



Anodic Dissolution of Aluminum in the Aluminum Chloride-1-Ethyl-3-methylimidazolium Chloride Ionic Liquid

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The anodic dissolution of aluminum metal was investigated in the Lewis acidic chloroaluminate ionic liquid, aluminum chloride-1-ethyl-3-methylimidazolium chloride. The investigation was conducted on aluminum rotating disk electrodes as a function of potential, ionic liquid composition, and temperature. Two different dissolution mechanisms were realized. At modest overpotentials, dissolution takes place under mixed kinetic-mass transport control. However, as the overpotential is increased to induce higher dissolution rates and/or the ionic liquid is made more acidic, the dissolution reaction transitions to a potential-independent passivation-like process ascribed to the formation of a porous solid layer of $\text{AlCl}_3(\text{s})$. At a fixed temperature and composition, the limiting passivation current density displays Levich behavior and also scales linearly with the concentration of AlCl_4^- in the ionic liquid. The heterogeneous kinetics of the Al dissolution reaction were measured in the active dissolution potential regime. The exchange current densities were independent of the composition of the ionic liquid, and the anodic transfer coefficients were close to zero and seemed to be independent of the Al grain size.

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Room-temperature chloroaluminate ionic liquids are obtained by combining aluminum chloride with certain anhydrous quaternary ammonium chloride salts. The most popular examples of these well-known salts are those based on the 1,3-dialkylimidazolium cations, notably 1-ethyl-3-methylimidazolium chloride (EtMeImCl).¹ A unique and very versatile feature of these ionic liquids is their adjustable chloroacidity, which is based on the extant anions. This property is directly tied to the AlCl_3 content and is commonly expressed as the AlCl_3 /organic chloride salt ratio, mole fraction of AlCl_3 (x_{Al}), or percent mole fraction (m/o) of AlCl_3 . In this article, all compositions will be reported using the latter two conventions. Mixtures that contain less than 50 m/o AlCl_3 ($x_{\text{Al}} < 0.50$) are Lewis basic due to excess unbound chloride ion, whereas those containing greater than 50 m/o AlCl_3 ($x_{\text{Al}} > 0.50$) are Lewis acidic because they contain the coordinately unsaturated species, Al_2Cl_7^- . Equimolar mixtures of the organic salt and AlCl_3 ($x_{\text{Al}} = 0.50$) contain only AlCl_4^- and are designated as “neutral” ionic liquids.

Acidic room-temperature chloroaluminates are of interest as solvents for the electroplating of aluminum and aluminum alloys due to the easily accessible redox reaction²



It is also possible to electrochemically reduce the coordinately saturated species, AlCl_4^- , but this reaction is normally accessible only in alkali chloride-based systems such as $\text{AlCl}_3\text{-NaCl}$ where this anion can be reduced at more positive potentials than the alkali cation.³ However, this does not seem to be the case in chloroaluminates based on organic cations. Room-temperature chloroaluminates are safer, more stable alternatives to the traditional plating baths based on mixtures of aromatic hydrocarbons, alkali halide salts, and pyrophoric aluminum alkyl compounds commonly used in commercial Al plating technology. In fact, BASF^c now supplies the 60 m/o $\text{AlCl}_3\text{-EtMeImCl}$ ionic liquid for this purpose (Basionic AL 01) along with suitable beneficial additives to improve the deposit morphology. The high-rate electroplating of aluminum from room-temperature chloroaluminate

ionic liquids and traditional plating baths has been comprehensively reviewed^{4,5} with practical comparisons of the plated products obtained from engineering studies using different plating baths⁶ and will not be discussed further herein.

An overlooked aspect of cell performance during the electroplating of Al is the limiting rate of the electrochemical dissolution process taking place at the anode. This issue was discussed in recent articles by Abbott, et al.^{5,7} An Al anode is of course necessary in order to replenish the aluminum-containing species that are reduced at the cathode and lost from the solution during the plating process. Anode rate limitations during the plating process are usually overcome by making the active area of this electrode much larger than the cathode. However, Al anode performance is important for applications involving chloroaluminate ionic liquid-based batteries and other cells where the active area of the anode may be constrained by cell design to mirror the area of the cathode. Thus, it is important to understand the mechanism of Al dissolution and the various factors that affect the rate of this process.

There have been a number of investigations of Al anodization or the anodic dissolution of bulk Al in Lewis acidic chloroaluminate/haloaluminate molten salts, including $\text{AlCl}_3\text{-NaCl}$ and related alkali chloride systems.^{2,8–12} But only few such investigations have been undertaken in the related room-temperature ionic liquids, e.g., $\text{AlCl}_3\text{-EtMeImCl}$ ¹³ and $\text{AlCl}_3\text{-BuMeImCl}$,⁷ with the former study conducted in the basic (Cl^- -rich) ionic liquid. However, the kinetics and mechanistic aspects of the anodization reaction remain unclear. Historical reports seem to conflict with some investigators observing classical Tafel behavior.⁸ Others have reported the formation of a passive layer of $\text{AlCl}_3(\text{s})$, which results in a limiting current governed by the diffusion of reacting ions to the electrode surface.¹⁰

In a recent article,¹⁴ we reported the anodic dissolution of Al in the Lewis neutral $\text{LiAlBr}_4\text{-NaAlCl}_4\text{-KAlCl}_4$ (30-50-20 m/o) haloaluminate molten salt as a function of temperature. This investigation was carried out by using rotating disk electrode voltammetry at a miniature Al electrode. In this case, both types of behavior described above were observed. For example, at small overpotentials, the Al dissolution process proceeds under mixed kinetic/mass-transport control, but at higher dissolution rates, the current decreases significantly due to the formation of a passive/blocking layer of $\text{AlCl}_3(\text{s})$, and the current becomes mass-transport limited.

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^cCertain trade names are mentioned for experimental information only; in no case does it imply a recommendation or endorsement by NIST.

In this investigation, we have examined the anodic dissolution of Al in Lewis acidic AlCl_3 -EtMeImCl as a function of the ionic liquid composition using the same experimental procedures. It was not possible to examine the composition dependence of this reaction during our previous investigation due to experimental limitations inherent to working with the higher-melting acidic LiAlBr_4 -NaAlCl₄-KAlCl₄ molten salt. However, there are no such limitations in the AlCl_3 -EtMeImCl system. In addition, we carried out experiments on polycrystalline Al samples of varying electrode construction that have undergone different processing conditions in order to assess whether the structural differences of these materials is reflected by their different dissolution rates.

Experimental

Preparation of the ionic liquid as well as all electrochemical experiments were carried out in a dry nitrogen-filled glove box (LC Technology Solutions, Inc.). The oxygen and moisture contents were monitored by the appropriate sensors and were scrupulously maintained at less than 1 ppm. Aluminum chloride (Fluka >99%) was purified by vacuum sublimation from the AlCl_3 -NaCl melt as described previously.¹⁴ EtMeImCl (Sigma-Aldrich, BASF, >95.0%) was purified from the yellow-orange commercial product by repeated recrystallization from dry, high-purity acetonitrile until a colorless product was obtained. AlCl_3 -EtMeImCl ionic liquids of the desired composition were prepared by mixing appropriate amounts of the two materials in a flask and stirring for ~2 hours at 50 °C. The Lewis acidic ionic liquids were purified by constant current electrolysis (< 2 V applied potential) between two 6-mm diam aluminum rods (Alfa Aesar, Puritronic grade) until the final product was water-clear, and cyclic voltammetry (CV) conducted at a Pt electrode indicated that it was free from electroactive impurities.

