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Temperature Molten Salt

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Electrochemistry of Gallium in the Lewis Acidic Aluminum Chloride-1-Methyl-3-ethylimidazolium Chloride Room-Temperature Molten Salt

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The electrochemistry of gallium at tungsten and glassy carbon was investigated in the 60.0/40.0 mol % aluminum chloride-1-methyl-3-ethylimidazolium chloride molten salt. The electroreduction of gallium produces a gallium(I) solution, which can be electrochemically oxidized to Ga(III). The formal potential for the Ga(III)/Ga(I) and Ga(I)/Ga(0) couples are 0.655 and 0.437 V, respectively. The Gal(I)/Ga(III) electrode reaction exhibits slow charge-transfer kinetics with an anodic transfer coefficient and a standard heterogeneous rate constant of 0.24 and 3.16 $\times 10^{-4}$ cm$^2$ s$^{-1}$, respectively, at tungsten, and 0.14 and 1.82 $\times 10^{-3}$ cm$^2$ s$^{-1}$, respectively, at glassy carbon. The electrodeposition of gallium at glassy carbon from solutions of Gal(I) exhibits instantaneous three-dimensional nucleation with diffusion-controlled growth of the nuclei. The Ga(III) species can react with gallium metal to form Gal(I). The diffusion coefficients for Ga(III) and Ga(I) species are 2.28 $\times 10^{-7}$ and 9.12 $\times 10^{-7}$ cm$^2$ s$^{-1}$, respectively.

Apparatus.

In prior studies, Wicelinski and Gale24 reported the electrodeposition of GaAs from acidic room-temperature chloroaluminate melts composed of AlCl$_3$ and 1-butylpyridinium chloride, but they gave few details about the electrochemistry of the gallium species. Therefore, we have re-examined the electrochemistry of different gallium species and the electrodeposition behavior (e.g., nucleation mechanism) of gallium metal at glassy carbon and tungsten electrodes in the acidic AlCl$_3$-MEIC melt. The results of this work are reported below.

All of the electrochemical experiments were performed at 30 $\pm$ 1°C. Controlled potential electrolysis experiments were conducted using a large surface area tungsten flag electrode as the working electrode. Electrodeposition experiments were carried out on tungsten (0.5 mm diam (Aldrich 99.999%) wires. The electroplated wires were washed in the glove box with dry benzene and acetonitrile in succession to remove the melt residue. The washed samples were then dried under vacuum. An Hitachi S-4200 field effect scanning electron microscope (SEM) working at 15 kV was used to examine the surface topography of the electrodeposits.

Chemicals.—Anhydrous aluminum chloride (Fluka 99%) was sublimed under vacuum three times. The MEIC was prepared and purified according to the method described in the literature.5 Anhydrous gallium(III) chloride (99.99%, Aldrich) and gallium metal (99.99+%, Strem Chemicals) were used as received.

Results and Discussion

Dissolution of gallium.—A staircase cyclic voltammogram recorded for a gallium electrode in unstirred 60.0/40.0 mol % AlCl$_3$-MEIC melt is shown in Fig. 1. This figure shows that the onset of the anodization of the gallium electrode begins at about 0.3 V and increases rapidly until the potential scan is reversed at about 0.5 V. To determine the oxidation state of the gallium species produced by the anodization process, redoxdissolution experiments were carried out in a stirred 60.0/40.0 mol % AlCl$_3$-MEIC melt at a potential of 0.4 V. In each experiment, the weight loss of the gallium electrode was measured after the passage of a certain charge. By comparing the number of moles of gallium corresponding to the weight change and the number of moles of charge passed, it was determined that $n = 1$,
indicating that gallium(I) is the anodization product. A Nernst plot was constructed for the Ga(I)/Ga couple in this melt by using controlled-potential electrolysis to vary the concentration of gallium(I) in solutions contained in an electrochemical cell equipped with the usual aluminum reference electrode and a gallium indicator electrode. As shown in Fig. 2, the resulting plot of $E$ vs. $\ln[\text{Ga(I)}]$ was linear, with a slope of 0.027 V. This experimental Nernst slope is in good agreement with the 0.026 V theoretical slope expected for a one-electron redox couple at 30°C. The intercept of the Nernst plot, which corresponds to the formal potential, $E^\circ$, of the Ga(I)/Ga couple is 0.437 V.

