Room-temperature ionic liquids (RTILs), which is a name synonymous with room-temperature molten salts, have received considerable attention as novel reaction media, liquid materials, and starting materials for functional carbon material. The name “ionic liquid” was arbitrarily chosen to represent what are actually salts that liquefy at temperatures below 373 K. The interest in these materials stems from their favorable physicochemical properties, such as low-flammability, negligible vapor pressure, relatively high ionic conductivity, and high electrochemical stability.\(^1\)\(^–\)\(^6\) It is now common knowledge in the chemistry community that many RTILs are stable in air or even water. The “first generation ionic liquids” were difficult to handle because the typical anions known at that time, e.g., AlCl\(_4\)\(^−\) and Al\(_2\)Cl\(_7\)\(^−\), reacted strongly with moisture in the air. Only a very limited number of laboratories with special skills for handling them could effectively use these RTILs. No doubt, the flourishing interest in RTIL chemistry was heavily abetted by the discovery of air and water stable systems, i.e., the so-called “second generation ionic liquids”.

However, we should not devalue the first generation systems such as those based on quaternary organic halide salts and aluminum halides, e.g., AlBr\(_3\) and AlCl\(_3\), known as haloaluminates. The activity of the haloaluminates as well as their adjustable Lewis activity is precisely what makes them interesting and very versatile. By contrast, the second-generation “inert” ionic liquids, are just that: inert and nonreactive, both chemically and electrochemically. Furthermore, the ionic conductivity and viscosity of the haloaluminates, which are important factors for the electrochemical applications described herein, exceed those for the comparable second-generation RTILs. For example, the ionic conductivity and viscosity for 60.0–40.0 mol\% [C\(_2\)mim]Cl is sometimes used as the bath to electroplate pure Al. In those early days, the electrochemical reaction leading to Al electroplating had not been clarified, but it is now known to be the three-electron reduction of the coordinately unsaturated Al\(_2\)X\(_7\)\(^−\) ion

\[
4\text{Al}_2\text{X}_7\text{Al}^+ + 3e^- \rightarrow 2\text{Al} + 7\text{AlX}_4\text{Al}^+ \quad [1]
\]

where X is either Br or Cl.\(^3\) Most modern research is carried out exclusively with chloroaluminate RTILs because those based on Br tend to undergo photodecomposition and show slightly lower ionic concentration of the reducible species, e.g., 3.06 M Al\(_2\)Br\(_7\) in 66.7 mol\% AlBr\(_3\)–[C\(_2\)mim]Br at 298 K.\(^13\) compared to the chloride-based system with 3.27 M Al\(_2\)Cl\(_7\) in 66.7 mol\% AlCl\(_3\)–[C\(_2\)mim]Cl as low as well as higher conductivity and higher viscosity at the same temperature.\(^14\) Traditionally, the organic component of these RTILs has been either 1-(1-butyl)pypyridinium chloride ([C\(_3\)pyp][Cl])\(^15\)\(^–\)\(^16\) or [C\(_2\)mim][Cl].\(^17\) 1-Butyl-3-methylimidazolium chloride ([C\(_2\)mim][Cl]) is sometimes used as the organic salt component because the synthetic preparation proceeds at atmospheric pressure without special equipment. However, due to its superior physical properties, AlCl\(_3\)–[C\(_2\)mim][Cl] is most commonly employed, particularly as the solvent for Al plating. The greater cost of the normally more expensive [C\(_2\)mim][Cl] salt has been mitigated to some extent by the commercial availability of the crude product. However, this material still needs considerable processing to be a useful component of plating baths. The much cheaper [C\(_3\)pyp][Cl] salt is often overlooked as well. Although it is of less academic interest than its 1,3-dialkylimidazolium cousins, the 66.7 mol\% eutectic makes a fine, inexpensive Al plating bath. In all chloroaluminate RTILs, Al and Al alloy coatings can only be prepared from those containing more than 50 mol\% AlCl\(_3\), i.e., Lewis
Acidic melts in which the reducible AlCl₃⁻ ion exists. Although the AlCl₃⁻ ion, which is a major constituent of these RTILs, is in principle reducible to Al, the organic cation component is reduced at more positive potentials than this ion. The electrodeposition of Al by reduction of AlCl₃⁻ is normally seen only in inorganic molten salts, such as AlCl₃–NaCl. Some other aluminum chloride-based solvents with properties similar to traditional chloroaluminate should also be recognized here. For example, the combination of certain polarizable organic compounds with AlCl₃ often produces nonaqueous solutions at or close to room temperature. These mixtures are often called solvate ILs and/or deep eutectic solvents. In the AlCl₃-based mixtures, the following reaction is believed to proceed spontaneously:

\[
2\text{AlCl}_3 + n\text{B} \rightarrow [\text{AlCl}_3-n\text{B}]^+ + [\text{AlCl}_3^-] \quad [2]
\]

where B is a polarizable organic compound. Unfortunately, the ionic conductivity and viscosity of these solvate systems do not reach those for commonly-used chloroaluminate RTILs, but the preparation cost is much lower. Major components for some haloaluminate RTILs and solvate mixtures are summarized in Fig. 1.

