ELECTROCHEMICAL DEPOSITION OF ALUMINUM AT VITREOUS CARBON IN A ROOM-TEMPERATURE MOLTEN SALT

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ABSTRACT

The electrochemical deposition of aluminum at vitreous carbon has been studied in the AlCl₃ : 1-ethyl-3-methylimidazolium chloride molten salt system. In a 1.2:1.0 acidic melt, multiple Al stripping peaks are observed at low coverage, which implies that there are several types of nucleation sites on the carbon surface. In neutral buffered (NaCl) melts, a symmetrical oxidation peak at -0.4 V (vs Al/1.5:1.0 melt) suggests aluminum stripping after initial deposition at -1.40 V. This oxidation process becomes two peaks, at -0.2 V and 0.0 V, if the potential is held for 180s at -1.40 V before scan reversal. This behavior is believed to be due to the loss by diffusion of NaCl, formed during Al₂Cl₇⁻ reduction, from the electrode surface during potential hold. As a result, aluminum stripping soon exhausts the supply of NaCl at the surface, and the remainder of the aluminum is stripping into an essentially acidic melt at 0.0 V. Scanning electron microscopy of long-term (3600 s) deposits on vitreous carbon show considerable amounts of chlorine and sodium, in addition to aluminum, suggesting that inclusion of melt has occurred during deposition.

INTRODUCTION

Studies of metal deposition at vitreous carbon have proven to be very interesting because of the nature of the surface functional groups found on the surface (1). In general, metal deposition, at least at low coverages, involves accumulation of metal in isolated areas rather than as uniform films (2). Prior studies of aluminum deposition in the aluminum chloride : 1-ethyl-3-methylimidazolium chloride molten salt system have involved work at both carbon and metal electrodes (3). Work by Wilkes at platinum in the neutral buffered melt investigated the effect of lowered acidity in this system on the deposition of aluminum from the melt (4). In the neutral buffered melt, sodium chloride is added to an acidic melt to form sodium tetrachloroaluminate, the result being that dissolved sodium ions are introduced into the system. The low solubility of NaCl in the melt provides some buffering to chloride introduction into the melt (5,6). The presence of a very low concentration of the acidic species Al₂Cl₇⁻ in the neutral buffered melt allowed the deposition of aluminum on platinum, although the deposit quality was not particularly high (4). Following a scan through the broad reduction processes encountered from -0.5 V to -2.0 V, symmetrical oxidation peaks at 0.0V and +0.7 V were observed (4). The present work was undertaken after studies of acid-catalyzed rearrangement reactions in...
the neutral buffered melt at 77°C showed that these types of oxidation processes are also observed at vitreous carbon, and that the number and potential of the peaks varies with time spent in the deposition region. This communication presents the details of further investigations into these initial findings.

**EXPERIMENTAL**

The molten salts used in this study were prepared by addition of aluminum chloride to 1-ethyl-3-methylimidazolium chloride (EMIC), which was prepared as described previously (7). Protonic impurities were removed from the melts by placing melts under vacuum at 75°C. Cyclic voltammograms were recorded at Tokai GC-20 vitreous carbon electrodes (3 mm diameter) and also at Cypress Systems platinum (1 mm diameter) electrodes. Potentials are referenced to an aluminum wire immersed in a 1.5:1.0 acidic melt (N = 0.60). A tungsten counter electrode was used in this work to prevent any unintentional introduction of platinum species into the melt. All reactions were carried out in a Vacuum Atmospheres drybox. Electrochemical experiments were carried out on a PARC Model 283 Potentiostat / Galvanostat. A JEOL Model JSM-6100 Scanning Electron Microscope, equipped with a Kevex Sigma X-Ray probe, was used to obtain images and elemental compositions of electrode deposits.

**RESULTS AND DISCUSSION**

**Studies in 1.2 : 1.0 Acidic Melt**

**Vitreous Carbon.** In appreciably acidic melts, the deposition and stripping processes for aluminum at vitreous carbon occur as single peaks, as shown in Figure 1. The potential of the stripping peak is very near 0.00 V, consistent with an aluminum deposit in contact with the acidic melt measured versus a similar situation at the reference electrode. At very small aluminum coverages, other oxidation processes are seen, at potentials markedly different from 0.00 V. Figure 2 shows the results of a scan to -0.15 V, corresponding to passage of 10 °C in the reduction process. The major oxidation peak is observed at +0.13 V, with two smaller oxidation peaks at more positive potentials. These small peaks are not observed in a background scan extending only to 0.00 V. The total charge for these oxidation peaks is 8 °C, which is considerably less than the 34 μC calculated for monolayer coverage of aluminum on a 3mm diameter electrode (~ 1 x 10¹⁵ sites / cm² ). For significantly more negative deposition potentials (-0.20 V, 1.26 mC), only one oxidation process is observed at +0.02 V (1.20 mC), although a low oxidation plateau (20 μA) is present beyond +0.10 V (Figure 2). These results indicate that low aluminum coverage involves deposition at active sites on the vitreous carbon surface, giving rise to oxidation processes at the various potentials seen in Figure 2. Such behavior is typical of metal deposition at vitreous carbon in other media and in this molten salt. At higher coverages, a uniform aluminum deposit is apparently achieved, giving only one oxidation peak as in Figure 2 (-0.20 V scan).