Electrochemistry of Ga(I) at a tungsten electrode.—A Ga(I) solution was prepared by dissolution of metallic gallium into 60.0/40.0 mol % AlCl$_3$-MEIC melt. A typical stationary staircase cyclic voltammogram recorded for the Ga(I) solution at a tungsten electrode is shown in Fig. 3a. When the voltammetric scan was initiated in the positive direction and reversed at 1.10 V, an oxidation wave, $a_1$, with a peak potential of ca. 0.853 V and a coupled reduction wave, $c_1$, with a peak potential of ca. 0.469 V were observed. In order to determine the number of electrons, $n$, transferred during the oxidation wave, exhaustive controlled potential electrolysis experiments were conducted with solutions of Ga(I) at an applied potential of 1.10 V. Based on the initial number of moles of Ga(I) present in the solution and on the total charge consumed during the electrolysis, the average $n$ value determined from three independent experiments was 2, suggesting that Ga(I) is oxidized to Ga(III) at wave $a_1$. The staircase cyclic voltammogram recorded for the oxidized solution (as shown in Fig. 3b) reveals that the same redox couples that were accessible in the Ga(I) solution are still accessible in the oxidized solution. However, the two-electron oxidation product of Ga(I) is now the principle electroactive species present in the solution. Solutions of Ga(III) could also be prepared by the direct dissolution of GaCl$_3$ into the melt. The staircase cyclic voltammograms of the solutions prepared by the direct dissolution of GaCl$_3$ are identical to those resulting from the electro-oxidation of Ga(I). A Nernst plot was constructed for the Ga(III)/Ga(I) couple by using controlled-potential electrolysis to adjust the Ga(III)/Ga(I) concentration ratio in a solution initially containing only Ga(III), and the equilibrium potentials were recorded as a function of the concentration ratio. As shown in Fig. 2, the resulting plot of $E$ vs. $\ln[\text{Ga(III)}]/[\text{Ga(I)}]$ was linear, with a slope of 0.014 V. This experimental Nernst slope is half of that observed for the Ga(I)/Ga couple and is in good agreement with the 0.013 V theoretical slope expected for a two-electron redox
Table I. Summary of electrochemical data for Ga(III) and Ga(I) in 60.0/40.0 mol % AlCl₃-MEIC at 30°C.

<table>
<thead>
<tr>
<th>Redox system</th>
<th>Solute</th>
<th>E° (V)</th>
<th>10⁷ D (cm² s⁻¹⁻¹)</th>
<th>10¹⁰ ηD/T (g cm² s⁻² K⁻¹)</th>
<th>k₁ (cm s⁻¹)</th>
<th>αₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(III)/Ga(I)</td>
<td>Ga(III)</td>
<td>0.655</td>
<td>2.28</td>
<td>1.01</td>
<td>3.16 × 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>Ga(I)/Ga(0)</td>
<td>Ga(I)</td>
<td>0.437</td>
<td>9.12</td>
<td>4.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These values were produced in a 41.2 mM solution of Ga(I) in 60.0/40.4 mol % AlCl₃-MEIC melt solution containing Ga(I) is shown in Fig. 5. The deposits shown in this figure varied from 3 to 12 μm in size. Energy-dispersive spectroscopy (EDS) analysis of these deposits indicated that they consisted of pure gallium with no trace of aluminum.