Aluminum and its alloy coatings can be used to improve the surface corrosion resistance of reactive ferrous metals such as iron and carbon steel. Today, most commercial Al plating is carried out by using technology that was originally developed by Siemens, AG (Germany). This technology, which is called the Sigal process, is currently licensed to AlumiPlate, Inc. in the USA. Rasant-Alcotec in Germany also provides commercial Al plating. The plating process involves pyrophoric mixtures composed of organoaluminum compounds, aromatic solvents, and other additives such as alkali halides or hydrides and quaternary onium salts. From both safety and environmental perspectives, the use of aromatic solvents leaves much to be desired. Thus, the plating of Al and Al alloys from room-temperature chloroaluminate has been explored with the goal of improving the current Al plating technology. (For more information on Al plating from conventional aromatic solvents, the reader is invited to examine the review by Zhao and VanderNoot.)

As described above, the most distinct characteristic of the haloaluminate RTIL systems is that aluminum metal can be deposited electrochemically through the reaction described by Eq. 1. It is interesting to note that the Al electrodeposition/stripping process proceeds at 100% coulombic efficiency, if the ionic liquid is reasonably pure and free from reducible protonic impurities. This suggests that we can use Al as a negative electrode for rechargeable Al energy storage systems based on chloroaluminates. However, it has not been easy to identify an appropriate active material for a positive electrode due to the very reactive nature of the Lewis acidic RTILs. There has simply not been enough research on the positive electrodes for use in these RTILs compared to for example Li-ion secondary batteries, although Al rechargeable batteries have the potential to be the next generation high-capacity electric storage system that is based on a relatively abundant element. In this article, we review the status of electrochemical technology based on haloaluminate RTILs and related solvate ILs that has taken place over the past decade. This review is intended to be a sequel to the many excellent reviews about these solvents.

**Aluminum Electrodeposition from Haloaluminate-Based RTILs and Solvate ILs**

**Aluminum electroplating.—** As noted above, aluminum electroplating has been studied extensively in the Lewis acidic AlCl₃–[C₄mim]Cl and AlCl₃–[C₆py]Cl RTILs. Chloroaluminate RTILs based on other types of organic chloride salts have also been studied for this purpose, but they have been found to offer little or no advantage over these systems. Recently, Fischer and Leadbetter, et al. provided a comprehensive report about Al electroplating from chloroaluminate RTILs under many different experimental conditions. We believe that this well-written report provides basic knowledge and many good suggestions for beginners who intend to explore Al deposition in chloroaluminate RTILs.

When moderate current densities (≤ ca. 40 mA cm⁻²) are applied during the electroplating process, relatively-dense and crystalline Al deposits are easily obtained. But dendritic crystals are observed on the cathode surface as the current density is increased above this value. This unfavorable surface morphology is apparently caused by changes in the Lewis acidity resulting from the depletion of AlCl₃⁻ at the electrode surface during the plating reaction. This is a huge issue for the industrialization of this technology. There are two avenues for overcoming this problem. One is to improve mass transport in the RTIL by raising the temperature of the plating bath. Referring back to our own experiences, these plating baths should not be heated above 373 K to avoid deterioration of the haloaluminate RTIL, which results in decomposition of the organic cation and subsequent sublimation of AlCl₃. Another approach for modifying the viscosity and increasing the conductivity of these plating baths is to add aromatic hydrocarbon co-solvents, such as benzene, toluene, xylene, or ethylene glycol. Surprisingly, the crystallographic texture of the resulting Al deposit depends on the co-solvent used. For example, as shown in Fig. 2, Takahashi, et al. found that the orientation indexes of the Al electrochemically obtained in chloroaluminate RTILs with benzene and toluene, respectively are 200 and 111 at applied current densities exceeding 1.5 A dm⁻². In the case of toluene, the crystallographic orientation does not change in the range of 0.75 to about 2.0 A dm⁻². Uii, et al. reported that the metallic luster of the plated Al produced in 66.7 mol% AlCl₃–[C₄mim]Cl containing ε- or m-, or p-xylene is closely related to the crystallographic orientation and surface morphology of the deposit. Other possible approaches for obtaining smooth Al layers are the use of leveling agents and the application of electrochemical pulse methods during the plating process. Figure 3 shows SEM images of Al electrodeposits produced from 60.0 mol% AlCl₃–[C₄mim]Cl containing different concentrations of nicotinamide (i.e., 3-pyridinocarboxamide). The surface morphology of the Al deposits depends on the concentration of the nicotinamide, and once the concentration of this leveling agent exceeds 6.0 mM, the substrate is covered with smooth, fine Al crystallites. As noted, pulsed current methods can also improve deposit morphology. Wang and Azumi report that a bipolar current pulse polarization (BCP) method, which slightly dissolves the developing Al deposit by applying a small anodic current pulse, improves the surface morphology of the deposits in 66.7 mol% AlCl₃–[C₄mim]Cl. They conclude that the best result is obtained with the following conditions: duty ratio = 0.5,

---

4Certain trade names are mentioned for experimental information only; in no case does it imply a recommendation or endorsement by NIST.

---

Figure 1. Typical components of haloaluminate room-temperature ionic liquids and their solvent mixtures.

