THE ELECTROCHEMISTRY OF ALUMINUM AND PROTONS IN ROOM TEMPERATURE CHLOROALUMINATE MOLTEN SALTS BUFFERED WITH SODIUM CHLORIDE

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ABSTRACT

As an electrolyte the Lewis neutral, room temperature, chloroaluminate molten salt, MEICI/AICI₃ (MEICI = 1-methyl-3-ethylimidazolium chloride) provides a voltage window of greater than 4V. To maintain this voltage window, the electrolyte must be buffered by a chloride salt such as NaCl. In the present work the electrochemistry of a NaCl buffered melt was studied using Pt, W, and glassy carbon electrodes. When excess NaCl is added to an N=0.55 melt a "neutral" melt results, saturated with NaCl. On Pt and W electrodes, the cyclic voltammetry shows several small overlapping reduction peaks which lead to a small, but distinct oxidation peak at about -0.1V (vs an Al/Al³⁺ N=0.6 melt reference). Comparison to the voltammogram of an N=0.5002 melt (no NaCl) suggests that the oxidation process is aluminum stripping. Voltammograms of the neutral melt and N=0.5002 melt after prolonged reductions both display very large, sharp stripping peaks. The potential of the stripping peaks does not match that of a very acidic N=0.55 melt. This is because the stripping peak shifts from about -0.1V to 0.3V as the Lewis acidity increases from neutrality to N=0.55. The presence of the Al stripping peak in the voltammogram of the buffered melt means that this melt is still slightly Lewis acidic even when saturated with NaCl.

Although treated with ethylaluminum dichloride, residual protons are still present in the buffered melts. Overlapping reduction peaks in the voltammograms lead to a sharp, intense oxidation at 0.8V on a Pt electrode. Using a W electrode the peak is less pronounced, and it is absent from voltammograms obtained using a glassy carbon electrode. On the metal electrodes protons are believed to be reduced leading to adsorbed H₂, which then is oxidized near 0.8V.

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INTRODUCTION

Lewis neutral room temperature chloroaluminate molten salts made by mixing 1-methyl-3-ethylimidazolium chloride (MEICl) and aluminum chloride are being investigated as possible battery electrolytes because of their wide potential windows (1,2). It has been shown that such Lewis neutral (N=0.5) MEICl/AlCl₃ melts can provide a voltage window of 4.4V(2). To maintain this voltage window, the electrolyte must be Lewis buffered, which can be achieved by the addition of alkali chloride salts such as NaCl(3). If the Lewis acid AlCl₃ is added to a buffered melt, reaction with NaCl produces the neutral species, AlCl₄⁻. If the Lewis base MEICl is added, the chloride ion is removed by precipitation with sodium ion. Thus, such a melt is buffered against the addition of both Lewis acids and bases and a wide voltage window can be maintained in the presence of other species.

Although a few studies of alkali metal reductions in neutral and/or buffered melts have appeared (4-7), no detailed examinations of the melts themselves have been made. We present here a detailed investigation of the electrochemistry of NaCl buffered MEICl/AlCl₃ melts at Pt, W and glassy carbon electrodes. Within the voltage window established by the buffered melt, the cyclic voltammograms show several small reduction and oxidation peaks which correspond to low concentrations of aluminum species and residual protons.

EXPERIMENTAL

Instrumentation

Cyclic voltammetry and chronoamperometry were performed using a Princeton Applied Research (PAR) Model 273 Potentiostat/Galvanostat interfaced to a personal computer using PAR 270 software. A three-electrode system was used. The working electrode was either a Bioanalytical Systems (BAS) model MF-2013 Pt electrode, a BAS model MF-2012 glassy carbon electrode, or a homemade W electrode consisting of a W wire, 0.5 mm dia., 99.98% (Alfa), sealed in a Pyrex tube and polished smooth. The auxiliary electrode was a Pt flag and the reference electrode was an aluminum wire, 0.58 mm dia., 99.999%, (Alfa), inserted into an N=0.60 MEICl/AlCl₃ melt in a Pyrex tube with an asbestos tip for the junction. All electrochemical experiments were carried out in a Vacuum Atmospheres dry box under a helium atmosphere estimated to contain combined oxygen and water of less than 10 ppm.

Scanning electron microscopy was carried out using an Amray Model 1830 scanning electron microscope. The SEM was fitted with an ECON IV EDAX detector from which energy dispersive spectra of electrode surfaces were obtained.
The data was processed with PV9900 software and ZAF corrections were made when possible.