Rotating disk electrode voltammetry experiments were carried out in an undivided three-electrode Pyrex glass cell with a Biologic SP-200 potentiostat/galvanostat. Three different Al working electrodes were used. The first (Electrode A) was a miniature rotating disk electrode (RDE) prepared from 2-mm diam annealed (soft temper) aluminum wire (Alfa Aesar, Puratronic, 99.9995%) and covered with several layers of heat-shrink Teflon tubing as described previously.¹⁴ The second working electrode (Electrode B) was a Teflon-sheathed aluminum RDE purchased from Pine Instruments Company with a diameter of 5.0 mm. The surface area of this electrode is 0.196 cm². A third Al RDE (Electrode C) was constructed in-house from a short length of 6-mm diam Al rod (Alfa Aesar, Puritronic, 99.9965%) and was mounted on a Pine Instruments electrode shaft and fitted with a machined Teflon sheath similar to the Pine RDE. All electrodes were polished with 1500 grit silicon carbide sandpaper before use inside the glove box. In addition, they were further pretreated before data collection by repeated anodic dissolution until the maximum currents were observed at a fixed potential and rotation rate. Furthermore, during data collection, the electrodes were checked frequently against a standard applied potential and electrode rotation rate to make sure that there were no gross changes in electrode area. A Pine Instruments electrode rotator was placed in the glove box and provided controlled electrode rotation. The same high-quality 2-mm diam Al wire was also used to prepare the reference (RE) and counter electrodes (CE). The CE was a very large surface area multi-coil spiral of this wire, and the RE was simply a short length of this Al wire immersed in the bulk ionic liquid. The temperature of the electrochemical cell was controlled within $\pm 0.5^\circ\text{C}$ with an Ace Glass temperature controller in a homemade furnace.

The three Al electrodes were analyzed using electron backscatter diffraction (EBSD). The samples were sectioned, mounted in epoxy, and polished. Final polishing included vibratory polishing with MasterMet colloidal silica for 5 hours to provide a 'deformation free' surface. EBSD patterns were recorded using Oxford Aztec Software. EBSD scans resulted in hit rates (number of indexed points divided by total number of points) of about 75%. Unindexed pixels were assigned using standard iterating techniques involving nearest neighbors. Note

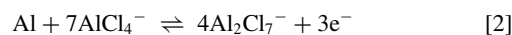
that this process creates artifacts in the grain size and shape, particularly at the boundaries of the image. Pole figures were created from the grain orientation and contour plots showing the relative intensities of different orientations in the pole figure. Microhardness measurements were performed (Electrodes A and B) on a Buehler Micromet 5124 machine using a Vickers microindenter and a load of 100 gram-force and indentation time of 15 seconds.

Results and Discussion

Characterization of the pre-electrolysis Al anode film in AlCl_3 -EtMeImCl.—As noted in the experimental section, the acidic AlCl_3 -EtMeImCl ionic liquid is conveniently purified by electrolysis between Al electrodes. During electrolysis, the anode rod sometimes developed a water-insoluble black coating. The formation of this black surface film on Al anodes in chloroaluminate molten salts and ionic liquids has been reported by many workers^{8,11,12,15,16} and has been attributed to finely divided Al resulting from the disproportionation of subvalent Al species produced during an initial one-electron oxidation reaction.^{15,16} Gale and Osteryoung¹¹ investigated this phenomenon in some detail in acidic AlCl_3 -NaCl, but were unable to confirm the participation of subvalent Al ions. Their analysis of this film by atomic emission spectroscopy indicated that it consisted of Si, B, Sn, Mn, as well as Al. Collection and subsequent analysis by energy dispersive X-ray spectroscopy (EDS) of the black material produced on the Al anode in acidic AlCl_3 -EtMeImCl indicated that it was almost completely carbonaceous. We found that by repeatedly removing the rod from the electrolysis cell and cleaning off this black material it was eventually possible to remove all of the impurities in the ionic liquid that produced the film, and the electrode remained bright throughout subsequent electrolysis. Thus, it seems unlikely in this case that the black film results from the disproportionation of subvalent species during the dissolution of Al in acidic AlCl_3 -EtMeImCl.

Anodic dissolution experiments.—The experiments used to characterize the anodization of aluminum electrodes in the AlCl_3 -EtMeImCl ionic liquid were similar in scope and function to those conducted in the LiAlBr_4 -NaAlCl₄-KAlCl₄ (30-50-20 m/o) molten salt at $t > 100^\circ\text{C}$ and are described in a recent article.¹⁷ However, the results were considerably different from those obtained in this previous study because the current density for the oxidation of Al in the ionic liquid was much smaller than observed in the higher melting salt mixture, owing to the significantly lower conductivity of the ionic liquid. As noted above, experiments were conducted in an undivided cell. In this cell, the equilibrium potential, E_{eq} , of the Al working electrode is 0 V. Thus, if the overpotential, η , is greater than this value, the anodization of Al will take place.

The current-time behavior of each Al electrode was studied by applying a series of potential steps and then observing the oxidation current as a function of time. The overpotentials, η , used varied from 0.045 to 1.273 V. Figure 1 shows current-time plots recorded during the anodization of the three Al electrodes at fixed temperatures and angular frequencies, ω (s⁻¹). For $\eta < 0.40$ V, the current densities reach constant values about 1 s after the potential is applied. These current densities are potential dependent, but time independent. However, for $\eta > 0.60$ V, the current densities increase at the beginning of the potential-step experiments, but then decrease sharply thereafter and become independent of both time and overpotential. These sharp decreases in current were attributed to a passivation-like process occurring on the Al electrode surface.¹⁰ The onset of this passivation process is potential-dependent at a given temperature, with passivation occurring sooner when the overpotential is larger. Thus, the oxidation of Al appears to involve two distinct mechanisms depending on the overpotential/anodic dissolution rate. The first is an active dissolution process represented by the overall reaction,