Figure 2. In the case of toluene, the crystallographic orientation does not change in the range of 0.75 to about 2.0 A dm⁻². Uii, et al. reported that the metallic luster of the plated Al produced in 66.7 mol% AlCl₃–[C₄mim]Cl containing ε- or m-, or p-xylene is closely related to the crystallographic orientation and surface morphology of the deposit. Other possible approaches for obtaining smooth Al layers are the use of leveling agents and the application of electrochemical pulse methods during the plating process. Figure 3 shows SEM images of Al electrodeposits produced from 60.0 mol% AlCl₃–[C₄mim]Cl containing different concentrations of nicotinamide (i.e., 3-pyridinocarboxamide). The surface morphology of the Al deposits depends on the concentration of the nicotinamide, and once the concentration of this leveling agent exceeds 6.0 mM, the substrate is covered with smooth, fine Al crystallites. As noted, pulsed current methods can also improve deposit morphology. Wang and Azumi report that a bipolar current pulse polarization (BCP) method, which slightly dissolves the developing Al deposit by applying a small anodic current pulse, improves the surface morphology of the deposits in 66.7 mol% AlCl₃–[C₄mim]Cl. They conclude that the best result is obtained with the following conditions: duty ratio = 0.5,
frequency = 2 Hz, \( j_a = -16.0 \text{ mA cm}^{-2} \), and \( j_c = +1.0 \text{ mA cm}^{-2} \) as depicted Fig. 4. These approaches could become options for producing non-dendritic Al platings.

Aluminum-coated steel produced from chloroaluminate RTIL exhibits the same corrosion resistance as Al-coated steel prepared by other physical coating methods. More than twenty years ago, a manufacturing pilot plant based on this RTIL technology was developed by Nisshin Steel Co., Ltd. (Japan), but at that time the plant was not economically viable due to the high cost of synthesizing the organic salt component. However, recent advances in small batch organic synthetic technology now make this commercial plating process viable. Thus, during this decade, the electroplating of pure Al from Lewis acidic chloroaluminates has drawn renewed attention from the chemical and aluminium industries because the cost of producing dialkylimidazolium chloride salts, e.g., [C2mim]Cl and [C4mim]Cl, is becoming significantly less costly compared to the 1990’s. (Of course, from an industrial standpoint, these are still not cheap chemicals!) In addition to this factor, improvements in the atmospheric control systems that can produce very low concentrations of water and oxygen also contribute to this revival. When the atmosphere in the electroplating cell is controlled appropriately, deterioration of the electroplating bath by chemical stress is not recognized at temperatures below 368 K. When the atmosphere in the electroplating cell is controlled appropriately, deterioration of the electroplating bath by chemical stress is not recognized at temperatures below 368 K. However, decomposition of the \([\text{C}_2\text{mim}]^+\) cation, especially through cleavage of the \(\text{C}_2\text{mim}^-\) anion, is initiated at 368 K.50 In order to simplify the conditions the physicochemical properties and ionic/chemical speciation in the electroplating bath during long-term operations. Thus, more investigations of this promising, but largely untested strategy are warranted.

A so-called “blind spot” related to large scale Al electroplating in RTILs is the anodic reaction that resupplies the reducible aluminum species during the plating process through the reverse of Eq. 1. Recent investigations of the dissolution of Al that are based on the seminal work by Holleck and Giner53 have been carried out in the low-melting mixed halide molten salt, LiAlBr4–NaAlCl4–KAlCl4,54 as well as Lewis acidic AlCl3–[C2mim]Cl. In both liquid systems, the anodization reaction is under mixed kinetic/mass-transport control at moderate overpotentials, but becomes a mass transport-limited process governed by the dissolution of a passive layer of solid AlCl3 on the anode at more positive overpotentials.55,56 Not surprisingly, in consideration of the reaction in Eq. 1, the anodic process is favored in slightly acidic melts, but highly disfavored under very acidic conditions. Thus, a truly high speed, efficient Al plating process must also take into account the limitations associated with the anode reaction. Designing a cell that gets the best out of both the anode and cathode reactions may require considerable ingenuity. There is no doubt that modeling of the Al electrode reactions from an electrochemical engineering perspective will be a valuable procedure for planning and designing large scale electrolysis cells.57

Of special note for Al plating is the lower preparation cost associated with the use of AlCl3-based solvent mixtures, e.g., sольвент ILs with polarizable organic molecules or deep eutectic solvents. The biggest disadvantage of these systems is that physicochemical properties such as conductivity and viscosity are inferior to those of conventional chloroaluminate RTILs. Some of the mixtures that have been explored include LiAlCl4–dimethylsulfoxide (DMSO),20 AlCl3–DMSO,20–25 AlCl3–diethylsulfone (DOSO),20 AlCl3–dipropylsulfone (DPSO),20,21 AlCl3–dialkylsulfone (RR’SOF2),21 AlCl3–urea,26,51 AlCl3–acetamide,26 AlCl3–diglyme,27 AlCl3–1,3-dimethyl-2-imidazolidinone (Me2imid),28 and AlCl3–4-propylpyridine (4-PrPy).29 Surprisingly, these mixtures usually show better thermal stability than the individual component compounds themselves. As an example, thermogravimetric analysis diagrams of
Figure 3. SEM images of Al electrodeposits obtained from 60.0 mol% AlCl₃–[C₄mim]Cl with (a) 0, (b) 2.0, (c) 4.0, (d) 6.0, and (e) 8.0 mmol L⁻¹ of added nicotinamide at 303 K. The current density was −3.4 mA cm⁻². Images reproduced by permission of Springer.

