RECHARGEABLE ALKALI METAL AND LI-AL ALLOY ANODES IN IONIC LIQUID ELECTROLYTES

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ABSTRACT

The room-temperature molten salts possess a number of unique properties that make them ideal battery electrolytes. In particular, they are nonflammable, nonvolatile, and chemically inert, and they display wide electrochemical windows, high inherent conductivities, and wide thermal operating ranges. Although the ionic liquids have excellent characteristics, the chemical and electrochemical properties of desirable battery electrode materials are not well understood in these electrolytes. In this paper, we present results for rechargeable lithium and sodium anodes in buffered neutral chloroaluminate melts and lithium and lithium-aluminum alloy anodes in a BF$_4^-$ ionic liquid.

INTRODUCTION

Room-temperature molten salts, also termed ionic liquids, are versatile solvents that have been employed in a variety of research applications, including electrochemistry, spectroscopy, gas separations, and homogeneous catalysis (1-5). Most studies have been performed in chloroaluminate room-temperature molten salts comprised of AlCl$_3$ and an organic cation, either 1-butylpyridinium chloride (BPC) or 1-ethyl-3-methylimidazolium chloride (EMIC) (1,2); however, recent efforts have focused on melts in which the chloroaluminate ions have been replaced with air-stable fluoroanions, such as BF$_4^-$, CF$_3$SO$_3^-$, (CF$_3$SO$_2$)$_2$N$, and (CF$_3$SO$_2$)$_3$C$^-$ (5-8). In addition, other heterocyclic organic cations have been substituted for BPC and EMIC to increase the cathodic end of the electrochemical window and to simplify the preparation of the organic cation (5,8-10).

The room-temperature molten salts possess several properties that make them ideal candidates for battery electrolytes:

- Nonvolatile: The negligible vapor pressure allows the ionic liquid electrolytes to be operated in sealed cells at elevated temperatures without venting. In addition, the lack
of organic vapors eliminates the possibility of vapor ignition, increasing the overall safety of ionic liquid batteries.

- **Nonflammable:** When a direct flame is applied to an ionic liquid soaked in a glass separator, it burns with a flame characteristic of the anion. However, upon removing the flame source, the ionic liquid immediately extinguishes, leaving the remaining electrolyte unaltered. Therefore, a room-temperature molten salt will not ignite and burn as in the case of organic solvents currently used in lithium and lithium-ion batteries.

- **Wide Electrochemical Windows:** The ionic liquid cations and anions are extremely resistant to electrochemical reduction and oxidation, respectively. Therefore, high-voltage anode and cathode materials can be employed in the ionic liquid electrolytes to create cells that operate in excess of 4 V.

- **High Inherent Conductivities:** The ionic liquids are single-component electrolytes that possess ionic conductivities equivalent to the best organic battery electrolytes; therefore, high-power battery systems can be achieved with the ionic liquid electrolytes. Also, the manufacture of these electrolytes is easier than many conventional organic electrolytes that contain both an organic solvent and an ionic salt.

- **Wide Thermal Operating Range:** The room temperature molten salts are thermally stable to greater than 200 °C and, in some cases, maintain liquid electrolyte properties at temperatures well below 0 °C. Therefore, these electrolytes can be safely and reliably employed in batteries intended for operation in harsh, fluctuating temperature environments.

- **Chemically Inert:** The ionic liquid electrolytes are compatible with metals and polymers used in common battery devices; therefore, they do not require any specialized materials of construction or manufacturing technologies.

Although the room-temperature molten salts are exceptional battery electrolytes, the chemical and electrochemical properties of desirable battery electrode materials are not well understood in these liquids. In this paper we will briefly discuss our results on rechargeable lithium and sodium electrodes in chloroaluminate melts containing thionyl chloride and then will present more recent results on lithium and lithium-aluminum alloy electrodes in the \((\text{EMI})(\text{BF}_4)\) ionic liquid.

**EXPERIMENTAL**

Melt preparations followed standard procedures (1,2,6,7). Unless stated otherwise, all experiments were performed under helium or nitrogen atmospheres inside a Vacuum Atmosphere glove box. Electrochemical experiments were accomplished with an EG&G PARC Model 273 Potentiostat/Galvanostat interfaced to a personal computer using the Model 270 software package. The electrodes and electrochemical cells are described in the appropriate references. Potentials are reported versus an Al/Al(III)
reference electrode (Al wire in 1.5:1.0 AlCl₃:EMIC) in chloroaluminate melts and versus an Al wire quasi-reference electrode in the (EMI)(BF₄) electrolyte.