**Platinum.** At platinum, the electrodeposition behavior of aluminum is much simpler than at vitreous carbon. For all coverages studied, only one stripping peak for aluminum was observed. This behavior indicates that the nucleation sites on platinum are
much closer in energy than are those at vitreous carbon. Further comparisons between behavior at vitreous carbon and platinum were made by chronoamperometric studies. Chronoamperometric curves were obtained by stepping from +0.50 V to −0.10 V, giving the responses shown in Figure 3. The rate of current increase is much higher for platinum than for vitreous carbon, implying a slower nucleation rate at vitreous carbon.

Studies in the Neutral Buffered Melt

Vitreous Carbon. A cyclic voltammetric scan at vitreous carbon in the neutral buffered melt is shown in Figure 4. As seen in other work at platinum (4), the current gradually increases as the potential is swept in the negative direction until considerable reduction current is observed past −1.5 V. As suggested by Wilkes, the neutral buffered melt is actually very weakly acidic, based on the correspondence of the small oxidation peak at −0.1 V with the aluminum stripping process observed in mildly acidic melts (4). At platinum, two stripping peaks were observed (−0.1 V and +0.8 V) following scanning to −1.4 V (vs Al / N = 0.60 melt). As is evident from the scan at vitreous carbon (Figure 4), there are no large oxidation peaks at room temperature. At 77°C, however, a symmetrical oxidation peak is observed at −0.4 V (Figure 5) after scanning to −1.40 V. An interesting situation develops when the scan is held at −1.40 V, after which two oxidation peaks are observed at −0.2 V and at 0.0 V (Figure 5). The relative peak currents of these oxidation peaks depend on the length of the hold period, there being more of the 0.0 V peak at longer hold times. Scanning electron microscope / X-ray spectroscopic studies of electrode surfaces held for 180 s showed very little if any aluminum, or other substances, deposited onto the surface. Based on the charge passed during the hold period, there should be approximately 150 monolayers of aluminum on the surface; however, the reduction process may be very inefficient in producing aluminum or the deposit may not be adherent under these conditions. At longer hold times (3600s), a dark porous deposit was found on the surface. After treatment with benzene and water, distinctive (dendritic, with nucleation islands) patterns were observed by SEM (Figure 6); however, the major elemental signal was for chlorine, with smaller amounts of aluminum and sodium. Similarly poor deposits were also seen at platinum (4), so it is likely that inclusion of melt components is responsible for these results.

The symmetrical shape of the peaks observed after deposition at −1.40 V and 77°C suggest that they are stripping peaks, although the assignment of definite processes to them seems difficult. One possibility considered is that they involve stripping of aluminum from different surface sites; however, at similar peak currents in the acidic melt, only one peak was observed. Multiple peaks there were seen only at very low coverages. Another possibility is that some of the peaks are due to admixtures or inclusions of melt components with deposited aluminum. In this case, one would not expect such well-defined peaks as those observed in the 0.0 V to −0.4 V region. In a few cases, very broad peaks at +0.8 V to +1.0 V were observed after the melt had been kept at 77°C for a few days, so it is possible that these responses are due to aluminum oxidation from aluminum / melt deposits. Such behavior would be analogous to de-alloying peaks seen, for instance, in stripping of nickel / aluminum deposits in room-temperature molten salts in which aluminum stripping was ascribed to a peak at 0.45 V.