Electrochemistry of Ga(I) at glassy carbon electrode.—A typical staircase cyclic voltammogram recorded at glassy carbon for a 60.0/40.0 mol % AlCl₃ MEIC melt solution containing Ga(I) is shown in Fig. 5. When the potential was initially scanned in the negative direction from the rest potential, voltammograms like that shown in Fig. 5a were obtained. This voltammogram exhibits a single reduction wave, c₁ (Eₚ = 0.157 V), and two oxidation waves, a₂ (Eₚ = 0.392 V) and a₁ (Eₚ = 1.889 V). While waves c₂ and a₂ are attributed to the electrodeposition and anodic dissolution of gallium, respectively, wave a₁ is due to the oxidation of Ga(I) to Ga(III). In comparison to that was electrodeposited from a 41.2 mM solution of Ga(I) at an applied potential of 0.260 V is shown in Fig. 4. The deposits shown in this figure varied from 3 to 12 μm in size. Energy-dispersive spectroscopy (EDS) analysis of these deposits indicated that they consisted of pure gallium with no trace of aluminum.

Figure 4. SEM micrographs of gallium electrodeposits on tungsten wires that were produced in a 41.2 mM solution of Ga(I) in 60.0/40.4 mol % AlCl₃-MEIC melt at 30°C and the following applied potentials. (a) 0.26 and (b) 0.23 V.
the voltammograms obtained at tungsten, this figure reveals that the anodic wave for the oxidation of Ga(I) to Ga(III) at GCE occurs at a potential more positive than at tungsten. Moreover, the cathodic wave for the reduction of Ga(III) to Ga(I) that is observed at tungsten is not obviously seen in Fig. 5. It was found, however, that if the potential was initially scanned in the positive direction from the rest potential and reversed after wave $a_1$, the current for the electrodeposition of gallium (wave $c_2$ in Fig. 5b) was significantly larger than that observed in Fig. 5a, whereas the currents for waves $a_2$ and $a_1$ remained constant. This suggests that wave $c_2$ actually resulted from two electrochemical processes, i.e., the Ga(III) was first reduced to Ga(I) which was further reduced to Ga(0) at this potential. Apparently, the Ga(III)/Ga(I) redox reaction at a GCE is a kinetic controlled charge-transfer process that requires a substantial overpotential. Because the peak potential separation observed in Fig. 5 is larger than that observed in Fig. 2, it is expected that the charge-transfer rate constant for the Ga(I)/Ga(III) couple at GCE would be smaller than that obtained at tungsten. To evaluate the charge-transfer kinetics of the Ga(I)/Ga(III) couple at GCE, RDE voltammetry experiments were conducted with a GCRDE. The average values for $k^o$ and $\alpha$, calculated using Eq. 2, and 3, from several experiments are collected in Table I. As expected, the values for $k^o$ obtained at GCE is smaller than that obtained at tungsten, indicating that the Ga(I)/Ga(III) reaction at GCE is less favorable than at tungsten.

In contrast to the results obtained at tungsten, the voltammograms recorded during the deposition of gallium at a GCE exhibit current loops indicative of a nucleation-rate controlled process. The nucleation process was examined in more detail by carrying out potential-step experiments using Ga(I) solutions. The current-time transients resulting from these experiments are typical of those observed for other nucleation-rate controlled electrodeposition processes. That is, after the application of the potential step and an induction period, the current increases until it reaches a broad maximum, $t_m$, at time, $t_m$. After $t_m$, the current decreases as the diffusion layer gets thicker. It has been shown that the electrodeposition of metals on glassy carbon from AlCl$_3$-MEIC melt is often involved instantaneous or progressive three-dimensional nucleation with hemispherical diffusion-controlled growth of the nuclei. An excellent method for discriminating between these two nucleation/growth models is to compare the dimensionless experimental $(i/t_m)^2$ vs. $(t/t_m)$ current-time transients to the theoretical transients for these two models. However, the dimensionless plots of $(i/t_m)^2$ vs. $(t/t_m)$ in Fig. 6 that were generated from experimental data fall between the theoretical curves for instantaneous and progressive nucleation. This indicates that the nucleation is a progressive three-dimensional nucleation on a finite number of active sites. The theoretical curve is represented by Eq. 4

$$
(i/t_m)^2 = (t_m/t)[1 - \exp(-x/t_m) + \alpha(1 - \exp(-x/t_m))]^2/
$$

$$
[1 - \exp(-x + \alpha(1 - \exp(-x/\alpha)))]^2
$$

In this equation, $\alpha$ and $x$ are adjustable parameters that give the information about the number density of active sites and the nucleation rate per active site.