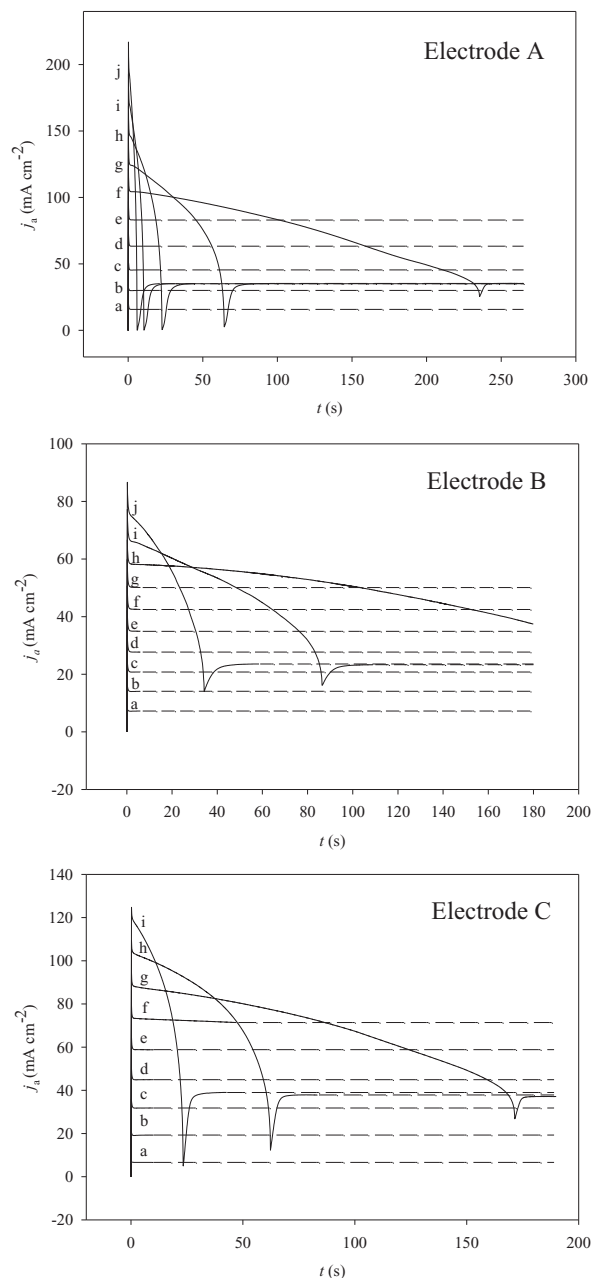


Figure 1. Current-time plots recorded during the anodization of Al rotating disk electrodes at different anodic overpotentials in the 65 m/o ionic liquid. Electrode A: (a) 0.045 V, (b) 0.096 V, (c) 0.143 V, (d) 0.181 V, (e) 0.213 V, (f) 0.478 V, (g) 0.578 V, (h) 0.678 V, (i) 0.778 V and (j) 0.878 V. Electrode B: (a) 0.028 V, (b) 0.060 V, (c) 0.093 V, (d) 0.125 V, (e) 0.153 V, (f) 0.178 V, (g) 0.202 V, (h) 0.428 V, (i) 0.668 V and (j) 0.766 V. Electrode C: (a) 0.028 V, (b) 0.089 V, (c) 0.151 V, (d) 0.208 V, (e) 0.256 V, (f) 0.318 V, (g) 0.893 V, (h) 1.086 V, and (i) 1.273 V. The temperature was 32°C, and the electrode rotation rates were 157 rad s⁻¹.

which is the reverse of Eq. 1,² and another process leading to the passivation-like behavior. We have addressed both of these scenarios below in more detail.

Dissolution of Al under passive conditions.—In order to study the passive dissolution process, additional experiments were performed as a function of temperature and composition. However, instead of plotting the resulting current densities as a function of time, the results are presented as current-sampled voltammograms. The results obtained with Electrode A (Al wire RDE) are shown in Fig. 2. In

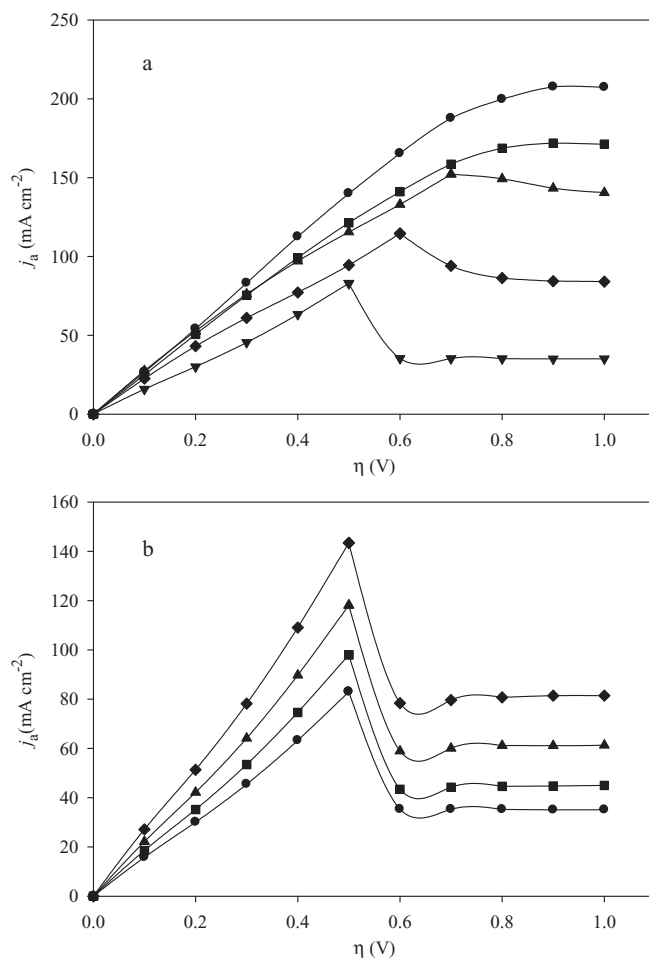


Figure 2. Current-sampled voltammograms constructed from steady-state current densities similar to those shown in Fig. 1 for Electrode A, but at different ionic liquid compositions and temperatures: (a) 32°C; (●) 51 m/o, (■) 54 m/o, (▲) 58 m/o, (◆) 62 m/o, and (▼) 65 m/o AlCl₃; (b) 65 m/o AlCl₃; (●) 32°C, (■) 41°C, (▲) 51°C, and (◆) 62°C. The electrode rotation rates were 157 rad s⁻¹.

each case, the currents were recorded after each potential step when they had reached a constant, time independent value. The results for the Electrode B (Pine Al RDE) and Electrode C (Al RDE prepared in-house) were similar, but passivation could not be achieved under all of the conditions as observed for Electrode A due to experimental limitations resulting from the higher current densities that were required. Figure 2 confirms the potential independence of the current densities at large overpotentials. Passivation is most readily achieved in the more acidic (higher AlCl₃ content) ionic liquids and can only be induced at higher overpotentials in the less acidic ionic liquids, i.e., < 55 m/o AlCl₃. We also investigated the effect of temperature, but were limited to a maximum of ~60°C to avoid physical damage to the larger Teflon-shrouded Electrodes (B and C).

From the graphs in Fig. 2, it is also possible to define a critical current density, j_{crit} , for the anodic dissolution reaction. At a fixed temperature and ionic liquid composition, this value is the largest current density that can be supported continuously by the anode reaction under the specified convective conditions without inducing passivation. Assuming that the cathode reaction does not control the cell current, this empirical parameter might be useful in the design of an Al plating bath so that the maximum plating rate might be maintained during processing without encountering the limitations arising from the anode reaction. As Fig. 2 implies, j_{crit} is clearly dependent on the ionic liquid composition and temperature. An example of a plot of j_{crit} versus composition at a fixed temperature and rotation rate is shown in

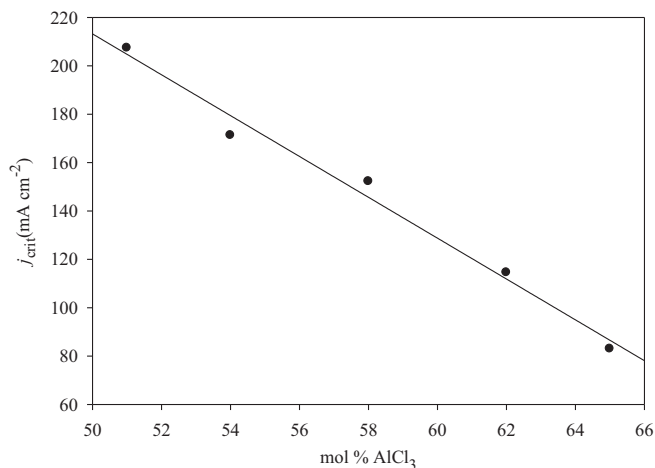


Figure 3. Plot of the critical current density, j_{crit} , versus the ionic liquid composition for Electrode A based on the data in Fig. 2. The temperature was 32°C, and the electrode rotation rates were 157 rad s⁻¹. The line is drawn to aid the eye.

Fig. 3. Not surprisingly, active dissolution of the anode proceeds more effectively when the ionic liquid composition is closer to $x_{\text{Al}} = 0.50$ because j_{crit} occurs at larger η . This is explained in part below. The parameter j_{crit} is likely to also depend significantly on other variables as well, including the convection rate, cell geometry, and/or current distribution. Thus, it would be necessary to experimentally determine this parameter for the practical plating cell under consideration.

