EQCM Studies of Aluminum and Aluminum Alloys in Room Temperature Molten Salts

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ABSTRACT

Room-temperature molten salts composed of aluminum chloride (AlCl₃) and 1-ethyl-3-methylimidazolium chloride (EMIC) are well suited to studying the electrodeposition of aluminum (Al) and as a codeposit with other metals (Al-Mₓ). We have employed an Electrochemical Quartz Crystal Microbalance (EQCM) to investigate, in situ, the deposition and stripping behavior of Al and Al-Mₓ in acidic AlCl₃:EMIC molten salts. The EQCM provides both mass and charge data during electrodeposition and stripping processes. This information can be used to determine codeposited metal composition and to model deposition and/or stripping processes.

INTRODUCTION

Our interest lies in the electrodeposition of various combinations of metals with aluminum. This grows from the planned use of these metal combinations to make thin multilayers and bulk deposits. These multilayers are being investigated for their various properties such as their utility as magnetic thin layered films as in the case of aluminum with cobalt, iron, or nickel. In order to understand these systems, their growth and film properties need to be investigated. A first step in this process is the growth of these films from room temperature molten salts. Application of room temperature molten salts to the deposition of various metals arises from their known use as an electroplating medium for aluminum production. Previous work with cobalt and nickel indicate that the growth of these films is by a underpotential deposition (UPD) mechanism, that is tempered by a three dimensional nucleation phenomena. The focus of the present work is the examination of the EQCM behavior of these aluminum metal combinations and the characterization of the resulting films produced by the above method.
EXPERIMENTAL

Purification of AlCl$_3$:EMIC melt components was performed as previously described.$^4$ Protonic impurities were removed by vacuum treatment at $1 \times 10^5$ Torr for several days.$^5$ Polycrystalline gold disk electrodes were made by vapor deposition of approximately 2000 Å of gold onto approximately 50 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 is 0.34 cm$^2$ and the piezoelectrically active area is 0.28 cm$^2$. The counter electrode was a 0.5 mm diameter platinum wire coil, and the reference electrode consisted of an Al wire immersed in $N=0.60$ AlCl$_3$-EMIC melt contained in a sealed glass compartments built into a homemade EQCM cell using a platinum wire connection to the built-in luggin capillary. Melt preparation and handling was performed in a nitrogen filled Vacuum Atmospheres two man drybox. All EQCM measurements were conducted using the air-tight glass electrochemical cells which were set up inside the drybox, then used outside the drybox. EQCM cyclic voltammetry was performed with an Intertech Systems HB-111 Analog Function Generator and a PS151 Potentiostat/Galvanostat controlled by the Asyst 4.01 software environment using a GTSI 486DX/33MHz computer. Data acquisition was done with a Data Translation DT-2801A D/A converter board and a DT-707 screw board. The oscillator circuit used was for a 5 MHz crystal in the normal mode$^6$ powered by a Hewlett Packard 20 volt power supply. All data collected in the above system was converted into Microsoft Excel 5.0 worksheets for data analysis by Microsoft Excel or Origin software.

RESULTS AND DISCUSSION

We have recently demonstrated the use of the EQCM in room-temperature molten salts.$^7$ Room-temperature molten salts are significantly more viscous than aqueous solutions. The acidic molten salts used in these studies had viscosities in the range of 15-20 centipoise. (This is comparable to the viscosity of ethylene glycol). The higher viscosity of the melts tends to slow down the EQCM indicated response time causing a separation to occur between the forward and reverse scans. However, we can somewhat compensate for this by slowing down the scan rate, which allows for the reaction to proceed to completion before scan reversal.

The nature of the EQCM frequency data can be evaluated by mathematically converting it to current response data; this gives a calculated cyclic voltammogram which can be compared with the experimental voltammogram. Differences between the two voltammograms may be an indication of solvent occlusion, mixed transport of ions, or the presence of other species (i.e. proton) which are electroactive in the region of interest. Consequently, these studies were performed on clean proton free acidic melts to minimize these problems.
The first effort in looking at the use of EQCM in room temperature molten salts involved an examination of the UPD of aluminum. The nature of the response would give us a good indication of the utility the EQCM would have in this relatively viscous medium. The answer to that question lies in the analysis of the data presented in Table I. The second column reports both the frequency and current data converted into grams per centimeter squared to give areal mass. The areal mass data indicates that the results of the frequency and current data don't have amplification (positive or negative) due to viscoelastic effects from the viscous electrolyte. The film remains a rigid layer as far as the system can detect with no indicated variable damping of the resonance frequency of the quartz crystal. The data representing the calculated and actual frequencies achieved indicate that this EQCM method is sensitive enough to detect monolayer amounts of material in the molten salt used for this study. Furthermore, this data indicates the viability of using EQCM as a tool to study rigid layers in this room temperature molten salt.

