA cm\(^{-2}\) with a 10 min charge remained essentially unchanged when a delay time of 10 min at open-circuit was imposed prior to discharge. Other experiments gave cycling efficiencies from 80 to 90% with 10 min charging and current densities. Using a charge/discharge current density of 0.2 mA cm\(^{-2}\) and charging times of 10 min to 2 hrs, cycling efficiencies from 70 to 90% were obtained. Importantly, the discharge potential was relatively flat and was centered around -0.35 V for all discharge curves.

**Organic Cation and Tetrachloroaluminate Intercalation into Graphite**

Staircase cyclic voltammograms illustrating EM\(\text{I}^+\) reductive intercalation and AlCl\(_4^\text{-}\) oxidative intercalation into graphite in the 1:1 AlCl\(_3\):EMICl (no LiCl) molten salt electrolyte are shown in Fig. 5. 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 EM\(\text{I}^+\) reduction and AlCl\(_4^\text{-}\) oxidation, respectively. The electrochemical process at -1.5 V (Fig. 5a) involves the intercalation and deintercalation of EM\(\text{I}^+\) into the graphite lattice. The electrochemical process at +1.8 (Fig. 5b) probably involves the intercalation and deintercalation of AlCl\(_4^\text{-}\) into the graphite lattice. Although
it has been proposed that graphite oxidation in this melt involves intercalation of Cl\(_2\) (6), the potential of the oxidative intercalation (0.6 V negative of AlCl\(_4^−\) oxidation to Cl\(_2\)) and the lack of known stable chlorine intercalates points towards the formation of an AlCl\(_4^−\) intercalation compound instead (7). Numerous chloroaluminate and other metal halide intercalation compounds are known (8,9).

The relevant parameters for EMI\(^+\) and AlCl\(_4^−\) intercalation, studied with chronopotentiometry, are presented in Table I. The EMI\(^+\) cycling efficiency decreases as the time delay between charging and discharging is increased. This instability of EMI\(^+\) may involve reaction of the relatively acidic C-2 proton with the negatively charged graphite lattice (10). This is supported by the high cycling efficiencies observed for the reductive intercalation of the DMPI\(^+\) cation in which the C-2 proton has been replaced by a methyl group (11).

Because both the cation and anion of the 1:1 AlCl\(_3\):EMICl molten salt can be intercalating in the same system, a battery cell can be constructed by simply inserting two graphite electrode into the melt. Charging of this cell causes oxidative intercalation of the organic cation into the graphite anode and reductive intercalation of AlCl\(_4^−\) into the graphite cathode. The molten salt electrolyte provides both intercalating species, and so, we have termed this cell a Dual Intercalating Molten Electrolyte (DIME) battery. The performance of such a cell using 1:1 AlCl\(_3\):EMICl as the electrolyte is summarized in Table II. Based on a comparison of cycling efficiencies in Tables I and II, it appears the instability of EMI\(^+\) limits the performance of this DIME battery configuration. As expected, better DIME battery performance can be achieved using the AlCl\(_3\):DMPICl molten salt electrolyte instead (11).

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| Intercalating Ion | I\text{charge} (mA cm\textsuperscript{2}) | E\text{charge} (V) | I\text{discharge} (mA cm\textsuperscript{2}) | E\text{discharge} (V) | Time Delay | Efficiency % |
|-------------------|-----------------|-----------------|-----------------|-----------------|------------|--------------|
| AlCl\textsubscript{4}\textsuperscript{-} | 1 | +2.01 | 1 | +1.64 | N/A | 68 |
| AlCl\textsubscript{4}\textsuperscript{-} | 1 | +1.97 | 0.5 | +1.64 | N/A | 79 |
| AlCl\textsubscript{4}\textsuperscript{-} | 1 | +1.95 | 0.25 | +1.65 | N/A | 79 |
| EMI\textsuperscript{+} | 1 | -1.72 | 0.5 | -1.51 | N/A | 49 |
| EMI\textsuperscript{+} | 1 | -1.73 | 0.25 | -1.52 | N/A | 57 |
| EMI\textsuperscript{+} | 1 | -1.73 | 0.25 | -1.51 | 30 min | 51 |
| EMI\textsuperscript{+} | 1 | -1.73 | 0.25 | -1.44 | 4 hr's | 29 |
| EMI\textsuperscript{+} | 1 | -1.73 | 0.25 | -1.27 | 10.5 hr's | 2 |

Table II. Performance parameters for a Dual Intercalating Molten Electrolyte (DIME) battery cell. All runs conducted at 31°C with a charging time of 30 min.

| E\text{open} (V) | I\text{charge} (mA cm\textsuperscript{2}) | E\text{charge} (V) | I\text{discharge} (mA cm\textsuperscript{2}) | E\text{discharge} (V) | Time Delay | Efficiency % |
|------------------|-----------------|-----------------|-----------------|-----------------|------------|--------------|
| -3.14 | 1 | -3.69 | 1 | -3.15 | N/A | 63 |
| -3.36 | 1 | -3.76 | 0.5 | -3.14 | N/A | 60 |
| -3.23 | 1 | -3.71 | 0.25 | -3.25 | N/A | 61 |
| -2.87 | 1 | -3.70 | 1 | -3.12 | 30 min | 62 |
| -2.62 | 1 | -3.70 | 1 | -2.80 | 4.3 hr's | 27 |
| -3.05 | 1 | -3.71 | 1 | -2.80 | 6.1 hr's | 25 |
| ---- | 1 | -3.70 | 1 | -1.40 | 17.5 hr's | 0 |

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Fig. 1. Staircase cyclic voltammograms at a graphite rod in (a) 1:1 AlCl₃:EMICl melt and (b) 1.1:1:0.1 AlCl₃:EMICl:LiCl melt, [Li⁺] = 0.45 M. Scan rate = 50 mV s⁻¹.

Fig. 2. Staircase cyclic voltammograms at (a) a graphite rod and (b) a glassy carbon disk in 1.1:1.0:0.1 AlCl₃:EMICl:LiCl melt. Scan rate = 50 mV s⁻¹.
Fig. 3. Staircase cyclic voltammogram in 1.1:1.0:0.1 AlCl$_3$:DMPICl:LiCl showing lithium intercalation/deintercalation at 1 mV s$^{-1}$.

Fig. 4. Chronopotentiometric (a) charge and (b) discharge curves for a lithium-graphite rod electrode in 1.1:1.0:0.1 AlCl$_3$:EMICl:LiCl melt. Current density is 0.5 mA cm$^{-2}$ for both charging and discharging.
Fig. 5. Staircase cyclic voltammograms at graphite in 1:1 AlCl₃:EMICl showing (a) reductive intercalation of EMI⁺ and (b) oxidative intercalation of AlCl₄⁻; scan rate = 50 mV s⁻¹.