The limiting current densities, j_l , similar to those shown in Fig. 2 were also investigated at $\eta = 1.0$ V as a function of the electrode rotation rate at a fixed temperature and ionic liquid composition for all three electrodes. The resulting Levich plots are shown in Fig. 4, and the linearity of these plots clearly indicates that the passive current densities at all three Al RDEs are limited by mass transport. In a previous investigation of Al dissolution conducted in the LiAlBr₄-NaAlCl₄-KAlCl₄ molten salt,¹⁴ we posited that the passive layer probably consists of a thin blocking layer of AlX₃(s) (X = Cl + Br) on the Al surface as the electrode diffusion layer becomes rich in this anodization product, and its solubility in the molten salt is exceeded. For the present case, this process can be represented by the reactions

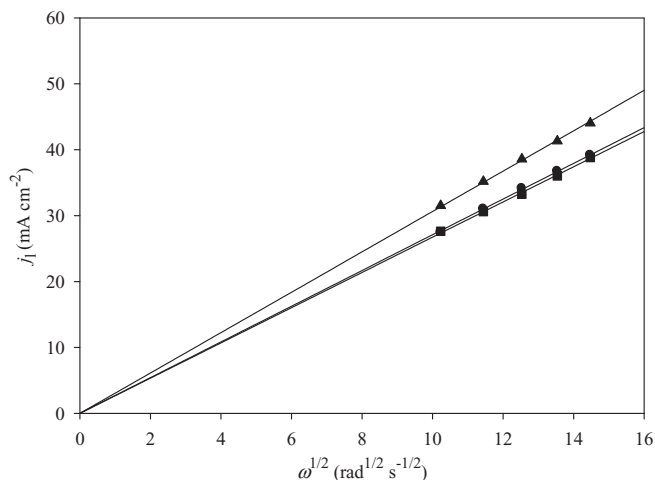
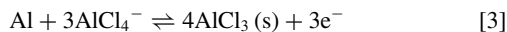
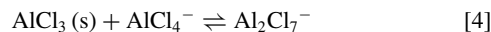


Figure 4. Levich plots for the passive limiting currents measured at (●) Electrode A, (■) Electrode B, and (▲) Electrode C in the 65 m/o ionic liquid at an anodic overpotential of 1.0 V. The temperatures were 32°C.



that when balanced together constitute the reaction in Eq. 2. It is a reasonable assumption that the accumulation of AlCl₃(s) on the electrode surface occurs because the supply of AlCl₄⁻ in the electrode diffusion layer becomes insufficient to convert all of the former into soluble Al₂Cl₇⁻ ions. (Note that Eq. 2 requires a total of seven AlCl₄⁻ ions overall to accommodate the three-electron oxidation of just one Al atom.) Thus, the limiting current is observed because the effective concentration of AlCl₄⁻ at the electrode surface is zero. If this is indeed the case, then at a fixed angular frequency, the steady-state or limiting current should show some regular dependence on the bulk concentration of AlCl₄⁻, although as pointed out previously,¹⁰ the Levich equation may not otherwise be strictly applicable in this case.

The bulk concentration of AlCl₄⁻, $C_{\text{AlCl}_4^-}^*$, (mol L⁻¹) can be readily calculated from the expression (see Appendix for derivation)

$$C_{\text{AlCl}_4^-}^* = 10^3 \rho (2 - 3x_{\text{Al}}) / [M_{\text{R}} + x_{\text{Al}}(M_{\text{Al}} - M_{\text{R}})] \quad [5]$$

where ρ is the density of the acidic AlCl₃-EtMeImCl ionic liquid at the specified temperature and ionic liquid composition. M_{Al} and M_{R} are the molecular weights of AlCl₃ (133.34 g mol⁻¹) and EtMeImCl (146.62 g mol⁻¹), respectively. The density information required for this calculation can be found in the classical paper by Fannin, et al.¹⁸ (Note that Eq. 5 can also be used for other aluminum halide organic salt mixtures with similar stoichiometry.) A complication associated with this approach is that the viscosity of the ionic liquid also changes with x_{Al} , which will influence the limiting current in two ways. First, the solution viscosity, which is linearly proportional to the kinematic viscosity, affects the diffusion layer thickness. Second, provided that the hydrodynamic radius of the diffusing species remains constant with changes in x_{Al} , the diffusion coefficient of the reacting species is itself inversely proportional to the solution viscosity. Thus, a strict comparison between j_l and $C_{\text{AlCl}_4^-}^*$ must also take into account the changes in the viscosity attendant to the variation of x_{Al} . By combining the Stokes-Einstein equation

$$D = kT / 6\pi\nu\rho r_s \quad [6]$$

where D is the diffusion coefficient, ν is the kinematic viscosity of the ionic liquid, and r_s is the hydrodynamic radius of the diffusing species, with the Levich equation, a “viscosity corrected” limiting current density, j_l' , can be defined as

$$j_l' = j_l \nu^{5/6} \rho^{2/3} \omega^{-1/2} = 1.86F(kT/6\pi r_s)^{2/3} C_{\text{AlCl}_4^-}^* \quad [7]$$

Datta and Vercruysse¹⁹ used a similar approach in a study of the transpassive dissolution of steel in concentrated aqueous acids with different viscosities. A plot of j_l' versus $C_{\text{AlCl}_4^-}^*$, is shown in Fig. 5. This plot exhibits a linear relationship between these variables with $j_l' \rightarrow 0$ as $C_{\text{AlCl}_4^-}^* \rightarrow 0$. This result lends strong support to a mechanism involving Eq. 3 and 4 in which the passive current is limited by the convective mass transport of AlCl₄⁻ to the electrode surface. Although this explanation is appealing, the results in Fig. 5 do not preclude the fact that the diffusion of the Al₂Cl₇⁻ product away from the electrode may be an equally important determinant of the steady-state current because the concentrations of these two species are inseparably related by the simple stoichiometric relationship (see Appendix for derivation).

$$C_{\text{AlCl}_4^-}^* / C_{\text{Al}_2\text{Cl}_7^-}^* = (2 - 3x_{\text{Al}}) / (2x_{\text{Al}} - 1) \quad [8]$$

Because AlCl₃(s) is an electrical insulator, this finding also suggests that the resulting electrode surface layer must be porous or spongy. The sharp peak-like drop in the current density seen in Fig. 1 just before the onset of the steady-state passive current may be due to the initial formation of a non-porous, insulating layer of liquid or gel-like AlCl₃(s), which then quickly converts into a more permeable layer of AlCl₃(s). However, there may be other explanations as well.

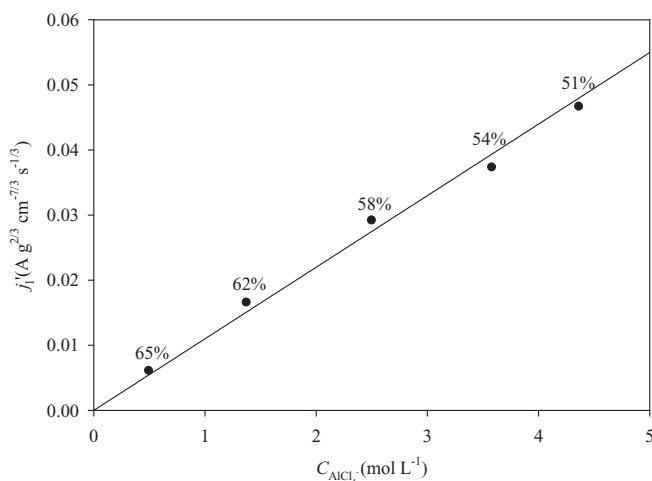


Figure 5. Viscosity-corrected passive limiting current densities versus the AlCl_4^- concentration for Electrode A. In each case, the temperature was 32°C , and the electrode rotation rate was 157 rad s^{-1} . The limiting currents were measured at anodic overpotentials of 1.0 V .

