Investigation of the Underpotential Deposition of Lead on Gold in Basic and Acidic Room-Temperature Chloroaluminate Molten Salts

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ABSTRACT

The underpotential deposition (UPD) of lead on polycrystalline gold was used to investigate the characteristics of the electrochemical quartz crystal microbalance (EQCM) in room-temperature chloroaluminate molten salts. The bulk and UPD reduction of lead on gold was observed in both acidic and basic molten salts. The mass of the lead UPD in both acidic and basic melts, as determined from both EQCM charge and frequency data, were essentially identical. These data indicate that the EQCM is well behaved in these systems.

INTRODUCTION

Ambient-temperature chloroaluminate molten salts have proven to be versatile solvents for a wide variety of chemical and electrochemical studies (1-9). The most popular member of this family of ionic liquids is made from mixtures of 1-ethyl-3-methylimidazolium chloride (EMIC) and aluminum chloride (AlCl₃). The physical and chemical properties of the EMIC:AlCl₃ molten salts can be varied greatly by changing the relative amounts of the two components. Acidic melts are produced when there is a molar excess of AlCl₃, and basic melts are produced when there is a molar excess of EMIC. The acidic melts contain heptachlorodialuminate ion, Al₂Cl₇⁺, which is a strong Lewis acid, while the basic melts contain chloride ion, a weak Lewis base.

We recently reported application of the Electrochemical Quartz Crystal Microbalance (EQCM) to the investigation of aluminum and aluminum alloy electrodeposition from acidic AlCl₃:EMIC molten salts (10-11). Acidic molten salts are significantly more viscous than the aqueous solutions the EQCM is normally used in (15 cP versus 1 cP). This increased viscosity appeared to cause some dampening of the EQCM quartz crystal oscillation. However it did not appear to effect the relationship
between the change in quartz crystal frequency ($\Delta F$) and the change in areal mass ($\Delta M$) at the surface of the crystal (equation 1),

$$\Delta F = C_f \Delta M$$  \[1\]

where $C_f = 55.6 \text{ Hz-cm}^2/\mu\text{g}$

Our initial studies clearly indicated the potential of EQCM measurements in AlCl$_3$:EMIC molten salts. However, because of the complex chemical and physical properties of these liquid systems we felt it was necessary to more thoroughly characterize the behavior of the EQCM in these ionic liquids. Towards this end we choose to use the EQCM look at the underpotential deposition of lead in the melts. The tendency of lead to undergo underpotential deposition (UPD) onto polycrystalline and single-crystal gold electrodes is well known (12). Hussey and Xu (13) have investigated the voltammetry and nucleation behavior of lead on nickel and glassy carbon electrodes in acidic EMIC:AlCl$_3$ melts. However, they did not investigate its electrochemistry on gold. In this paper we report on our investigations of lead UPD on gold electrodes in both acidic and basic EMIC:AlCl$_3$ molten salts.

**EXPERIMENTAL**

Purification of AlCl$_3$:EMIC melt components was performed as previously described (14). PbCl$_2$ (Johnson Matthey puratronic, 99.999%) was used as received. Following addition of PbCl$_2$ to the basic and acidic melts, protonic impurities were removed by vacuum treatment at $1 \times 10^{-5}$ Torr (15). Polycrystalline gold disk electrodes were made by vapor deposition of approximately $2000 \text{ Å}$ of gold onto approximately $50 \text{ Å}$ of chromium. The support material was AT-cut 5 MHz Quartz crystals, which were highly polished and 1.0 inch in diameter. The electrochemically active area was $0.34 \text{ cm}^2$ and the piezoelectrically active area was $0.28 \text{ cm}^2$. The counter electrode was a $0.5 \text{ mm}$ diameter aluminum wire coil. The reference electrode consisted of an Al wire immersed in an $N = 0.60 \text{ AlCl}_3$:EMIC; this melt was contained in a sealed glass compartment in a custom made EQCM cell. A platinum wire in-glass was used to connect the reference compartment to a built-in luggin capillary. Melt preparation and handling was performed in a nitrogen filled Vacuum Atmospheres drybox. All EQCM measurements were conducted using the air-tight EQMC cells that were set up inside the drybox, and then used outside the drybox. The EQCM system consisted of an EG&G PARC model 263A potentiostat/galvanostat with floating ground option. Electrochemical experiments were controlled with the EG&G PARC 270 software package running under DOS on an Intel-Pentium based computer. The oscillator circuit used was for a 5 MHz crystal in the normal mode (16). Frequency data was collected with a Fluka frequency counter; the
resulting voltage output was feed into the auxiliary input of the PAR 263A. After the experiment the voltage data was transferred into Microsoft Excel were it was converted back into frequency data.

RESULTS AND DISCUSSION

The staircase cyclic voltammograms for the bulk reduction of Pb(II) on the EQCM gold electrode in basic and acidic melts are shown in Figure 1. Interestingly, lead is one of the few metals which is reducible in both the basic and acidic melts (1). Figure 1 clearly shows a shift in the main reduction wave of approximately 1.15 V between the basic and acidic melts. This shift can be ascribed to the change in the chloride activity between the two melt compositions. In Figure 1 UPD waves are evident in both melts prior to the main bulk reduction waves. These UPD waves are more clearly shown in Figure 2. The shape of the voltammograms in Figure 2, in both the acidic and basic melts, are characteristic of lead UPD. The various UPD peaks result, in part, from deposition onto the multiple crystal faces of the polycrystalline gold electrode (17-19).