Reagents and Melt Synthesis

Sodium chloride (Aldrich, 99.999%) was dried in an oven before use. Acetonitrile (Fisher, HPLC grade) was refluxed over P₂O₅ before use.

The melt components, MEICl and AICI₃ were made and purified as described earlier (1,3). The melts were made in the glove box by the slow addition of AICI₃ to MEICl. Protons were removed from Lewis neutral melts by the dropwise addition of ethylaluminum dichloride (Aldrich, 97%) (8). Neutral buffered melts were made by first slowly adding enough AICI₃ to MEICl to form an N=0.55 (acidic) melt. Based on the calculated concentration of Al₂Cl₇⁻, a 20% excess of NaCl was added and the melt was stirred overnight before use. Cyclic voltammetry indicated that the melt was neutral by the absence of both the reduction peak for Al₂Cl₇⁻ and the oxidation peak for Cl⁻. For plating experiments followed by SEM examination, the buffered melts were filtered before use to remove the excess NaCl.

RESULTS AND DISCUSSION

Several steps are involved in preparing a NaCl buffered neutral melt (3). A neutral melt is first made by adding AICI₃ to MEICl to reach a 1:1 stoichiometry, (N (mole fraction AICI₃) = 0.5). Since such melts always contain some protonic impurities, EtAlCl₂ is added to reduce the protons to a residual level (8). The cyclic voltammogram of the resulting melt is flat and has a voltage limit of greater than 4V. At a Pt electrode the window is 2.4V to -2.2V (7). Because of their activity on Pt, the residual protons still show up as two low current, broad, overlapping reduction peaks between 0.0 and -1.0V. Less pronounced oxidation peaks sometimes are evident at positive potentials.

The next step in preparing a buffered melt is to make the melt Lewis acidic by adding AICI₃. More acidic melts will give higher buffer capacities since more chloride salt is required to neutralize the Al₂Cl₇⁻. Typically an N=0.55 melt is used. The cyclic voltammogram of such a melt is given in Fig. 1. The Al₂Cl₇⁻ is reduced to Al⁰ at -0.38V. The plated aluminum is stripped from the electrode at 0.30V. The crossing of the two scan segments at -0.2V is indicative of a plating/stripping couple. Integration of the peaks indicates that 97.6% of the Al is stripped off. (Note that integration of the reduction peak includes the area under part of the reverse scan segment.)
To buffer the melt, NaCl is added to neutralize the Lewis acid:

\[ \text{NaCl} + \text{Al}_2\text{Cl}_7^- \rightarrow \text{Na}^+ + 2\text{AlCl}_4^- \]

Based on a 1:1 stoichiometry, NaCl is added in a 20% molar excess over Al₂Cl₇⁻. The melt is stirred >12 hours to ensure equilibration. (The melt may also be heated up to 90°C to promote more rapid reaction.)

For the present work, buffered melts were prepared as described above and the resulting cathodic scan cyclic voltammogram using a Pt electrode is shown in Fig 2. Besides small proton reduction peaks in the 0.0 to -1.0V region, two new reduction peaks and two new oxidation peaks appear. The reduction peak at -1.2V is present on all cathodic scans, while the -1.6V reduction peak is not present on voltammograms using a freshly polished electrode. The anodic scan segment shows a small but distinct oxidation peak at about -0.1V and a large oxidation spike at 0.8V. (See also Fig. 1, ref. 7.) The rest potential of the system is about 1.0V, which is positive of both oxidation peaks. Thus, an initial anodic scan shows no oxidations (Fig. 3). This means that the oxidation peaks must be a result of the reduction processes rather than due to species originally present in the melt.

To determine which reduction peaks lead to the oxidations, a negative scan limit study was done. Several cathodic scan voltammograms were recorded, reversing the scans just after each reduction peak, proceeding more negatively with each experiment. The 0.8V oxidation first appeared when reversing the scan at -0.54V, while the -0.1V oxidation only appeared on scans going to -1.40V or more negative. The oxidation peaks get larger with more negative scans, but scanning beyond -2.0V leads to a black passivating film on the electrode. The reduction process at -0.3V and other small peaks may be proton reductions and seem to lead to the 0.8V oxidation. (This will be discussed later, in comparison to the results on W and glassy carbon electrodes.)

