STUDIES OF THE CATHODIC LIMIT OF PROTON-MODIFIED ROOM TEMPERATURE CHLOROALUMINATE MOLTEN SALT ELECTROLYTES

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ABSTRACT

When protons in the form of HC12 are added to a 1-methyl-3-ethylimidazolium chloride/A1C13 melt, buffered with sodium chloride, the negative voltage limit shifts farther negative from -2100 mV to -2400 mV (vs. a reference of Al in an N = 0.6 melt). When protons are added to a similar neutral melt without NaCl present, no such shift occurs. It has previously been shown that in the proton-modified melts sodium is plated on Pt electrodes, and it is believed that the limiting reduction process is for the methylethylimidazolium cation (MEI+). Thus, both added protons and a sodium surface are necessary to shift the reduction of MEI+ and widen the voltage limit. FTIR studies are underway to try to identify the product of MEI+ reduction.

INTRODUCTION

Sodium chloride buffered room temperature chloroaluminate molten salts made by mixing 1-methyl-3-ethylimidazolium chloride (MEICl) and AlC13 are being evaluated as possible battery electrolytes. These buffered melts provide a stable 4V window and a water-free environment needed for the use of alkali metal anodes. In spite of this wide voltage window (approximately +2.2V to -2.2V vs a reference electrode of Al in an N=0.6 melt) the window does not extend to negative enough voltages to observe the reversible reduction of Na+. Riechel and Wilkes [1] have shown that the voltage window can be extended about 200 mV more negative by the addition of a proton-rich melt, 1-methyl-3-ethylimidazolium hydrogen dichloride (MEIHCl2) [2]. The resulting proton-modified melt allows the reversible plating and stripping of sodium at Pt and W electrodes [1].

To be useful in a rechargeable battery the sodium deposited on these inert electrodes must be stable, but also easily stripped. Riechel and Wilkes showed that the
plated surface was stable for over five hours, but the stripping process often exhibited two peaks. It was suggested that the product of MEI+ reduction is plated and stripped along with sodium, and that the resulting organic film protects the sodium metal from reacting directly with the melt.

In this paper we explore the redox chemistry of MEI+ and its relationship to plated sodium. Electrochemical studies will be reported concerning the cathodic voltage limit change as MEIHC12 is added to the buffered melt. FTIR studies are underway to help identify the MEI+ reduction product that coats the electrodes.

EXPERIMENTAL

Cyclic voltammetry and controlled potential electrolysis were performed using a Bioanalytical Systems (BAS) Model 100A Electrochemical Analyzer. A three electrode cell was used with a BAS Pt working electrode, a Pt flag auxiliary electrode, and a reference electrode consisting of an Al wire in an N=0.6 MEICI/AlCl3 melt. All electrochemical experiments were carried out in a Vacuum Atmospheres glove box under a dry nitrogen atmosphere.

Preparation of the sodium chloride buffered MEICI/AlCl3 melt and the MEIHC12 melt have been described previously [1-3] and are straightforward. The formation of the protonic melt with the extended voltage window requires the dropwise addition of MEIHC12 to the NaCl buffered MEICI/AlCl3 melt until the melt becomes thick and cloudy in appearance. This physical change corresponds to the observation of sodium plating and stripping via cyclic voltammetry [1].

For FTIR examination of coated electrodes an air tight electrode cap has been made and fitted with a 13x2 mm KCl window. FTIR spectra will be recorded using a Perkin Elmer Model 1800 spectrometer integrated with a Spectra Tech IRPLAN microscope.

RESULTS AND DISCUSSION

Gray, Winnick, and Kohl [4] have also investigated the proton-modified melt by bubbling HCl(g) directly through the neutral, NaCl buffered melt. They found that an HCl partial pressure of at least 6mm Hg was necessary to shift the voltage limit and observe sodium plating. But the sodium reduction peak was difficult to resolve from the MEI+ reduction peak and the product of MEI+ reduction has not been identified. Scordilis-Kelley and Carlin [5] used a similar melt modification (MEIHC12 added to a LiCl buffered melt) to separate the reduction peak for Li+ from the solvent window and measure the standard reduction potential for lithium. To avoid overlap and measure the standard reduction potential for sodium they modified a 1,2-dimethyl-3-
propylimidazolium chloride/AlCl₃ melt, which has a more negative potential window. These workers concluded that HCl₂⁻ causes the reduction potential of MEI⁺ to shift negatively, and may slow down the oxidation of Li(s) and Na(s) by organic cations. Since the stability of Na(s) and its reversible plating and stripping are critical for its use in such electrolytes, we are attempting to characterize the process occurring near the voltage limit and to identify the MEI⁺ reduction product that sometimes coats the electrode.