Figure 3 shows the EQCM frequency change observed in an acidic melt ($N = 0.60$) containing 20 mM Pb(II) when the gold electrode potential was scanned through the lead UPD region. As expected the deposition of a lead monolayer, and corresponding increase in surface mass, resulted in a decrease in the crystal resonance frequency. When this lead UPD monolayer was stripped off, the crystal resonance frequency returned to its original value. Figure 4 shows the EQCM frequency change observed during a double potential-step chronoamperometric experiment in this same acidic melt. The potential was stepped for 10 s from a point prior to the UPD ($E_{\text{initial}} = 1.2V$) to a potential negative of the UPD, but before the bulk wave, ($E_{\text{step}} = 0.5 V$). The potential was then stepped back to $E_{\text{initial}}$ for an additional 10 s. The charge and frequency data for this experiment are given in Table I. The mass of the lead from its UPD may be calculated from the charge data assuming a two electron reduction of Pb(II), and it may also be calculated from the observed frequency change using equation 1. As shown in Table I, the mass calculated by both these methods are in very good agreement. The observed mass change is significantly less than expected for a hexagonal close-packed monolayer of lead. However, it is reasonably close to that expected for a monolayer on single crystal Au 110 (17). The polycrystalline nature of the electrode surface may explain the smaller observed mass change. Also, some of the electrode surface may be masked due to adsorption of impurities.

The staircase cyclic voltammetric and chronoamperometric experiments were repeated for the lead UPD in the basic melt ($N = 0.44$). These data are shown in Figures 5 and 6. The charge and mass data for the chronoamperometric experiment are given in Table I. As was the case with the acidic melt, we have excellent agreement between the

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mass change calculated from charge and frequency change. More importantly, the mass change observed in the basic melt is essentially identical to that observed in the acidic melt. Thus indicating the amount of lead reduced during the UPD process remains unchanged when going from an acidic to a basic melt. Furthermore, this indicates that the EQCM is gives consistent data in the molten salts studied.

If the EQCM in is well behaved in the molten salts then the observed peak currents for the staircase cyclic voltammograms of the lead UPD should increase as the scan rate increases, while the observed frequency change should remain constant. Figure 7 shows the effect of changing scan rate on the current and frequency data for the lead UPD in an acidic ($N = 0.60$) melt. As expected the voltammetric current increases while the frequency remains unchanged.

CONCLUSIONS

The UPD of lead on polycrystalline gold was used to investigate the characteristics of the EQCM in room-temperature chloroaluminates molten salts. The bulk and UPD reduction of lead on gold was observed in both acidic and basic molten salts with an approximately 1.15 V shift between both melts. The mass of the lead UPD as calculated from both charge and frequency data were in very good agreement. Furthermore, the measured mass of the lead UPD was essentially identical between the acidic and basic melts.

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Table I. Chronoamperometric Charge and Mass Data for the UPD of Lead in Basic and Acidic Melts.

|                     | Basic Melt (N = 0.44) | Acidic Melt (N = 0.60) |
|---------------------|-----------------------|------------------------|
| Charge              | 70 µC                 | 71 µC                  |
| Frequency Change (ΔF) | 12.2 Hz              | 10.9 Hz               |
| Mass From Charge    | 199 ng/cm²            | 202 ng/cm²             |
| Mass from ΔF        | 215 ng/cm²            | 192 ng/cm²             |
| Expected Mass for hcp Monolayer (320 µC/cm²) |                          | 340 ng/cm²             |
| Expected Mass for Monolayer on Au 110 (220 µC/cm²) |                          | 237 ng/cm²             |
Figure 1. Staircase cyclic voltammograms for the reduction of 20 mM Pb(II) on polycrystalline gold in an (a) acidic ($N = 0.60$) EMIC:AlCl$_3$ melt. (b) basic ($N = 0.44$) EMIC:AlCl$_3$ melt. Scan rate was 20 mV/s.

Figure 2. Staircase cyclic voltammograms for the UPD of lead on polycrystalline gold in (a) acidic ($N = 0.60$) EMIC:AlCl$_3$ melt. (b) basic ($N = 0.44$) EMIC:AlCl$_3$ melt. The melt was of 20 mM Pb(II), and the scan rate was 20 mV/s.
Figure 3. Cyclic staircase voltammogram and corresponding EQCM frequency data for the UPD of lead on polycrystalline gold in an acidic \((N = 0.60)\) EMIC:AlCl\(_3\) melt containing 20 mM Pb(II). Scan rate was 20 mV/s.
Figure 4. Double potential-step chronoamperogram and corresponding EQCM frequency data for the UPD of lead on polycrystalline gold in an acidic (N = 0.60) EMIC:A1C13 melt containing 20 mM Pb(II). $E_{\text{initial}} = 1.2$ V, $E_{\text{step}} = 0.5$ V.
Figure 5. Cyclic staircase voltammogram and corresponding EQCM frequency data for the UPD of lead on polycrystalline gold in a basic \((N = 0.44)\) EMIC:AlCl, melt containing 20 mM Pb(II). Scan rate was 20 mV/s.
Figure 6. Double potential-step chronoamperogram and corresponding EQCM frequency data for the UPD of lead on polycrystalline gold in a basic \((N = 0.44)\) EMIC:AlCl\(_3\) melt containing 20 mM Pb(II). \(E_{\text{init}} = -0.1\) V, \(E_{\text{step}} = -0.625\) V.
Figure 7. Cyclic staircase voltammograms and corresponding EQCM frequency data for the UPD of lead on polycrystalline gold in an acidic (N = 0.60) EMIC:AlCl₃ melt containing 20 mM Pb(II). Scan rate (a) 5 mV/s. (b) 10 mV/s. (c) 20 mV/s.