Dissolution of Al under active conditions.—As shown in Fig. 2, at smaller overpotentials, i.e., $< 0.40 \text{ V}$, the oxidation of Al appears to proceed without the intermediate formation of a passive-like layer. We investigated the dissolution of Al in this potential region at each of the three RDE electrodes by applying different overpotentials and rotation rates. Levich plots were constructed from the resulting data, and examples are shown in Fig. 6. Although these plots are mostly linear, it is clearly obvious that they do not pass through the origin. This data is typical of that seen for the anodic dissolution of metals under mixed kinetic/mass transport control,²⁰ and is similar to that reported for the anodic dissolution of Al in $\text{LiAlBr}_4\text{-NaAlCl}_4\text{-KAlCl}_4$ (30-50-20 m/o).¹⁴

Information about the kinetics of the dissolution reaction can be extracted from this data by constructing Koutecky-Levich plots,²⁰ i.e., plots of j_a^{-1} versus $\omega^{-1/2}$

$$j_a^{-1} = j_k^{-1} + [k_c / (k_a - k_c C_{\text{Al}^{3+}}^*)] [0.538 (F D^{2/3})^{-1} \nu^{1/6}] \omega^{-1/2} \quad [9]$$

where the inverse of the intercept of these plots is $j_k = 3F(k_a - k_c C_{\text{Al}^{3+}}^*)$. In this expression, k_a and k_c are the potential-dependent anodic and cathodic heterogeneous rate constants, respectively. Consistent with Eq. 1, $C_{\text{Al}^{3+}}^*$ is $1/4(C_{\text{Al}_2\text{Cl}_7}^*)$. Example plots for each electrode based on the corresponding Levich plots are shown in Fig. 7. Because of contributions to the net current density from the back reaction, i.e., Eq. 1, it was necessary to construct graphs of $\log j_k$ versus η , i.e., classical Tafel plots, to determine the exchange current density, j_0 , by extrapolation of the linear portions of these graphs to $\eta = 0$

$$\log j_k = \log j_0 + \alpha_a F \eta / 2.303 RT \quad [10]$$

Examples of these graphs with the extrapolated anodic Tafel lines are shown in Figs. 8 and 9. Each data point was carefully corrected for the iR drop in the solution. The slopes of these plots, $\partial \log j_k / \partial \eta$, also give information about the apparent anodic transfer coefficient, α_a .²¹ The value of j_0 obtained from this extrapolation is directly related to the heterogeneous anodic rate constant, referenced to $\eta = 0$, or E_{eq} and defined here as $k_{a,0}$, by the relationship $j_0 = 3Fk_{a,0}$.

The resulting values of j_0 , α_a , and $k_{a,0}$ for each of the three electrodes in four to five different ionic liquid compositions are given in Table 1. Although there is unavoidable scatter in the data collected in this table due to the inherent inaccuracies associated with the extrapolation needed to avoid the very facile back reaction, it is a reasonable conclusion that j_0 is about the same for the two large disk electrodes, Electrodes B and C, but larger for the small annealed wire electrode, Electrode A. It is not clear if these results reflect structural differences

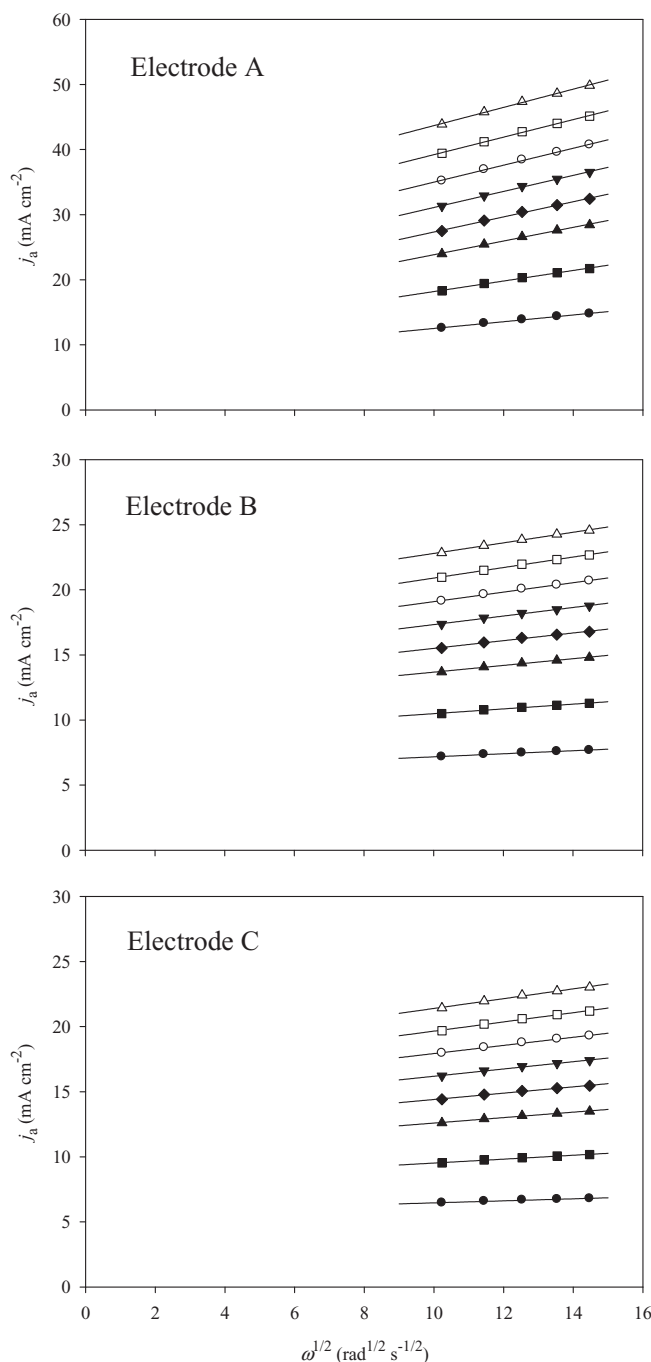


Figure 6. Examples of Levich plots for the anodization of Electrodes A, B, and C at 32°C in the 65 m/o ionic liquid. The currents were sampled at 300 s . The anodic overpotentials were Electrode A: (●) 0.053 V , (■) 0.082 V , (▲) 0.111 V , (◆) 0.130 V , (▼) 0.144 V , (○) 0.160 V , (□) 0.174 V , and (△) 0.190 V ; Electrode B: (●) 0.025 V , (■) 0.040 V , (▲) 0.055 V , (◆) 0.065 V , (▼) 0.075 V , (○) 0.086 V , (□) 0.097 V , and (△) 0.108 V ; Electrode C: (●) 0.028 V , (■) 0.043 V , (▲) 0.058 V , (◆) 0.068 V , (▼) 0.078 V , (○) 0.088 V , (□) 0.098 V , and (△) 0.108 V .

in the Al used to fabricate these electrodes. Thus, we have examined each of the electrodes with Electron Backscatter Diffraction (EBSD), and the results are given in the next section.

