SHORT COMMUNICATION

AMALGAMATED ALUMINUM ELECTRODES IN ACIDIC CHLOROALUMINATE MOLTEN SALTS

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(Received 17 December 1987)

Abstract--Aluminum was electrochemically deposited in and stripped from mercury substrates in acidic 1-methyl-3-ethylimidazolium chloride-AlC13 molten salts. Electrodedissolution occurred at 220 and 45 mA cm⁻² 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⁻² in LiClO₄-propylene carbonate electrolytes. Leger and Blomgren [10] reported that protective surface oxides on aluminum were removed by mercury treatment, thereby activating the electrode for NH₄NO₃-dimethylformamide electrolytes. Furthermore, Gileadi et al [11] demonstrated that aluminum can be electrodeposited into a hanging mercury drop electrode from KBr-AlBr₃-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 \( \text{P}_2\text{O}_5 \) 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 \( \text{w/o} \) \( \text{HgCl}_2 \) 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 \( X_{\text{AlCl}_3} = 0.505 \) 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-N₂ atmosphere glove box with continuous moisture and oxygen removal.

Results and Discussion

Cyclic voltammetry of the mercury pool electrode in an \( X_{\text{AlCl}_3} = 0.60 \) 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 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 \(X_{\text{AlCl}_3} = 0.26\) electrolyte. In these experiments, the working electrode, rotated at 1000 RPM, was scanned anodically at 5 mV s\(^{-1}\). After several cycles, the scans were repeatable, and currents as high as 45 mA cm\(^{-2}\) were obtained. Under identical conditions, an aluminum RCE had a passive current of 11-13 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-AlCl\(_3\) molten salt (5 mV s\(^{-1}\)).
Acknowledgement

Funding for this research was provided by the United States Air Force Office of Scientific Research under grant no. AFOSR-85-0027.

References