EQCM measurements give simultaneous current and frequency data as a function of potential. By making certain assumptions, the frequency data can be converted to mass data. Figure 1 shows the staircase cyclic voltammogram of aluminum and chromium electrodeposited from a $N=0.52$ acidic melt. The corresponding frequency verses potential plot for the staircase cyclic voltammogram in Figure 1 is shown in Figure 2. As stated earlier, the frequency is proportional to the mass, and as Figure 2 clearly shows, there is a significant mass increase as the potential is scanned negative of zero volts. This corresponds to the first reduction wave in Figure 1. This mass increase continues through the rising part of the second reduction wave and also upon scan reversal out to approximately 0.25 V. At that point, the process is reversed and all the mass is stripped off. This corresponds to the two oxidation waves observed upon scan reversal in Figure 1. This is important because this indicates that nothing is left on the surface and no stripping of the electrode surface is occurring either.

Similar results to figures 1 and 2 are seen in figures 3 and 4, when the voltage is scanned only out through the first reduction wave. This gives a better look at the voltammetry of the first wave. Of interest is to figure out what component, the Al or Cr, is the main contributor to the electrochemical events taking place.

Also present is a secondary frequency change seen in both figures 2 and 4. This secondary frequency change at 0.8 to 1.5 V is hypothesized to be from the $\text{Cr}^{2+}$ to $\text{Cr}^{3+}$ transition which formed an insoluble compound. This compound precipitates out to give a frequency decrease which indicates an increased mass is sensed. The process is reversible and the material is completely removed.

EQCM measurements can be used to ascertain the composition of the deposited material. If we assume a uniform codeposit, analysis of mass and current data can be used to characterize deposition and stripping processes. The total mass change during deposition or stripping ($\Delta W_{\text{Total}}$) is equal to the sum of the masses of the individual metals; $\Delta W_{\text{Mx}}$ is...
the weight for added metal (other than aluminum) and $\Delta W_{Al}$ is the weight for aluminum (equation 1).

$$\Delta W_{Total} = \Delta W_{Mx} + \Delta W_{Al}$$ [1]

$$\Delta Q_{Total} = \Delta Q_{Mx} + \Delta Q_{Al}$$ [2]

The total charge ($\Delta Q_{Total}$) is equal to the charge from the added metal ($\Delta Q_{Mx}$) and from Al ($\Delta Q_{Al}$) (equation 2). Conversion of charge to weight and substitution of equation 2 into equation 1, gives equation 3. $K_1$ and $K_2$ are constants for Al and $M_X$, respectively.

$$\Delta W_{Mx} = (\Delta Q_{Total} - K_1*\Delta W_{Total})/(K_2 - K_1)$$ [3]

Once the $\Delta W_{Mx}$ is known, it is substituted back into equation 1 to get $\Delta W_{Al}$. From the ratio of the mass changes we can calculate the composition of the deposit. In addition, the mass changes can be plotted against the potential to determine mass loss and charge loss, upon stripping, of the codeposited Al and $M_X$ and individual metals.

Using the data from the frequency-potential plot shown in figure 4, we calculated the mass versus potential using the above equations for both Cr and Al. The data are plotted in figure 5 as moles of Cr and moles of Al. The plots for the Al and Cr are almost superimposable indicating that for the first reduction wave Al and Cr are deposited simultaneously and in similar molar quantities.

**SUMMARY**

We have concluded several issues from the above discussed work.
1. EQCM is a viable technique to use in a medium such as the room temperature EMIC-$AlCl_3$ molten salts.
2. The UPD of aluminum can be measured in this electrolyte system and the results are fairly close to the expected values.
3. Aluminum and chromium can be codeposited from the room temperature EMIC-$AlCl_3$ molten salts even though the potential at which they deposit occurs after normal bulk aluminum deposition.
4. EQCM can give us insight into the deposition and stripping behavior of metal deposits.

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Table I EQCM data of the underpotential deposition of aluminum.

| Scan | Q vs Freq (g/cm²) | Frequency Expected | Frequency Actual |
|------|-------------------|--------------------|-----------------|
| 1    | 6.5/5.5x10⁻⁸      | 3.6 Hz             | 3.8 Hz          |
| 2    | 5.4/5.8x10⁻⁸      | 3.6 Hz             | 4.0 Hz          |
| 3    | 6.8/6.1x10⁻⁸      | 3.6 Hz             | 4.2 Hz          |
Fig. 1 Staircase cyclic voltammogram of aluminum and chromium electrodeposited from $N=0.52$ room temperature EMIC-$\text{AlCl}_3$ molten salt using an aluminum wire in $N=0.60$ EMIC-$\text{AlCl}_3$ as a reference electrode.

Fig. 2 The accompanying frequency data of Aluminum and Chromium electrodeposited during the EQCM experiment depicted in figure 1.
Fig. 3 Staircase cyclic voltammogram of first peak from aluminum and chromium electrodeposited out of a $N=0.52$ room temperature EMIC-$\text{AlCl}_3$ molten salt using an aluminum wire in $N=0.60$ EMIC-$\text{AlCl}_3$ as a reference electrode.

Fig. 4 The accompanying frequency data of aluminum and chromium electrodeposited during the EQCM experiment depicted in figure 3.
Fig 5  The modeled frequency and charge data for chromium and aluminum. Depicted are curves for the moles of aluminum or chromium present during the electrochemical events.