Equation 4 was fit to the data in Fig. 6 by adjusting the values of $\alpha$ and $x$ to obtain the minimum variance between the experimental curves and the theoretical curve generated from Eq. 4. The best fit was obtained for values of $\alpha = 0.08$ and $x = 1.47$. The small value of $\alpha$ is consistent with the fact that it is very close to the instantaneous nucleation model. These results are similar to those found for Hg$^9$ and Sn$^{12}$ on GCE in the 66.7/33.3 AlCl$_3$-MEIC melt and for In$^{14}$ on GC and W electrodes in the 44.4/55.6 AlCl$_3$-1,2-dimethyl-3-propylimidazolium chloride melt.

**Diffusion coefficients.**—Experimental diffusion coefficients, $D$, and Stokes-Einstein products, $\eta D/T$, where $\eta$ is the absolute viscosity of the melt, for both of the Ga(III) and Ga(I) species in the 60.0/40.0 mol % AlCl$_3$-MEIC melt at 30°C were estimated from...
RDE limiting currents using the Levich equation and from chronoamperometry experiments using the Cottrell equation. The resulting average values are summarized in Table I. Although the crystal ionic radius of Ga(III), 62 pm, is only slightly smaller than that of Ga(I), 81 pm, the Ga(III) species exhibits fairly smaller diffusion coefficient and Stokes-Einstein product than Ga(I). This indicates that there may be a significant structural difference between these two solvated ions.

**Reaction of gallium(III) with gallium metal.**—It was found that when gallium metal was added to solutions containing gallium(III), the gallium metal dissolved and the rest potential of the solution shifted to a more negative direction. Moreover, it is noted that as the gallium metal dissolved, the voltammetric reduction wave due to the reduction of Ga(III) to Ga(I) decreased in size as the potential was scanned in a negative direction from the rest potential, and the oxidation wave due to the oxidation of Ga(I) to Ga(III) started to grow if the potential was scanned in a positive direction from the rest potential. Eventually, when excess amounts of gallium metal were added, the voltammogram of the solution was identical to that obtained for a pure Ga(I) solution. By comparing the currents of the solution before and after the addition of gallium metal, it was found that for each mole of Ga(III) present in the solution initially, three moles of Ga(I) and after the addition of gallium metal, it was found that for each mole of Ga(III) present in the solution initially, three moles of Ga(I) were produced in the final solution. Thus, it is concluded that Ga(III) in the solution reacts with gallium metal to give Ga(I)

\[ \text{Ga}^{3+} \text{(solv)} + 2 \text{Ga} \rightarrow 3 \text{Ga}^{+} \text{(solv)} \]  

**Conclusion**

The electrodissolution of gallium metal in the 60.0/40.0 mol % AlCl₃-MEIC melt produced solutions of Ga(I) which could be further oxidized to Ga(III). The Ga(III)/Ga(I) redox reaction in both tungsten and glassy carbon involves slow charge-transfer kinetics, and the standard heterogeneous rate constant obtained at glassy carbon was smaller than that obtained at tungsten. The diffusion coefficient found for Ga(III) is smaller than that for Ga(I). The electrodissolution of gallium from Ga(I) at glassy carbon was found to involve instantaneous three-dimensional nucleation with diffusion-controlled growth of the nuclei. Gallium metal could react with Ga(III) to produce Ga(I) in this melt. The results show that the electrochemical behavior of gallium species in the acidic AlCl₃-MEIC melt is similar to that reported in the AlCl₃-NaCl-KCl mixture, but is different from that reported in the LiCl-KCl and the basic GaCl₃-MEIC melts due to the difference in the Lewis acidity of these systems.

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**References**