Figure 4. (a) Examples of the current pulse waveform and resulting potential response observed during the application of a bipolar current pulse-polarization method. SEM images of Al electrodeposited from 66.7 mol% AlCl₃–[C₂mim]Cl using the BCP method with duty ratio = 0.5, frequency = 2 Hz, \( j_a = −16 \text{ mA cm}^{-2} \), and \( j_a = (b) 0.3, (c) 0.5, \) and (d) 1.0 mA cm⁻²; and (e) cross-section image of the deposit in Fig. 4d. Images reproduced by permission of Elsevier.

Figure 5. Chromatograms of (A) a test mixture consisting of 1-methylimidazole, 1-ethylimidazole, 1,3-dimethylimidazolium acetate, 1,3-dimethylimidazolium chloride (1 mg L⁻¹), (B) fresh AlCl₃–[C₂mim]Cl ionic liquid, (C) long-term stored ionic liquid, and (D) the ionic liquid after electrodeposition stress. The detailed analytical procedures are described in Ref. 49. Images reproduced by permission of Wiley-VCH.

AlCl₃, 4-PrPy, and their mixtures are shown in Fig. 6. The onset of the evaporation of the two AlCl₃–4-PrPy mixtures is ca. 523–543 K, whereas those for AlCl₃ and 4-PrPy are 433 and 368 K, respectively. This behavior is likely due to the formation of Al-containing cations and AlCl₄⁻ anions by the following reaction:

\[
2\text{AlCl}_3 + 2(4\text{-Pr-Py}) \rightleftharpoons [\text{AlCl}_2(4\text{-Pr-Py})_2]^+ + [\text{AlCl}_4^-] \quad [3]
\]

Excess AlCl₃ may induce the formation of [AlCl₂(4-Pr-Py)]⁺ according to the reaction mechanism:

\[
2\text{AlCl}_3 \rightleftharpoons [\text{AlCl}_2]^+ + [\text{AlCl}_4^-] \quad [4]
\]

\[
[\text{AlCl}_2]^+ + [\text{AlCl}_2(4\text{-Pr-Py})_2]^+ \rightleftharpoons 2[\text{AlCl}_2(4\text{-Pr-Py})]^+ \quad [5]
\]

In AlCl₃–DMSO₂ mixtures, a thin film of electrolytic Al is obtained by reduction of the Al-containing cations in a mixture containing 10 mol AlCl₃ + 3 mol DMSO₂ + 0.01 mol trimethylamine hydrochloride (Fig. 7). The resulting Al film consists of fine crystals, and a film thickness of up to 27 μm is easily attained. Hirato, et al., postulated that in AlCl₃–Me₂imdn mixtures, excess AlCl₃ simply reacts with [AlCl₄⁻] anions in the well-known acid-base

Figure 6. Thermal gravimetric analysis diagrams of AlCl₃, 4-propylpyridine, and their complexes at different ratios under a helium atmosphere. The heating rate was 20 K min⁻¹. Images reproduced by permission of Elsevier.
Figure 7. (a) Photograph and (b) SEM image of electrolytic Al thin films prepared in a 23–77 mol% mixture of AlCl₃–DMSO containing 0.01 mol trimethylamine hydrochloride. The electroplating bath was agitated at 368 K. Images reproduced by permission of the Surface Finishing Society of Japan.

Figure 8. (a) Photograph and (b) SEM image of an Al electrodeposit obtained from a 54.5–45.5 mol% AlCl₃–Me2imdn mixture at 353 K. Images reproduced by permission of Elsevier.

Reaction

\[ \text{AlCl}_3 + [\text{AlCl}_4]^- \rightarrow [\text{Al}_2\text{Cl}_7]^- \]  \hspace{1cm} \text{(6)}

and that Al with a bright metallic luster is electroplated by reduction of the \([\text{Al}_2\text{Cl}_7]^-\) species (Fig. 8). It is difficult to reduce Al-containing cations to the metallic state in Me₂imdn-rich chloroaluminate mixtures. The reason is not entirely clear, but the strong coordination of the \([\text{AlCl}_2]^+\) cations by the polarizable organic molecules may contribute to this result.

Deposition of Al nano/microstructures.—There are several recent articles describing the electrodeposition of Al nano/microstructures from chloroaluminate RTILs. These structures can be produced by both templated and non-templated processes. Detailed information about the use of templates is available elsewhere. Templated electroplating is not an unusual process, but it is difficult to apply the methods that are employed in aqueous solutions to Lewis acidic chloroaluminate RTILs and solvate mixtures. This is because only a limited number of template materials are stable in the Lewis acidic melts.

Deposition of Al nano/microstructures.—There are several recent articles describing the electrodeposition of Al nano/microstructures from chloroaluminate RTILs. These structures can be produced by both templated and non-templated processes. Detailed information about the use of templates is available elsewhere. Templated electroplating is not an unusual process, but it is difficult to apply the methods that are employed in aqueous solutions to Lewis acidic chloroaluminate RTILs and solvate mixtures. This is because only a limited number of template materials are stable in the Lewis acidic melts.