The data in this table do not seem to show any obvious dependence of j_0 on the ionic liquid composition at any of the electrodes, within the experimental precision of these measurements. The implication of this result seems to be that neither AlCl_4^- nor Al_2Cl_7^- ions are directly

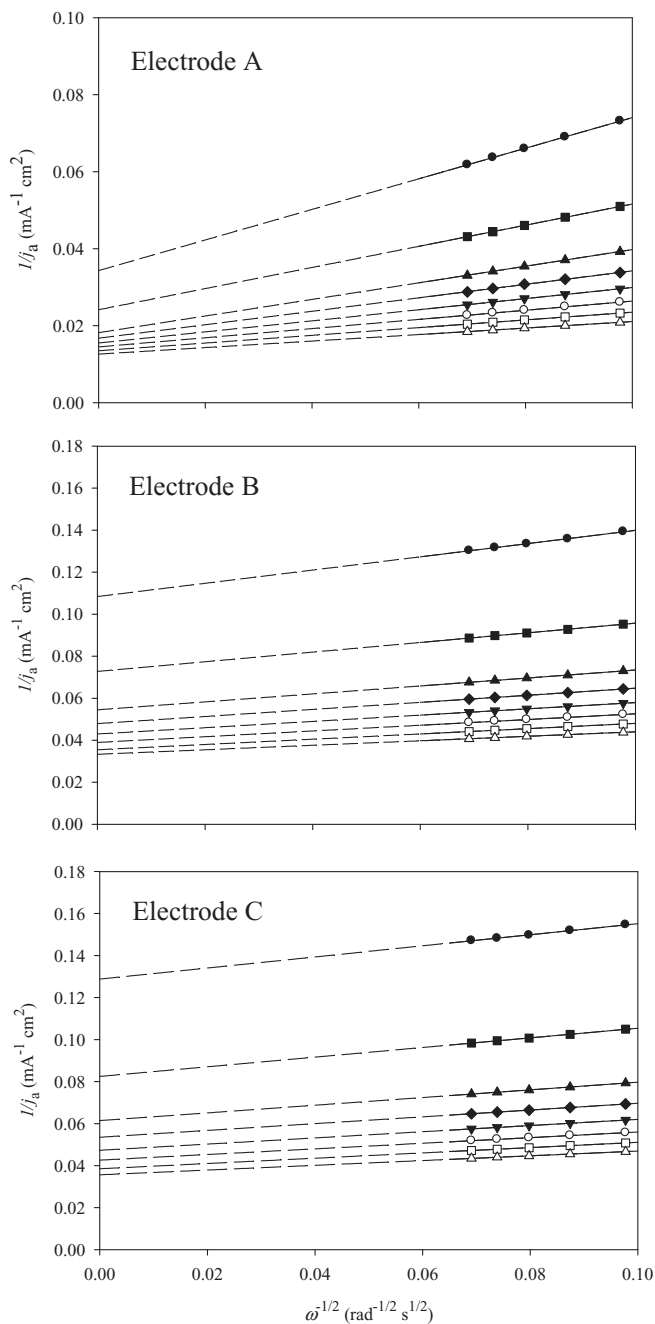


Figure 7. Examples of Koutecky-Levich plots for Electrodes A, B, and C constructed from the data in Fig. 6: The anodic overpotentials were the same as those given in this figure. The dashed lines are drawn to aid the eye.

involved in the rate-determining step of the fundamental Al dissolution process. In addition, the apparent anodic transfer coefficient is close to zero in all of the measurements. Although this result defies ready interpretation, similar small α_a values were found during an investigation of the Al dissolution reaction in the $\text{LiAlBr}_4\text{-NaAlCl}_4\text{-KAlCl}_4$ (30-50-20 m/o) molten salt at $t > 100^\circ\text{C}$. The microscopic pathway for the dissolution of Al in chloroaluminates is without doubt very complex. However, the application of techniques beyond the classical electrochemical methods used in this investigation will likely be required to fully realize this mechanism.

In order to estimate the apparent activation energy, $\Delta G_{a,0}^\ddagger$, for the Al dissolution process under the described conditions, we determined j_0 at several additional temperatures at each ionic liquid composition

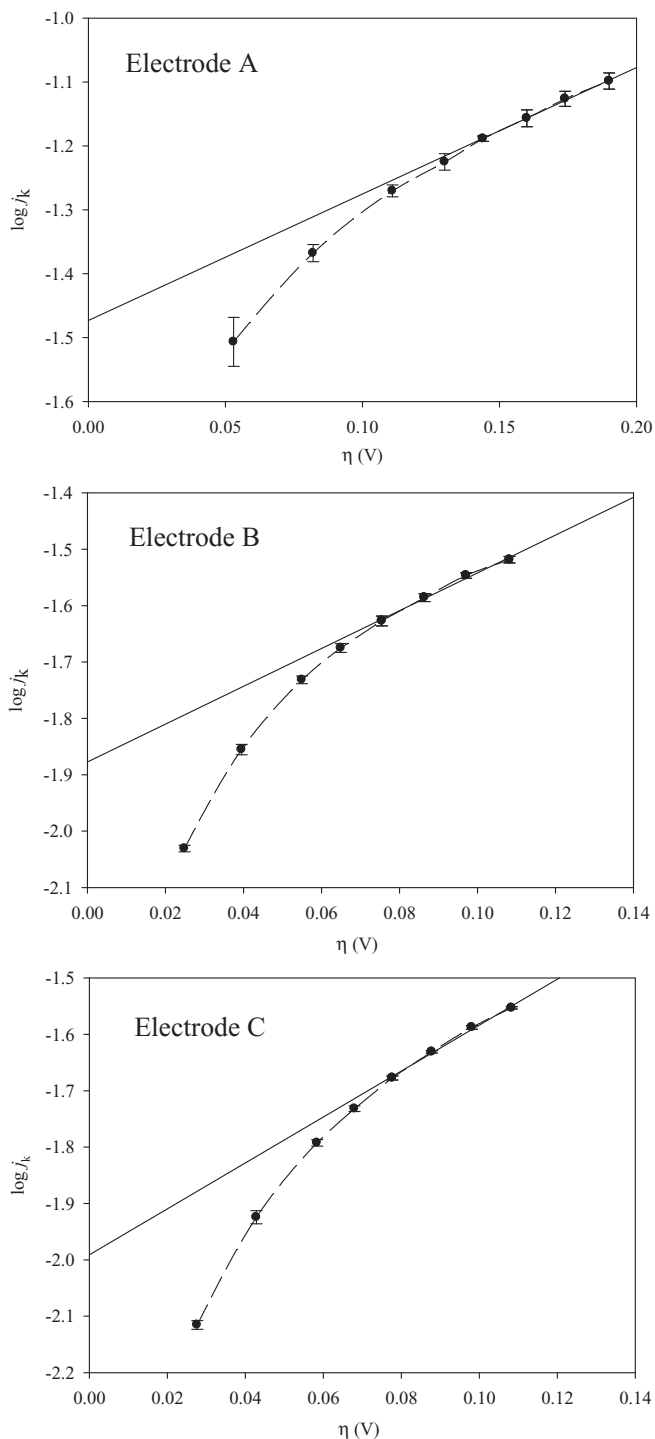


Figure 8. Examples of Tafel plots for Electrodes A, B, and C prepared from the data in Fig. 7. The error bars represent the 95% C.I. The dashed lines are drawn to aid the eye.

by using the same experimental procedures described above. As noted previously, the temperature range accessible with the Teflon-shrouded disk electrodes is limited because these electrodes are easily damaged by heating above $\sim 60^\circ\text{C}$. Unfortunately, the small temperature range available for experiments with these electrodes degraded the precision of these results. (Because the experimental data were very similar to those obtained at 32°C , and for reasons of space and repetition, the numerous Tafel plots are not reproduced here.) Arrhenius plots of $\log j_0$ versus $1/T$ that were constructed from this data were linear,

