

## SHORT COMMUNICATION

### AMALGAMATED ALUMINUM ELECTRODES IN ACIDIC CHLOROALUMINATE MOLTEN SALTS

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**Abstract**--Aluminum was electrochemically deposited in and stripped from mercury substrates in acidic 1-methyl-3-ethylimidazolium chloride-AlCl<sub>3</sub> molten salts. Electrode dissolution occurred at 220 and 45 mA cm<sup>-2</sup> from mercury pool and amalgamated aluminum rotating cylinder electrodes, respectively. In contrast to pure aluminum electrodes, neither of these electrodes exhibited passive behavior.

#### Introduction

Aluminum is an attractive anode candidate for secondary electrochemical energy conversion devices due to its high specific energy, and electrochemical reversibility in acidic chloroaluminate molten salts [1-4]. Unfortunately, anodic passivation of aluminum was found to occur in aluminum chloride molten salts containing ethylpyridinium bromide or NaCl [5], KCl-NaCl [6], LiCl [7], or 1-methyl-3-ethylimidazolium chloride (MEIC) [8]. This passivity may exclude aluminum/chloroaluminate batteries from certain high rate applications.

The performance of aluminum electrodes is improved in organic electrolytes by amalgamation. Takada and Miyake [9] found that amalgamation decreased the anodic overpotential of an aluminum electrode polarized up to 10 mA cm<sup>-2</sup> in LiClO<sub>4</sub>-propylene carbonate electrolytes. Leger and Blomgren [10] reported that protective surface oxides on aluminum were removed by mercury treatment, thereby activating the electrode for NH<sub>4</sub>NO<sub>3</sub>-dimethylformamide electrolytes. Furthermore, Gileadi et al [11] demonstrated that aluminum can be electrodeposited into a hanging mercury drop electrode from KBr-AlBr<sub>3</sub>-toluene electrolytes; a Hg electrode super-saturated with aluminum assumed the potential of the reversible aluminum electrode. These results prompted us to determine if amalgamation can eliminate anodic aluminum passivation in the acidic MEIC-aluminum chloride room temperature molten salt. Elimination of the passivation would allow for high dissolution rates at large overpotentials.

### Experimental

1-Methyl-3-ethylimidazolium chloride was prepared with a modification to the procedure outlined by Wilkes [12]. Aluminum chloride (Fluka, puriss.) was sublimated over NaCl and aluminum wire at 170-190 °C in a vacuum sublimation apparatus equipped with a cold finger. Mercury (II) chloride (Fluka, Purum p.a.) was sublimated under vacuum in a similar apparatus. Acetonitrile (Fisher, HPLC) was refluxed over  $P_2O_5$  prior to use.

Rotating cylinder working electrodes and counter electrodes were fabricated from high purity aluminum stock (Johnson Matthey, m5N). The rotating cylinder electrode was amalgamated by immersion in a solution containing 11.4 w/o  $HgCl_2$  in acetonitrile [13]. The rotating cylinder electrode was controlled with a Pine Instruments MSR electrode rotator. Mercury (Alfa, electronic grade) was used as received. A glass thimble was used to contain the mercury pool electrode. A platinum button electrode was immersed in the mercury pool for contact. Reported potentials are IR free and are measured with respect to an aluminum-plated platinum wire in contact with an  $X_{AlCl_3} = 0.505$  electrolyte. The reference electrolyte was separated from the working electrolyte by an ultra fine porosity glass frit.

The working electrode was controlled electronically with a Princeton Applied Research Model 273/97 potentiostat, equipped with current interruption IR compensation. Data were saved on floppy diskette with an IBM/PC computer. All experiments were conducted in a He- $N_2$  atmosphere glove box with continuous moisture and oxygen removal.