Electrodeposition Aluminum Alloys from Haloaluminate RTILs

In the recent past, we reviewed the electrodeposition of Al alloys from haloaluminate ILs, mostly Lewis acidic AlCl₃–[C₂mim]Cl. ©

Thus far, only two materials have been found suitable for templates in chloroaluminate ionic liquids under these conditions. One material is porous/ordered alumina, and the other is a polycarbonate (PC) membrane. In practice, the alumina template method requires a specialized electroplating arrangement. The use of PC membranes entails pretreatment by sputtering Au on one surface before Al electroplating can be carried out. Both methods require a template dissolution process. What is interesting about the PC membrane approach is that Al is electrodeposited on both sides, i.e., both on the PC membrane side and on the Au-coated side as shown in Fig. 9 during the electroplating process. Self-standing Al wires are obtained if the electroplating is carried out under the appropriate conditions. Interestingly, longer Al wires coalesce to form Al wire bundles (Fig. 9b). Without doubt, the use of templates during the electrodeposition of Al is an important and fascinating process for nano/microstructure electroplating of this important metal. The electroplating of ordered nano/microstructures of Al without templates may seem to be a fantasy. However, Sun and his colleagues have succeeded in the electrodeposition of Al nanowires from Lewis acidic AlCl₃–[Me₂HN]Cl (Figure 10). The wire diameter, which can be controlled with the Lewis acidity and applied potential, ranges from 170 ± 23 to 510 ± 96 nm. These deposits can be produced on tungsten, glassy carbon, platinum, and aluminum substrates. Sun’s group concluded that the key factors for making the Al nanowires without templates are simply stationary solutions and constant bath temperatures (303 K). Under such conditions, unique electric double layer structures by specific adsorption of anions are formed during the electroplating process, which may contribute to one-directional Al electrodeposition and growth. More recently, Sun and coworkers have demonstrated that constant current methods result in the electrodeposition of interesting “worm-like” structures in the very same IL system (Fig. 11). The process seems to be driven by a potential oscillation during the galvanostatic deposition.
During this decade, the electroplating of several new binary (Al-M1) and ternary (Al-M1-M2) alloys has been reported. Included in this list are Al-Hf, Al-W, Al-In-Sb, Al-Mo-Ti, and Al-W-Mn. As discussed in our previous review, we categorized Al alloy electrodeposition from haloaluminate RTILs into three main types. Here, we focus only on “overpotential-driven” Al-M and Al-M1-M2 alloy deposition because the most significant results are obtained only in this area.

**Binary Al alloy deposition.**—In most cases, this alloying process results in dense, adherent corrosion-resistant alloys because the resulting electrodeposits are thermodynamically stable in Lewis acidic haloaluminate RTILs. These alloys are formed at or less than 0 V vs. Al(III)/Al without difficulty. Many Al alloy systems have been prepared by this route, including Al-Mg, Al-Ti, Al-Zr, Al-Hf, Al-V, Al-Cr, Al-Mo, Al-W, Al-Mn, Al-In, and Al-La. It has been determined by X-ray diffraction techniques that Al-Zr, Al-Cr, Al-Mo, Al-W and Al-Mn in particular form amorphous glass phases. Normally, metal cations having the lowest oxidation number are employed for the alloy electroploating process because the cations are reduced directly to the metal and alloyed with Al. Although the reason is not entirely clear, the lowest oxidation state of these metal ions is often stabilized by the strong Lewis acidity of the plating bath. For example, during the dissolution of TiCl4 in 60.0 mol% AlCl3–[C2mim][Cl], a small amount of purple precipitate identical to solid TiCl3 is present in the 60.0 mol% RTIL. However, the TiCl3 was not obvious under the more acidic conditions provided by the 66.7 mol% RTIL. The presence of TiCl3 in solutions of TiCl4 could arise through several different routes, including slow disproportionation of the dissolved Ti(II) as shown in Eq. 7.

\[ 3[\text{Ti(AlCl4)}]^- + 3[\text{AlCl}_4^-] \rightarrow 2\text{TiCl}_3(s) + \text{Ti} + 6[\text{Al}_2\text{Cl}_7]^- \]  

Serfi and Öye reported that Ti(II) tends to disproportionate in AlCl3–KCl molten salts containing less than 60.0 mol% AlCl3, where the [AlCl4]− concentration is large, but it is stable in strongly Lewis acidic melts.

The transition metal content of the resulting Al-M1 alloys generally decreases with increasing current density because at low reduction current densities and correspondingly less negative potentials, the partial current density for the metal ion reduction is a larger fraction of the total current. As the current density is increased, the partial current for the reduction of the metal ions reaches a limiting value, whereas the partial current for AlCl3− reduction continues to increase. This is because the AlCl3− concentration is usually massively larger (3.27 mol L−1 in 66.7 mol% AlCl3–[C2mim][Cl] at 298 K) than the metal ion concentration (usually 10–100 mmol L−1). This behavior is a common feature of overpotential alloy deposition in chloroaluminate RTILs. Figure 12 shows an example of this behavior. In this case, the tungsten content of the Al-W alloy prepared electrochemically in 66.7 mol% AlCl3–[C2mim][Cl] containing dissolved K3[W2Cl9] as the source of tungsten is shown as a function of the applied current density. As described above, the W content of the alloy decreases with increasing current density.