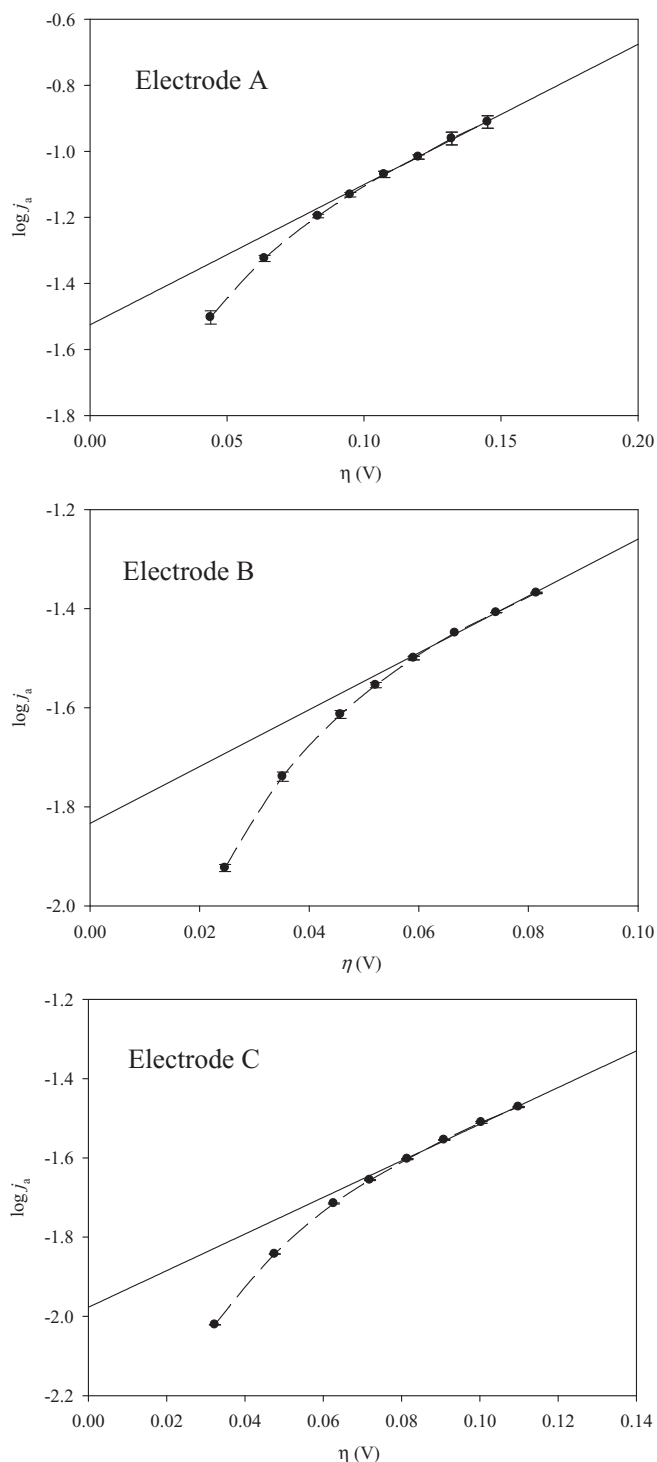


Figure 9. Examples of Tafel plots for Electrodes A, B, and C prepared from data recorded in the 54 m/o ionic liquid. The error bars represent the 95% C.I. The dashed lines are drawn to aid the eye.

and $\Delta G_{a,0}^\#$ was estimated from the slopes of these plots with the expression²²

$$\Delta G_{a,0}^\# = -2.303R \left[\partial \log j_0 / \partial (1/T) \right] \quad [11]$$

Given the independence of $\log j_0$ on the ionic liquid composition, it seemed valid to average the values of $\Delta G_{a,0}^\#$ obtained at different melt compositions at each electrode and given temperature. The results were 18.0 ± 0.9 , 17 ± 5 , and 16.3 ± 0.8 kJ mol⁻¹ for Electrodes A, B,

and C, respectively. The average of these three values is 17.3 kJ mol⁻¹ and is in reasonable agreement with the value of $\Delta G_{a,0}^\#$ measured for Al anodization in the LiAlBr₄-NaAlCl₄-KAlCl₄ molten salt, 17.1 kJ mol⁻¹.¹⁴

Electron backscatter diffraction.—In an effort to determine why the kinetic results obtained at the wire electrode were somewhat different from those observed at the two larger disk electrodes, the electrode materials were subjected to structural analysis with Electron Backscatter Diffraction (EBSD) as described in the Experimental section. Figure 10 shows the inverse pole maps and the pole figures of the three aluminum electrodes that were examined in cross-section; (a) electrode A (2-mm diameter aluminum wire), (b) electrode B (Pine Instruments RDE), and (c) electrode C (in-house, 6-mm diam Al rod). The pole figures show similar 100 fiber texture aligned with the wire/rod axis for all three electrodes. The 110 and 111 pole figures demonstrate the axisymmetry expected in a drawn or extruded wire or rod. While the 100 pole figure for electrode C has a more intense peak, the small number of grains makes a quantitative comparison with the other electrodes unreliable. The grain structure of the small wires (electrode A) exhibits a bimodal distribution, with smaller grains embedded in larger grains. The wires appear to have been only partially annealed after drawing or extrusion, as indicated by the smaller grain size and areas of similar orientation, but with misorientation boundaries of 2° to 4°. Grains range in size from 4 to 340 μm, with an average size of 21 μm. Electrode B has a higher density of small grains, but some larger grains are also present. Grain sizes range from 4 to 200 μm, with an average size of 14 μm. The inverse pole map of electrode C is quite different from the other samples, showing a large, equi-axed grain structure. The grain size and shape, as well as the high degree of texture (the 100 axis aligned with the rod axis) indicate that this sample was fully annealed. Grain sizes in this sample range from 40 to 880 μm, with an average size of 90 μm.

In order to quantify the extent of possible work-hardening in the wire (A) sample, the microhardness was measured and compared to that of the large-grained sample (C). The average microhardness (H_v) for sample C was 17.69 ± 0.78 (one standard deviation), while for sample A was 19.44 ± 1.58 . The measured difference in microhardness is slight, and not statistically significant. The slight hardness differences imply that the small wires do not have a large degree of cold work and dislocations. Since smaller grain size typically increases hardness, this may be the primary cause for the small difference in hardness.

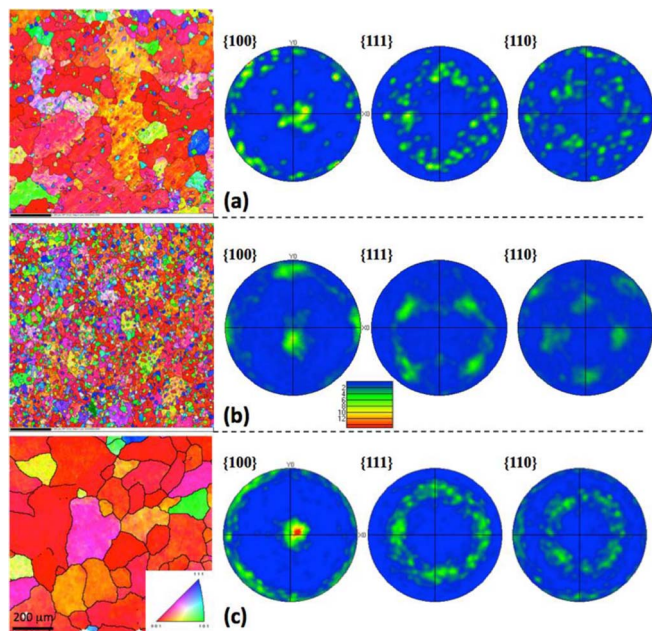
The EBSD analysis does not explain the enhanced dissolution kinetics of the sample (A) wire electrode. All three samples have a similar 100 fiber texture aligned with the wire/rod. Although the three samples appear to have different thermal history, based on the grain size distribution, the grain size alone does not correlate to the aluminum dissolution kinetics. At this point we can only attribute the enhanced kinetics to artificially larger current densities at the miniature electrode as the result of edge effects.