As seen in Figure 1, for the proton-modified NaCl buffered melt, sharp plating and stripping peaks for sodium are observed if the potential is not scanned too far negatively. When a scan proceeds too far into the limiting voltage process, the sodium reduction peak appears as only a shoulder, and no stripping peak is observed (Fig. 2). Following controlled potential electrolysis to plate sodium, two peaks are often observed when anodic stripping is subsequently performed (Fig. 3). These data show that it is difficult to separate the reduction of Na⁺ from that of MEI⁺.

In order to optimize the separation of these two reduction processes we have attempted to correlate the shift in the potential window limit to the amount of HCl present in the melt. Since the definition of the voltage limit depends on the amount of current deemed allowable, we have carried out preliminary experiments monitoring the decrease in current at a fixed potential on the leading edge of the limiting reduction process. The data given in Table 1 clearly indicate that as the Wt. % HCl in the melt increases, the potential of the limiting reduction process shifts negatively, and the current at —2.10V drops by a factor of ten. This means that the reduction of MEI⁺ becomes progressively more difficult as the presence of HCl₂⁻ impedes that process.

From another series of experiments, we have plotted the potential corresponding to a current of 10 µA, representing the negative voltage limit, when various amounts of MEIHC1₂ have been added. Figure 4 shows that the limiting voltage changes linearly from about —2100 mV to —2400 mV. This represents a 300 mV shift in the reduction potential of MEI⁺.

A similar experiment was carried out adding MEIHC1₂ to a neutral, unbuffered (no NaCl) melt. In this case (Figure 5) the background currents rose significantly and chloride oxidation was apparent at 1.3V (because the melt was not buffered), but there was no shift in the negative voltage limit. This means that the sodium surface on the plated electrode is required for the shift in the MEI⁺ reduction potential observed in proton-modified buffered melts.

In efforts to identify the MEI⁺ reduction product by FTIR spectroscopy, we are examining neutral, neutral buffered, and neutral buffered proton-modified melts. Lewis basic, neutral, and acidic melts have been examined previously and their IR spectra reported [6]. We are recording spectra of the melts between KCl windows and have
constructed an air-tight electrode cap for use with plated electrodes. If reduction of MEIr leads to significant structural changes, this should be observable in the IR spectra.

From the above studies we hope to learn how to stabilize the sodium plated on inert electrodes in the proton-modified melts.

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Fig. 1. Cathodic scan cyclic voltammogram of a Lewis neutral, NaCl buffered, MEICl/AlCl₃ melt after the addition of MEIHC₆, at a Pt working electrode. Scan rate: 100mV/sec.

Fig. 2. Cathodic scan cyclic voltammogram of the melt described in Fig. 1. (Scan rate: 100mV/sec.) The scan proceeds beyond the negative potential limit of the electrolyte.
Fig. 3. Anodic scan cyclic voltammogram of the melt described in Fig. 1 after plating for 1 min. at $-2.5V$. Scan rate: 100mV/sec.

Table 1
Current for the Cathodic Solvent Peak at $-2.10V$

| Wt. % HCl in Melt | Current (amps) |
|------------------|----------------|
| 0                | $1.05 \times 10^{-5}$ |
| 0.014            | $1.02 \times 10^{-5}$ |
| 0.055            | $9.66 \times 10^{-6}$ |
| 0.137            | $7.73 \times 10^{-6}$ |
| 0.259            | $4.83 \times 10^{-6}$ |
| 0.299            | $3.95 \times 10^{-6}$ |
| 0.406            | $9.88 \times 10^{-7}$ |
Fig. 4. Plot of the limiting potential corresponding to a 10 \( \mu \)A current in cyclic voltammograms of a Lewis neutral, NaCl buffered, MEICl/AlCl\(_3\) melt as a function of the amount of MEIHCl\(_2\) added.

Fig. 5. Cathodic scan cyclic voltammogram of a Lewis neutral, unbuffered, MEICl/AlCl\(_3\) melt after the addition of MEIHCl\(_2\), at a Pt working electrode. Scan rate: 100 mV/sec.