In many cases, the electrochemical reduction of quadrivalent transition metal ions, M(IV), e.g., Ti(IV) and Zr(IV), is complicated in the Lewis acidic chloroaluminate RTILs. The reason is that the reaction involves a chemical step that produces insoluble MCl3(s). It is difficult to produce M(II) ions from M(IV) species for elements with high atomic numbers, since the higher oxidation state species become favored going down a group in the periodic table. In Group 4 (Ti, Zr, Hf), we found that Ti(II) and Zr(II) can be produced chemically from the tetravalent species, but not Hf(II). Even if the lowest oxidation state is unstable, it is possible to use the M(IV) species to produce Al-M alloys, and Al-Hf is a good example. As indicated in Fig. 13, the surface morphology is dependent on the applied current density and the bath temperature, but seems to be independent of the HF content in the alloy samples for a given bath temperature. The deposited crystals become finer as the current density increases and/or the bath temperature decreases. In solutions of M(IV) ions, the alloying mechanism is likely different from that obtained by direct reduction from the lower oxidation state ions, M(II), but the result is nevertheless the same. The electrode reaction for the M(IV)/M(III) couples, wherein an EνEνCν-type reaction is observed, may simply be an anomaly.

The properties of nonequilibrium aluminum alloys resulting from this electrodeposition process, except Al-W, are virtually identical to those prepared by conventional nonequilibrium alloying methods (sputtering, melt spinning, plasma spraying, and ion implantation). These coatings typically show excellent chloride-induced pitting potential compared to pure Al. The favorable corrosion resistance of the Al-M alloys prepared in the Lewis acidic AlCl3–[C2mim][Cl] has been thoroughly investigated by recording potentiodynamic anodic polarization curves in Na2-saturated aqueous 0.1 M NaCl. All electrodoped Al-M1 and Al-M1-M2 alloys display a stable passive region, characterized by a small potential-independent current, followed by a sudden rise in current at the pitting potential. Among the electrodoped aluminum binary alloys, Al-Mo alloys containing more than 8 atomic fraction (a/o) Mo exhibit the most positive chloride-corrosion pitting potential of about +0.7 − 0.8 V against pure Al. Unfortunately, the Al-W alloy system, which on paper would seem to be superior to almost all of the other alloys investigated to date, in

---

**Figure 11.** Typical SEM images of Al wires electrodeposited on a tungsten wire electrode in 58–42 mol% AlCl3–[Me3HN]Cl at 0.25 mA cm−2 at a bath temperature of 311 K. Images reproduced by permission of The Electrochemical Society, Inc.

**Figure 12.** Relationship between the applied current density and W content of Al-W electrodeposits prepared in Cu rotating electrodes in 66.7 mol% AlCl3–[C2mim][Cl] containing K3[W2Cl9] under various conditions at 533 K. K3[W2Cl9] concentration: 8.0 mmol L−1, rotation rate: 105 rad s−1; K3[W2Cl9] concentration: 3.2 mmol L−1, rotation rate: 105 rad s−1; K3[W2Cl9] concentration: 3.2 mmol L−1, rotation rate: 209 rad s−1. Graph reproduced by permission of The Electrochemical Society, Inc.
fact suffers from a powdery morphology and poor resistance to pitting corrosion, especially at higher W content.\textsuperscript{73}

**Ternary Al alloy deposition.** There is little research on this topic, because the deposition of Al-M1-M2 alloys presents certain experimental problems in that the composition of these materials is difficult to control, owing to the presence of two alloying components, M1 and M2, in the plating bath. Nevertheless, Ueda, et al.,\textsuperscript{74} succeeded in controlling the composition of the Al-Ni-Cr ternary alloy produced from Lewis acidic AlCl3-[C2mim]Cl by using pulse techniques. By examining the partial current densities for Al, M1, and M2, we can gain considerable insight into the mechanism by which the ternary alloys, Al-M1-M2, are produced in chloroaluminate RTIL. The alloy composition data are conveniently converted to partial current densities by using the following expressions:

\[
\begin{align*}
\dot{j}_{M1} &= \frac{\dot{j} n_{M1} x_{M1}}{n_{M1} x_{M1} + n_{M2} x_{M2} + n_{Al} x_{Al}} \quad [8] \\
\dot{j}_{M2} &= \frac{\dot{j} n_{M2} x_{M2}}{n_{M1} x_{M1} + n_{M2} x_{M2} + n_{Al} x_{Al}} \quad [9] \\
\dot{j}_{Al} &= \dot{j} - \dot{j}_{M1} - \dot{j}_{M2} \quad [10]
\end{align*}
\]