### Results and Discussion

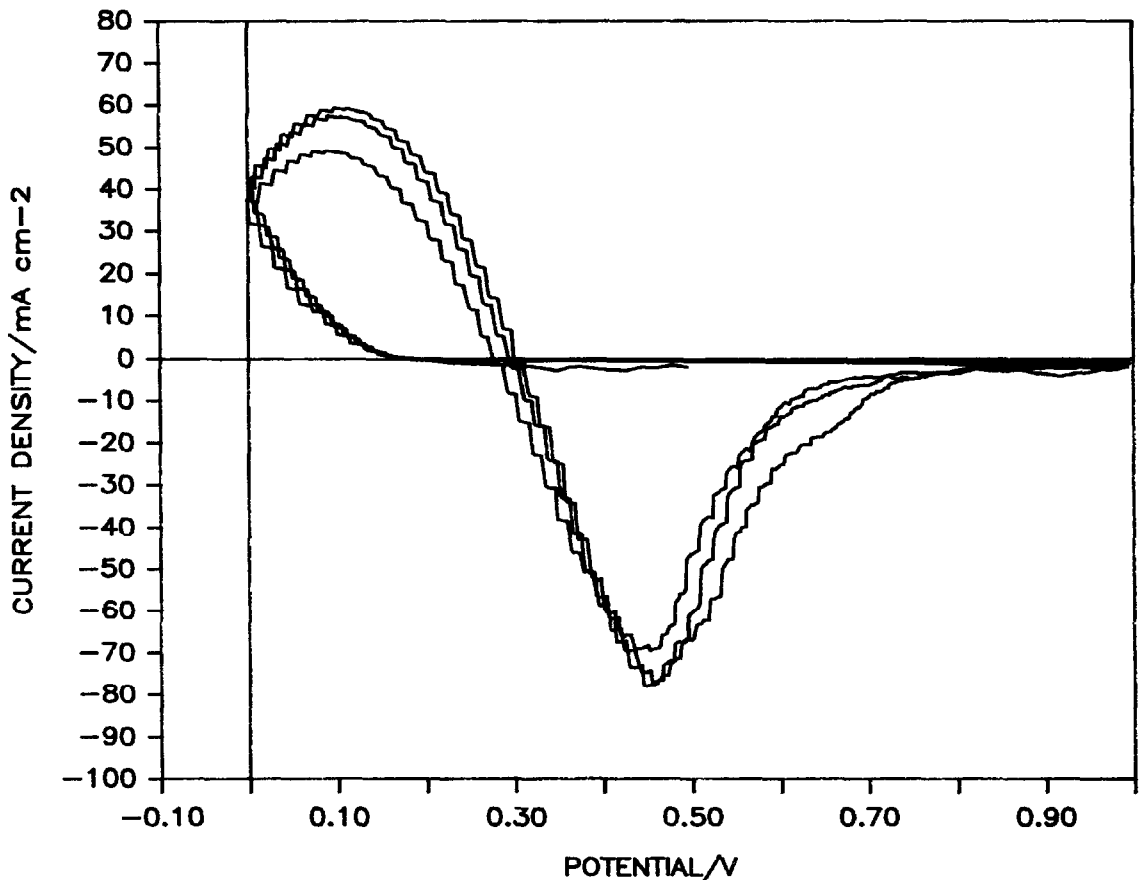
Cyclic voltammetry of the mercury pool electrode in an  $X_{AlCl_3} = 0.60$  electrolyte was limited cathodically by aluminum deposition at +140 mV, and anodically by mercury dissolution at +1100 mV. Figure 1 shows three successive cyclic voltammograms of the mercury electrode between 0 and +1000 mV. The cathodic current maximum on the reverse scan is typical of electrochemical nucleation [14], and the anodic stripping peak illustrates the reversibility of the process.

The mercury pool electrode was tested for cyclability by repetitive 2-3 minute cathodic and anodic pulses of 20 mA  $cm^{-2}$ . The current was reversed when the potential rose above +800 mV during the stripping half cycle. Except for the first cycle, the anodic transition times were in agreement with the deposition time. This suggests that a critical concentration of aluminum in the mercury is required to obtain an amalgam electrode that is well-behaved.

Rate capability of the Al-Hg electrode was determined by galvanostatic deposition, followed by the potentiostatic stripping of aluminum. During the 8 hour deposition half cycle at 20 mA  $cm^{-2}$ , 0.754 millimoles  $cm^{-3}$  were deposited into the Hg pool. The potential of

the Al-Hg electrode after the deposition was +141 mV, the potential of an aluminum electrode in this electrolyte. Then the aluminum was stripped at +900 mV, a potential that is cathodic of mercury dissolution (+1100 mV). Over a period of 20 minutes, the anodic current was approximately  $220 \text{ mA cm}^{-2}$  and consumed about 45 % of the deposited aluminum.

The rate capability of a solid electrode was tested using an amalgamated aluminum rotating cylinder electrode in an  $X_{\text{AlCl}_3} = 0.58$  electrolyte. In these experiments, the working electrode, rotated at 1000 RPM, was scanned anodically at  $5 \text{ mV s}^{-1}$ . After several cycles, the scans were repeatable, and currents as high as  $45 \text{ mA cm}^{-2}$  were obtained. Under identical conditions, an aluminum RCE had a passive current of  $11\text{--}13 \text{ mA cm}^{-2}$ , clearly demonstrating the utility of amalgamation.



**Figure 1.** Cyclic voltammogram of Hg-pool electrode in  $X_{\text{AlCl}_3}=0.60$  MEIC- $\text{AlCl}_3$  molten salt ( $5 \text{ mV s}^{-1}$ ).

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