The reduction peak at -1.2V or a process buried under the broad reduction envelope, gives rise to the oxidation peak at -0.1V. The potential and shape of this peak suggest that it may be an Al stripping peak. To pursue this, a variety of chronoamperometry experiments were carried out at -1.4V. In most cases the electrodes were rinsed in acetonitrile after plating, to remove the melt. The plated electrodes were then examined with a scanning electron microscope and deposits on the surface were analyzed by collecting energy dispersive spectra. Although some spectra indicated excess aluminum (compared to that expected for residual AlCl₃) the results did not conclusively show Al plating.
Further electrochemical experiments were done to identify the -0.1V oxidation peak. Chronoamperometry was again carried out at -1.4V. Immediately after this reduction process, a two-cycle anodic voltammogram was recorded (Fig. 4). On the first cycle there is a very sharp, intense, oxidation peak near the potential of the -0.1V oxidation of the original voltammogram. On the second cycle this peak is gone. This data suggests that Al is plated during the chronoamperometry step and stripped completely by one voltammetric scan.

Although the shape of the -0.1V oxidation peak is indicative of a stripping process, it does not match the shape or potential of Al stripping in an N=0.55 melt (Fig. 1). To investigate these differences, incremental additions of AlCl$_3$ were made to a neutral, unbuffered (no NaCl) melt. The first addition of AlCl$_3$ resulted in an N=0.5002 melt, whose voltammogram is given in Fig. 5. The reduction and oxidation peaks are quite similar to those seen in Fig. 2 for a buffered melt. Anodic scans produced no oxidations until a few complete cycles had been completed. Cathodic scans to -0.7V led to the 0.8V oxidation, while scanning to -1.6V was required before the -0.1V oxidation appeared.

Chronoamperometry at -1.6V was carried out in an experiment analogous to that for the buffered melt. The resulting voltammogram recorded immediately after the reduction step is shown in Fig. 6. Clearly, a stripping process occurred just as in the buffered melt experiment (Fig. 4). (A chronoamperometry experiment was also carried out at -1.3V on a neutral, unbuffered melt as a blank. No stripping peak was observed on the subsequent voltammogram.) These data indicate that a buffered melt is slightly Lewis acidic and permits the plating and stripping of Al.

Further additions of AlCl$_3$ were made to the neutral, unbuffered melt to investigate the shape and potential of the stripping peak as the concentration of Al$_2$Cl$_7^-$ is increased. Melts with compositions of N=0.501, 0.510, and 0.530 were investigated. As the Lewis acidity increased, the Al plating and stripping peaks began to resemble those of the N=0.55 melt (Fig. 1). (The small reduction peaks and the oxidation at 0.8V disappeared due to the compressed current scale.) Specifically, the stripping peak became broader and shifted to more positive potentials, verifying its assignment to Al.

Nearly all of the experiments described above were also carried out on W with similar results. Figure 7 is a cathodic scan cyclic voltammogram of the NaCl buffered melt. It is quite similar to the Pt voltammogram (Fig. 2) except that the 0.8V oxidation peak is much less pronounced. An anodic scan shows no oxidations until after the scan proceeds through the reduction waves. The results of a negative scan limit study were similar to those on Pt, indicating that the reduction process at -1.4V is responsible for the -0.1V oxidation. The results of a plating
experiment at -1.4V are shown in Fig. 8. This anodic scan voltammogram was recorded immediately after plating and shows the -0.1V stripping peak as seen on Pt (Fig. 4). A similar plating experiment was done at -1.6V on W in the N=0.5002 melt. The resulting voltammogram again showed the sharp stripping peak at -0.1V. (The blank experiment on a neutral, unbuffered melt showed no peak).

The potential of the -0.1V oxidation peak was also monitored as a function of melt composition. As on Pt, the peak shifted positively as more AlCl₃ was added to the N=0.5002 melt.

Table I compares the Al stripping potentials for buffered, slightly Lewis acidic, and neutral unbuffered melts at Pt and W electrodes. In Lewis acidic melts Al₂Cl₇⁻ is reduced via the reaction:

\[
4\text{Al}_2\text{Cl}_7^- + 3e^- \rightarrow \text{Al} + 7\text{AlCl}_4^- \tag{9}
\]

For an N=0.5002 melt, [Al₂Cl₇⁻] = 3.70 x 10⁻³M. The data indicate that for the buffered melt Al₂Cl₇⁻ is near this concentration and hence the melt is slightly Lewis acidic.