where \( \dot{j} \) is the applied current density used for the electrodeposition process; \( \dot{j}_{M1}, \dot{j}_{M2}, \) and \( \dot{j}_{Al} \) represent the partial current densities for M1, M2, and Al, respectively; \( n_{M1}, n_{M2}, \) and \( n_{Al} \) represent the number of electrons involved in the alloy deposition; and \( x_{M1}, x_{M2}, \) and \( x_{Al} \) are the atomic fractions of M1, M2, and Al in the alloys, respectively. Here we show for an example plots of \( \dot{j} vs. j_{Al} \) and \( \dot{j} vs. j_{M1} \) for the Al-W-Mn alloys electrodeposited from Lewis acidic AlCl3-[C2mim]Cl with K3[W2Cl9] and/or MnCl2 in Fig. 14.\textsuperscript{76} Note that \( j_{Al} \) is a linear function of \( j \), but the plots of \( j_{M1} \) versus \( j \) and \( j_{M2} \) versus \( j \) display a more interesting behavior. While \( j_{M1} \) for the binary Al-W alloy is an approximately constant value of \( 0.4 \pm 0.1 \text{ mA cm}^{-2} \), that for the ternary Al-W-Mn alloys decreases at higher \( j \) and then reaches a limiting value of \( 0.1 \text{ mA cm}^{-2} \). This behavior results from the fact that \( j_{Al} \) and \( j_{M2} \) increase at much higher fraction of \( j \) at higher applied current densities. This result was noted during previous studies of Al alloy electrodeposition from this same RTIL system.\textsuperscript{74,75,84} and it is based on the fact that the concentration of K3[W2Cl9] in the solvent is much smaller than the concentration of the reducible Al(III) and Mn(II) species. Figure 14 also shows that \( j_{M2} \) increases with \( j \) and decreases with a decrease in MnCl2 concentration in the solutions containing both K3[W2Cl9] and MnCl2. For values of \( j \) less than 10 mA cm\textsuperscript{-2}, it appears that \( j_{M2} \) decreases due to an increase in \( j_{M1} \).

**Figure 13.** SEM images of Al-Hf alloys prepared in 66.7 mol% AlCl3-[C2mim]Cl under different electrodeposition conditions: (a) 28.9 mmol L\textsuperscript{-1} HfCl4, 20 mA cm\textsuperscript{-2}, 298 K, Al87.6Hf12.4; (b) 28.9 mmol L\textsuperscript{-1} HfCl4, 20 mA cm\textsuperscript{-2}, 298 K, Al86.6Hf13.4; (c) 28.9 mmol L\textsuperscript{-1} HfCl4, 20 mA cm\textsuperscript{-2}, 298 K, Al88.4Hf11.6.\textsuperscript{72} The electrode rotation rate was 2000 rpm. Reproduced by permission of Springer.

**Figure 14.** Plots of the partial current densities for the deposition of (a) Al, (b) W, and (c) Mn vs. the total current density prepared in the 66.7 mol% AlCl3-[C2mim]Cl with K3[W2Cl9] and/or MnCl2.\textsuperscript{76} The salt concentrations added to the IL were: (●) 3.2 mmol L\textsuperscript{-1} K3[W2Cl9]; (■) 100 mmol L\textsuperscript{-1} MnCl2; (▲) 3.2 mmol L\textsuperscript{-1} K3[W2Cl9] + 25 mmol L\textsuperscript{-1} MnCl2; (△) 3.2 mmol L\textsuperscript{-1} K3[W2Cl9] + 50 mmol L\textsuperscript{-1} MnCl2; (●) 3.2 mmol L\textsuperscript{-1} K3[W2Cl9] + 100 mmol L\textsuperscript{-1} MnCl2. The rotation rate was 1,000 rpm. The temperature was 353 K. Graph reproduced by permission of The Electrochemical Society, Inc.
information about the nature of mass transfer processes in the overall electrode reaction.

The most important reason for adding the second alloying element to binary Al alloys often leads to improvement of the surface morphology and the chloride-induced pitting potential. Recently, we demonstrated that the pitting corrosion resistance of the Al-W and Al-Mn alloy electrodeposits is enhanced by the addition of manganese and tungsten, respectively. We also determined that Mn addition to the Al-W alloy results in much more adherent electrodeposits. Consequently, the Al-W-Mn alloys show better chloride-induced pitting potentials than Al-W and Al-Mn binary alloy electrodeposits. This suggests that Al-M1-M2 alloy systems have great potential as materials for next-generation surface finishing processes.

**Energy Storage Devices Using Haloaluminate RTILs**

Some interesting research about aluminum secondary batteries based on haloaluminate ILs electrolytes was reported by Koura, et al., and Gifford, et al., in the 1980’s and 1990’s. Although a bit dated, these articles still provide useful information about positive electrodes based on polyaniline, FeS2, and graphite. There is additional early research in this area not discussed here, but available in the review article by Li and Bjerrum. Unfortunately, this classical work received only minimal attention from scientists and engineers in the energy storage field when it was first presented. However, with the announcement of rechargeable batteries with anodes based on multivalent active metals, e.g., Mg and Al, interest in this research area has been rekindled. In fact, these new battery systems have been touted as next-generation high-capacity battery systems because they have the potential to greatly exceed the capabilities of the current generation of lithium-ion rechargeable batteries. It is not possible to electrochemically reduce metal ions such as Mg2+ or Al3+ to the metallic state in aqueous solutions due to their very negative deposition potentials, which results in hydrogen generation before these metals are reduced. Even if they are somehow reduced under these conditions, we do not expect useful coulombic efficiency in the charge-discharge cycle because the resulting highly reactive metals react readily with the electrolyte. Another problematic issue is that there are a limited number of choices for active materials that can serve as the positive electrode.