After considering these possibilities, attention was focused on the melt composition immediately next to the electrode surface as deposition and subsequent
stripping occurred. Upon reduction of $\text{Al}_2\text{Cl}_7^-$ to form aluminum, release of chloride ions would result in formation of $\text{NaCl}$ at the electrode surface, until the region next to the electrode is neutral. Even with stirring, the reductive current was seen to decrease rather rapidly (100 μA to 15 μA in 60 s), so replenishment of $\text{Al}_2\text{Cl}_7^-$ would seem to be slow. The solubility of $\text{NaCl}$ in the neutral melt is 8 mM (4) at room temperature, and larger values would be expected at 77°C. When the scan is immediately reversed at $-1.40 \text{ V}$, the deposit strips at $-0.4 \text{ V}$ into an effectively neutral melt. Most of the $\text{NaCl}$ formed during the deposition process would still be relatively near the electrode surface, and the $\text{Al}^{3+}$ ions formed during oxidation of the deposit would react with the $\text{NaCl}$ in a sort of titration type of interaction. In acidic melts, of course, stripping occurs at 0.0V, because the aluminum is in contact with a melt composition close to that in the reference electrode. That the stripping potential in the present case is so different from 0.0V indicates that the melt composition is indeed neutral, or at least not appreciably acidic. This supports the proposed interaction of aluminum ions with $\text{NaCl}$ during stripping, thereby preventing buildup of $\text{Al}_2\text{Cl}_7^-$ at the electrode surface. When the scan is held at $-1.40 \text{ V}$ for significant periods (180 s), however, some of the $\text{NaCl}$ has time to diffuse away from the electrode surface, so that as stripping occurs on the next sweep, the local amount of $\text{NaCl}$ is depleted before aluminum oxidation is completed. This allows formation of $\text{Al}_2\text{Cl}_7^-$ at the surface, so that the later stages of stripping occur near 0.0 V, as observed in an acidic melt. In the experiment in which the potential is held at $-1.40 \text{ V}$ for 180 s, the first oxidation peak is actually observed at $-0.2 \text{ V}$ (Figure 4), again supporting the loss by diffusion of $\text{NaCl}$ during the hold period, leading to slightly more acidic conditions at the electrode surface. Further support is obtained from the fact that only one stripping peak, at $-0.25 \text{ V}$, is seen at room temperature in the neutral buffered melt after a 180 s hold at $-1.40 \text{ V}$. (As mentioned above, no oxidation peaks are observed at room temperature without a potential hold at $-1.40 \text{ V}$.) At this lower temperature, diffusion of $\text{NaCl}$ would be slower than at 77°C so that enough $\text{NaCl}$ remains to prevent $\text{Al}_2\text{Cl}_7^-$ buildup. An oxidation peak at 0.0 V is not then observed.

Platinum. Analogous experiments were also carried out at platinum in the neutral buffered melt at 77°C. With a potential hold at $-1.30 \text{ V}$ for 180s, a broad oxidation peak centered at +0.40V, with indications of multiple components, was observed. An extremely broad oxidation process was present at $+1.3 \text{ V}$ to $+1.8 \text{ V}$. Although the oxidation peak at $+0.40 \text{ V}$ is not as well resolved as at vitreous carbon, the behavior appears similar to that at vitreous carbon. With no potential hold at $-1.40 \text{ V}$, very small oxidation peaks at $-0.4V$, $-0.1V$, and $+0.4 \text{ V}$ were observed. These peaks, however, are small compared to those at vitreous carbon, so further comparisons are not warranted in this case.

CONCLUSIONS

In 1.2 : 1.0 acidic melts, evidence of active sites on vitreous carbon has been obtained in the form of multiple oxidation peaks for very low aluminum coverages. In the neutral buffered melt, the potential of the stripping peak, presumably due to aluminum oxidation, varies with the time at which the potential is held at the $-1.40 \text{ V}$ deposition potential. A single oxidation peak at $-0.4 \text{ V}$ is observed for immediate scan reversal, whereas two oxidation peaks, at $-0.2 \text{ V}$ and 0.0 V, are observed for a 180 s potential hold at $-1.40 \text{ V}$. This behavior can be explained by changes in the layer immediately next to the electrode surface caused by aluminum reduction. Release of chloride ions in this
process leads to the formation of NaCl at the electrode surface, and with no delay in scan reversal, this chloride is available for quantitative reaction with Al$^{3+}$ ions formed in the stripping process. The potential for this process (-0.4 V) is not characteristic for stripping into an acidic melt (0.0 V), consistent with the presence of considerable NaCl at the surface with a significant delay at the switching potential, however, some of the NaCl has a chance to diffuse away, so that conditions are now more acidic at the electrode surface. Part of the stripping process occurs at -0.2 V, and when the NaCl remaining after diffusion has run out, stripping into an essentially acidic melt occurs and an oxidation peak at 0.0 V is observed. SEM runs on deposits formed at -1.30 V show definite metal-like dendritic patterning, but the composition is largely chlorine with some aluminum, suggesting that a very finely divided aluminum deposit, with considerable melt inclusions, is formed. From acidic melts (1.2:1.0, or $N = 0.55$), adherent deposits could occasionally be obtained, as judged from SEM scans giving elemental compositions of primarily aluminum.

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Figure 1. Cyclic voltammogram at vitreous carbon, in 1.2 : 1.0 (N = 0.55) melt. 50 mV/s, 20°C

Figure 2. Cyclic voltammograms in 1.2 : 1.0 acidic melt, 50 mV/s, at 20°C. Current for scan to -0.15 V has been multiplied by 50.
Figure 3. Chronoamperometric data for potential step +0.50 V to -0.16 V, 20°C.

Figure 4. Cyclic voltammogram at vitreous carbon, in neutral buffered melt, 20°C. Scan rate = 50 mV / s
Figure 5. Cyclic voltammogram at vitreous carbon, in neutral buffered melt, 77°C. 50 mV/s

Figure 6. SEM image of vitreous carbon electrode, after 3600 s deposition at -1.30 V in a neutral buffered melt at 77°C (no stirring). Electrode was rinsed with benzene to remove melt, then dipped in water for further cleaning.