Conclusions

At small anodic potentials, the anodization of aluminum in AlCl₃-EtMeImCl ionic liquid proceeds under mixed kinetic and mass-transport control. At larger anodic potentials and higher oxidation rates, the anodization reaction transitions to a mass-transport limited process resulting from the formation of a steady-state passive layer of AlCl₃ on the Al electrode. Under conditions such as those encountered in a plating bath, the formation of this passive layer would significantly limit the overall rate of the cell reaction. Thus, because of these anode limitations, careful choices must be made about the temperature, ionic liquid composition, and applied potential when using this and related chloroaluminate ionic liquids for Al plating. In fact, for a given set of conditions, it is possible to define a critical current density above which the passivation is likely to be observed. Although the three Al samples examined in this investigation exhibited somewhat different

Table I. RDE results for the anodization of Al in the Lewis acidic AlCl₃-EtMeImCl ionic liquid.

	mol % AlCl ₃	31°C		41°C		51°C		61°C	
		log <i>j</i> ₀	α _a	log <i>j</i> ₀	α _a	log <i>j</i> ₀	α _a	log <i>j</i> ₀	α _a
Electrode A	51%	-1.622	0.246	-1.505	0.214	-1.403	0.221	-1.356	0.223
	54%	-1.525	0.256	-1.364	0.230	-1.294	0.223	-1.217	0.226
	58%	-1.445	0.339	-1.248	0.246	-1.187	0.226	-1.164	0.214
	62%	-1.294	0.150	-1.153	0.145	-1.132	0.164	-1.015	0.145
	65%	-1.473	0.120	-1.412	0.140	-1.293	0.129	-1.195	0.120
avg		-1.47 ± 0.11 ^a	0.222	-1.34 ± 0.12 ^a	0.195	-1.26 ± 0.09 ^a	0.193	-1.19 ± 0.11 ^a	0.186
<i>k</i> _{a,0} (cm s ⁻¹)		1.2 × 10 ⁻⁷		1.6 × 10 ⁻⁷		1.9 × 10 ⁻⁷		2.2 × 10 ⁻⁷	
Electrode B	51%	*	*	*	*	*	*	*	*
	54%	-1.834	0.348	-1.798	0.355	-1.689	0.401	-1.644	0.405
	58%	-1.885	0.311	-1.769	0.256	-1.706	0.362	-1.583	0.348
	62%	-1.883	0.191	-1.766	0.233	-1.650	0.240	-1.525	0.182
	65%	-1.877	0.203	-1.751	0.193	-1.722	0.168	-1.656	0.205
avg		-1.87 ± 0.02 ^a	0.263	-1.77 ± 0.02 ^a	0.259	-1.69 ± 0.03 ^a	0.292	-1.60 ± 0.06 ^a	0.285
<i>k</i> _{a,0} (cm s ⁻¹)		4.7 × 10 ⁻⁸		5.9 × 10 ⁻⁷		7.0 × 10 ⁻⁷		8.6 × 10 ⁻⁸	
Electrode C	51%	*	*	*	*	*	*	*	*
	54%	-1.980	0.088	-1.873	0.299	-1.787	0.401	-1.727	0.405
	58%	-1.945	0.378	-1.850	0.329	-1.759	0.362	-1.702	0.348
	62%	-1.987	0.269	-1.882	0.334	-1.820	0.240	-1.746	0.182
	65%	-1.991	0.244	-1.848	0.226	-1.806	0.168	-1.710	0.205
Avg		-1.98 ± 0.02 ^a	0.245	-1.86 ± 0.02 ^a	0.297	-1.79 ± 0.03 ^a	0.292	-1.72 ± 0.02 ^a	0.285
<i>k</i> _{a,0} (cm s ⁻¹)		3.7 × 10 ⁻⁸		4.7 × 10 ⁻⁸		5.6 × 10 ⁻⁸		6.6 × 10 ⁻⁸	

^a95% C.I.**Figure 10.** EBSD data showing the inverse pole maps of the sample direction normal to the cross section and calculated pole figures for (a) Electrode A; (b) Electrode B; and (c) Electrode C. An inverse pole figure key is shown as a sidebar in (c). The superimposed black lines represent misorientations of 10° or greater.

dissolution kinetics and grain size, there was no obvious correlation between these properties.

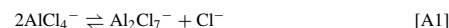
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Appendix

Because the equilibrium constant for the autosolvolytic reaction



is very small,²³ it is possible to neglect the concentration of Cl⁻ in Lewis acidic AlCl₃-EtMeImCl (and conversely the concentration of Al₂Cl₇⁻ in the basic composition, which is not considered here). Thus, the concentrations of Al₂Cl₇⁻ and AlCl₄⁻ in the ionic liquid can be obtained from simple considerations of stoichiometry. The derivation of Eq. 5 is as follows. In the Lewis acidic ionic liquid, the number of moles of AlCl₄⁻ is given by

$$n_{\text{AlCl}_4^-} = 2n_{\text{R}} - n_{\text{Al}} \quad [\text{A2}]$$

where *n*_R and *n*_{Al} represent the moles of EtMeImCl and AlCl₃, respectively, in a given ionic liquid mixture. The bulk concentration of AlCl₄⁻ (mol L⁻¹) is then

$$C_{\text{AlCl}_4^-}^* = 10^3 \rho (2n_{\text{R}} - n_{\text{Al}}) / w_{\text{m}} \quad [\text{A3}]$$

where *w*_m is the weight of the ionic liquid. The mole fraction of AlCl₃, *x*_{Al}, is

$$x_{\text{Al}} = n_{\text{Al}} / (n_{\text{Al}} + n_{\text{R}}) \quad [\text{A4}]$$

and therefore

$$n_{\text{Al}} = [x_{\text{Al}} / (1 - x_{\text{Al}})] n_{\text{R}} \quad [\text{A5}]$$

which gives

$$2n_{\text{R}} - n_{\text{Al}} = [(2 - 3x_{\text{Al}}) / (1 - x_{\text{Al}})] n_{\text{R}} \quad [\text{A6}]$$

Combining Eqs. A3 with A6 and substituting with *w*_R/*M*_R = *n*_R where *w*_R and *M*_R represent the weight and molecular weight of EtMeImCl, respectively, results in the relationship

$$C_{\text{AlCl}_4^-}^* = 10^3 \rho (2 - 3x_{\text{Al}}) w_{\text{R}} / [(1 - x_{\text{Al}}) w_{\text{M}} M_{\text{R}}] \quad [\text{A7}]$$

Eq. A8 is obtained from Eq. A5 by substituting for *n*_R as above and with (*w*_M - *w*_R)/*M*_{Al} = *n*_{Al} where *M*_{Al} is the molecular weight of AlCl₃ to yield

$$w_{\text{R}} / w_{\text{M}} = (1 - x_{\text{Al}}) M_{\text{R}} / [M_{\text{R}} + x_{\text{Al}} (M_{\text{Al}} - M_{\text{R}})] \quad [\text{A8}]$$

Finally, combining Eq. A7 with A8 yields Eq. 5.

An expression for the concentration of Al_2Cl_7^- , $C_{\text{Al}_2\text{Cl}_7^-}^*$, can be derived using the same approach. In this case, stoichiometric considerations show that the number of moles of Al_2Cl_7^- in a Lewis acidic mixture of EtMeImCl and AlCl_3 is given by

$$n_{\text{Al}_2\text{Cl}_7^-} = n_{\text{Al}} - n_{\text{R}} \quad [\text{A9}]$$

and it follows that

$$C_{\text{Al}_2\text{Cl}_7^-}^* = 10^3 \rho (n_{\text{Al}} - n_{\text{R}}) / w_{\text{M}} \quad [\text{A10}]$$

Consideration of Eq. A5 gives

$$n_{\text{Al}} - n_{\text{R}} = [(2x_{\text{Al}} - 1) / (1 - x_{\text{Al}})] n_{\text{R}} \quad [\text{A11}]$$

Combining Eq. A10 with A11 and substituting for n_{R} and n_{Al} , gives the following expression for $C_{\text{Al}_2\text{Cl}_7^-}^*$ (mol L^{-1})

$$C_{\text{Al}_2\text{Cl}_7^-}^* = 10^3 \rho (2x_{\text{Al}} - 1) / [M_{\text{R}} + x_{\text{Al}} (M_{\text{Al}} - M_{\text{R}})] \quad [\text{A12}]$$

Division of Eq 5 by Eq. A12 gives Eq. 8.

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