RESULTS AND DISCUSSION

Lithium and Sodium Rechargeable Anodes

High concentrations of alkali metal ions can be introduced into the chloroaluminate room-temperature molten salts by adding an alkali metal chloride (MCI), usually LiCl or NaCl, to a melt initially containing an excess of Al₂Cl₇⁻. The alkali metal salt effectively neutralizes the Lewis-acidic Al₂Cl₇⁻ via the reaction

$$\text{MCl(s)} + \text{Al}_2\text{Cl}_7^- \rightarrow \text{M}^+ + 2\text{AlCl}_4^-$$

[1]

Because the alkali metal chloride is not soluble in the resulting melt, the only anion present is the Lewis-neutral AlCl₄⁻ species. The cations are M⁺ and the heterocyclic organic cation, usually EMI⁺. In these melts, any Al₂Cl₇⁻ ions produced by an electrochemical process are neutralized by excess solid MCl, and any chloride ions formed are precipitated as MCI. Therefore, the ionic liquid is maintained in the Lewis-neutral state, and the system is termed a buffered neutral room-temperature molten salt (11). A number of ternary room-temperature melts with compositions AlCl₃-EMIC-MCI (MCI = LiCl, NaCl, KCl, RbCl, and CsCl) have been prepared and studied (10-13).

We have examined the alkali metal couples in the buffered neutral melts and have found that only lithium and sodium with standard reduction potentials of -2.066 (± 0.005) and -2.097 (± 0.050) V vs. Al/Al(III), respectively, can be electrodeposited before reduction of the organic cation (12). Despite these thermodynamic indications, elemental lithium and sodium cannot be electrodeposited from the pure buffered neutral melts. Instead, researchers have found it necessary to add a source of hydrogen chloride -- HCl₂ (10,13-15), gaseous HCl (16), or a hydrogen chloride salt (17) -- to the melt before elemental lithium and sodium can be deposited and stripped at an inert substrate electrode. However, because hydrogen chloride volatilizes from the melts, the desired deposition-stripping behavior can only be maintained by adding HCl₂ at regular intervals, controlling the gaseous HCl partial pressure, or introducing a large excess of a hydrogen chloride salt. Therefore, addition of hydrogen chloride is not an ideal method for achieving rechargeable alkali metal anodes in these melts.

More recently we have achieved reversible lithium and sodium deposition-stripping behavior in chloroaluminate ionic liquids by adding small quantities (< 100 mM) of thionyl chloride, SOCl₂, to the electrolyte (18). The cycling efficiencies in the presence of the thionyl chloride solute are > 90%, and the deposited alkali metals exhibit improved stability under open-circuit conditions. In addition, the low volatility of SOCl₂ (b.p. =
75.8 °C) maintains the high cycling efficiencies, even in an open vessel, for extended times. A more detailed discussion of this system is presented in an accompanying paper by Fuller and Carlin in this proceedings.

The dramatic improvements in the cyclability of lithium and sodium in the presence of SOCl\(_2\) have been attributed to the formation of a thin, stabilizing solid-electrolyte interphase (SEI) at the electrode-electrolyte interface. This SEI has been extensively studied for lithium and lithium-ion electrodes in organic solvents (19), but less so for sodium (20,21). The SEI is formed by reaction of the alkali metal with components in the electrolyte to produce inorganic salts, such as LiCl, Li\(_2\)O, and Li\(_2\)CO\(_3\). To achieve a stable rechargeable system, the SEI must be a good ionic conductor for the ion of the alkali metal comprising the active electrode. In chloroaluminate ionic liquids containing SOCl\(_2\), we believe the SEI is composed of LiCl or NaCl, depending upon the alkali metal ion present in the melt. Figure 1 illustrates the formation and function of the SEI at lithium: (A) bare substrate electrode in buffered neutral AlCl\(_3\)-EMIC-LiCl containing SOCl\(_2\); (B) electrodeposited Li; (C) reaction of Li with SOCl\(_2\) to produce a protective LiCl SEI layer; (D) Li\(^+\) transport through the SEI during charge and discharge.

**Lithium Anodes in (EMI)(BF\(_4\)).**

We have recently found that < 100 mM H\(_2\)O in (EMI)(BF\(_4\)) + 0.2 M LiBF\(_4\) promotes the electrodeposition and stripping of lithium metal from this non-chloroaluminate ionic liquid (22). A cyclic voltammogram at Pt (area = 0.02 cm\(^2\)), illustrating the deposition-stripping of lithium and the wide electrochemical window afforded by this system (> 5 V), is shown in Fig. 2. The Li/Li\(^+\) couple found at -3 V is referenced to a quasi-reference electrode. The cycling efficiency in this voltammogram is only 60%; however, this may be improved by future optimizations.

The H\(_2\)O is believed to form a Li\(_2\)O or LiOH SEI on the electrodeposited lithium metal in a manner similar to the LiCl SEI depicted in Fig. 1. In addition, a number of reduction processes occur at the Pt working electrode before lithium deposition. Figure 3 shows an expanded view of the cathodic portion of Fig. 2 overlaid with additional scans in which the potential was switched before lithium deposition. Several small waves are found in this region and are attributed to direct reduction of water at Pt and/or to electrochemical alloying of lithium with the Pt surface. We believe these initial reduction processes act to passivate the Pt electrode towards reduction of the EMI\(^+\) cation and cause the cathodic window limit of the melt to shift to more negative potentials.