Table II shows that in unbuffered melts the Al stripping peak potential shifts positively with increasing Lewis acidity, thus explaining the difference in potential between the N=0.55 melt and the buffered melt. Considering the data from both tables, it is clear that the buffered melt is acidic, but its composition is probably somewhat less acidic than N=0.5002 and thus [Al₂Cl₇⁻] is less than 3.70 x 10⁻³M.

To help identify the oxidation peak seen at 0.8V on Pt (and much less pronounced on W) the buffered melt was also examined using a glassy carbon electrode. Glassy carbon is very insensitive to protons as verified by the voltammogram for a neutral, unbuffered melt on which the residual protons were not seen. An N=0.55 melt showed the Al plating and stripping peaks at very high currents, but no smaller peaks. Also, the voltammogram of the buffered melt on glassy carbon was featureless. This means that low concentrations of Al₂Cl₇⁻ and protons are inactive on glassy carbon.

In summary, the residual proton reduction peaks and the 0.8V oxidation peak are pronounced on Pt, weak on W, and not observed on glassy carbon. Thus, it is proposed that on Pt, protons are reduced to H₂(g) which is adsorbed on the electrode. The sharpness of the 0.8V oxidation peak suggests that it is a "stripping" peak for the oxidation of adsorbed H₂ back to a protonic species.
Table I

A1 Stripping Potentials*

| Melt Composition         | Working Electrode |           |
|--------------------------|-------------------|-----------|
|                          | Pt                | W         |
| Buffered                 | -0.1582V          | -0.1212V  |
| N=0.5002                 | -0.0642           | -0.0872   |
| Neutral unbuffered (blank) | No peak           | No peak   |

*From anodic cyclic voltammograms recorded immediately after chronoamperometry.

Table II

A1 Stripping Potentials of Unbuffered Melts*

| Melt Composition | Working Electrode |           |
|------------------|-------------------|-----------|
| N                | Pt                | W         |
| 0.5002           | -0.1122V          | -0.0872V  |
| 0.5010           | -0.0872           | -0.0232   |
| 0.5100           | 0.0508            | 0.0018    |
| 0.5300           | 0.1988            | 0.0998    |
| 0.5500           | 0.3088            | 0.1238    |

*From cathodic cyclic voltammograms.
CONCLUSIONS

It has been shown that NaCl buffered MEICl/AlCl₃ melts remain slightly Lewis acidic when equilibrated. The buffering of an acidic melt with NaCl is analogous to buffering a basic melt with a metal chloride (10). In both cases true Lewis neutrality is probably not reached. Nonetheless, NaCl buffered melts have been shown to resist change upon the addition of a Lewis acid or base (3) and the currents resulting from low concentrations of Al₂Cl₇⁻ do not appear to limit the useful voltage window of the electrolyte.

The effect of residual protons appears to depend on the working electrode material. As with the small concentration of Al₂Cl₇⁻, the residual protons do not appear to affect the useful voltage window of the electrolyte. On the other hand, these species may result in unwanted side reactions or short lifetimes for operating batteries.

ACKNOWLEDGEMENT

This work was supported by the Air Force Office of Scientific Research.
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Fig. 1 Cathodic scan cyclic voltammogram of an N=0.55 MEICl/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec.

Fig. 2 Cathodic scan cyclic voltammogram of a NaCl buffered MEICl/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec.
I (Amps) I (Amps)
(E-4) ns hrj (E-4)

0.12
2.00 1.20 0.40 -0.40 -1.20 -2.00

E (V vs Al/0.6 melt)

Fig. 3 Anodic scan cyclic voltammogram of a NaCl buffered MEICl/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec.

Fig. 4 Two continuous anodic scan cyclic voltammograms of a NaCl buffered MEICl/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec. Recorded immediately after chronoamperometry at -1.40V for 600 sec. with stirring.
Fig. 5 Cathodic scan cyclic voltammogram of an N=0.5002 MEICI/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec.

Fig. 6 Two continuous anodic scan cyclic voltammograms of an N=0.5002 MEICI/AlCl₃ melt at a Pt electrode. Scan rate: 100 mV/sec. Recorded immediately after chronoamperometry at -1.60V for 600 sec. with stirring.
Fig. 7 Cathodic scan cyclic voltammogram of a NaCl buffered MEICI/AICI3 melt at a W electrode. Scan rate: 100 mV/sec.

Fig. 8 Two continuous anodic scan cyclic voltammograms of a NaCl buffered MEICI/AICI3 melt at a W electrode. Scan rate: 100 mV/sec. Recorded immediately after chronoamperometry at -1.40V for 3600 sec. with stirring.