**Lithium-Aluminum Alloys in (EMI)(BF\(_4\)).**

The extraordinary interest in Li-carbon anodes for Li-ion batteries with organic electrolytes prompted us to examine the possibility of using an intercalating lithium-graphite anode in an AlCl\(_3\)-EMIC-LiCl room-temperature molten salt. Initial results...
appeared to show a lithium ion intercalation at -1.4 V, but the process assigned as the deintercalation occurred at -0.1 V (23). Subsequent studies in our laboratory have shown that the process at -1.4 V is not the intercalation of lithium into the graphite lattice, but instead, it is the reduction of $\text{AlCl}_4^-$ from the buffered neutral melt. This reduction is promoted by the presence of the lithium ion in the melt and results in the formation of an, as yet unidentified, Li-Al alloy phase (Eq. 2).

$$ (4 + x) \text{Li}^+ + \text{AlCl}_4^- + (3 + x) e^- \rightarrow 4 \text{LiCl(s)} + \text{Li}_x\text{Al(s)} \quad [2] $$

Unfortunately, the products of Eq. 2 slowly coated the graphite surface with a film of solid LiCl and a black Li$_x$Al alloy, making it impossible to use the Li-Al alloy as a reversible electrode (24). Also, it eliminates the possibility of using an aluminum current collector in the buffered neutral chloroaluminates melts and precludes the possibility of accessing the $\beta$-LiAl phase which should form at +0.35 V from the Li/Li$^+$ couple (25).

To overcome these limitation inherent to the AlCl$_3$-EMIC-LiCl melts, we have performed preliminary studies of Li-Al alloy formation in an (EMI)(BF$_4$) melt containing 0.2 M LiBF$_4$. In these studies, an Al wire (area $\approx 1 \text{ cm}^2$) was used as the working electrode and experiments were performed on a lab bench and were exposed to the ambient atmosphere. Cyclic voltammetric scans at the Al wire in (EMI)(BF$_4$) + 0.2 M LiBF$_4$ are shown in Fig. 4. Formation of a Li-Al alloy at -2.72 V (versus an Al quasi-reference electrode) is clearly present, while the anodic window limit at Al is at ca. +2.5 V. The cycling efficiency for the $\beta$-LiAl anode was measured consistently at $\geq 90\%$, even under these unoptimized studies.

The potential for alloy formation is compared to the Li/Li$^+$ reduction potential in Fig. 5 where the Li/Li$^+$ couple is measured at a Pt electrode in the same melt and under identical experimental conditions. The Li/Li$^+$ potential is at -3.07 V. Therefore, the reduction potential for the Li-Al alloy is +0.35 V more positive than elemental lithium and is in agreement with the potential expected for the $\beta$-LiAl alloy phase (25). This alloy has an electricity storage capacity of 790 Ah kg$^{-1}$. At this time it is not clear if water is needed for alloy formation; however, preliminary data indicates that water is required only to shift the EMI$^+$ reduction to more negative potentials, discussed above, and not to form an SEI on the alloy surface.

Finally, chronopotentiometric experiments were performed in the (EMI)(BF$_4$) + 0.2 M LiBF$_4$ ionic liquid at an Al wire as the $\beta$-LiAl anode substrate and at a commercial Li$_4$CoO$_2$ cathode material. The charge and discharge chronopotentiometric curves for these two electrode materials are shown in Fig. 6. The $\beta$-LiAl electrode is well behaved with charge and discharge potentials (0.5 mA cm$^{-2}$) of -2.81 and -2.52 V, respectively. The Li$_4$CoO$_2$ electrode displays charge and discharge potentials of 1.46 and 1.05 V with
an open-circuit potential of ca. 1.34 V. Therefore, a properly engineered β-LiAl\((\text{EMI})(\text{BF}_4)\) + LiBF\(_4\) | Li\(_x\)CoO\(_2\) cell is expected to have an operating voltage of ca. 4 V.

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Figure 1. SEI formation and function at lithium. See text for description.

Figure 2. Cyclic voltammetry at Pt (area = 0.02 cm²) in (EMI)(BF₄) containing 0.2 M LiBF₄ and < 100 mM H₂O.
Figure 3. Expanded view of the cathodic portion of Fig. 2.

Figure 4. Cyclic voltammograms at an Al wire in (EMI)(BF₄) + 0.2 M LiBF₄.
Figure 5. Cyclic voltammograms at Al (curve A) and at Pt (curve B) in (EMI)(BF₄) + 0.2 M LiBF₄.

Figure 6. Chronopotentiometry at an Al wire anode (charge A; discharge B) and at a LiₓCoO₂ cathode (charge C; discharge D) in the (EMI)(BF₄) + 0.2 M LiBF₄.