**Figure 15.** (a) SEM image showing a graphitic foam with an open frame structure; scale bar: 300 μm. (Inset) photograph of graphitic foam; scale bar: 1 cm. (b) Galvanostatic charge and discharge curves of an Al/graphitic-foam pouch cell at a current density of 4,000 mA g⁻¹. (c) Long-term stability test of an Al/graphitic-foam pouch cell over 7,500 charging and discharging cycles at a current density of 4,000 mA g⁻¹. (d) An Al/graphitic-foam pouch cell charging at 5,000 mA g⁻¹ and discharging at current densities ranging from 100 to 5,000 mA g⁻¹. The electrolyte was 56.5 mol% AlCl₃-[C₅mim]Cl. Images and graphs reproduced by permission of the Nature Publishing Group.
Figure 16. Performance of a beaker cell-type Al rechargeable battery with 60.0 mol% AlBr$_3$−[C$_2$ mim]Br$_3$. The cutoff voltages were 1.7 and 0.2 V; the temperature was 298 K. (a) Charge-discharge curves resulting from charge-discharge at an applied current of ±2.0 mA. (b) Self-discharge behavior of the Al rechargeable battery after charging at 3.0 mA. (c) Coulombic efficiency of the Al rechargeable battery after each charge-discharge cycle. The applied current was ±2.0 mA. (d) Discharge capacity of the Al rechargeable battery at each cycle number. The applied current was ±2.0 mA. Graphs reproduced by permission of The Electrochemical Society, Inc.

In Lewis acidic haloaluminate RTILs, we can expect the deposition/stripping of pure Al with 100% coulombic efficiency, suggesting that it is a highly favorable negative electrode reaction for rechargeable Al battery systems. For this reason, there are great hopes that Al rechargeable battery systems based on chloroaluminate RTILs will be one of the future energy storage devices. However, as noted, the one big issue that remains to be solved is the identification of a suitable positive electrode, making the search for such an electrode a major research topic. In the past years, several cathode materials have been proposed for use with rechargeable Al batteries. These materials are metal chlorides,\textsuperscript{101,102} haloaluminate-doped conducting polymers,\textsuperscript{103,104} crystalline vanadium oxides (V$_2$O$_5$ and VO$_2$),\textsuperscript{105–109} FeS$_2$ nanoparticles,\textsuperscript{110} and functional carbon materials.\textsuperscript{111–114} The former research areas are similar to the classical work described previously, whereas the others represent new efforts. Vanadium(V) oxide has long been identified as an active positive electrode material for Li or Mg ion batteries.\textsuperscript{115–117} Jayaprakash, et al.,\textsuperscript{105} claimed that a V$_2$O$_5$ nanowire electrode using a stainless steel current collector works as a positive electrode and that the capacity reaches 305 and 273 mAh g$^{-1}$ at the 1$^{st}$ and 20$^{th}$ cycles, respectively. Wang, et al.,\textsuperscript{107} reported similar results, but using a nickel foam current collector. However, a different research group concluded that V$_2$O$_5$ does not function as a cathode at all under these conditions.\textsuperscript{106} What has apparently been observed in experiments with V$_2$O$_5$ is only participation by the Fe and Cr components of the stainless steel current collector through the following half-cell reactions:

\begin{equation}
4[AlCl$_4$]$^{-}$ + Fe $\rightleftharpoons$ 2[Al$_2$Cl$_7$]$^{-}$ + FeCl$_2$ + 2e$^{-}$ \text{ [11]}
\end{equation}

\begin{equation}
4[AlCl$_4$]$^{-}$ + Cr $\rightleftharpoons$ 2[Al$_2$Cl$_7$]$^{-}$ + CrCl$_2$ + 2e$^{-}$ \text{ [12]}
\end{equation}

These unexpected reactions are the likely source of the observed charge-discharge behavior for Al batteries utilizing V$_2$O$_5$ cathodes. Thus, the cell reaction is very similar to that found in the Al-metal chloride battery systems.\textsuperscript{101,102,118} Interestingly, Chiku, et al.,\textsuperscript{119} recently demonstrated that when combined with a molybdenum current collector, amorphous V$_2$O$_5$ does function as a useful cathode for Al secondary batteries, but only with an electrolyte consisting of AlCl$_3$, dipropylsulfone, and toluene in a 1:10:5 mole ratio.\textsuperscript{119} The key factors leading to this success, either the amorphous structure of the V$_2$O$_5$ or the composition of the electrolyte, cannot be stated with any certainty at this point.

Graphite is commonly employed as a negative electrode material in commercial Li ion batteries. Because of its layered structure, various ionic species, including Li$^+$, can be electrochemically inserted into the graphite. A great number of papers on electrochemical ion intercalation have been reported to date. Carlin, et al.,\textsuperscript{120} were the first to investigate the electrochemistry of graphite in chloroaluminate ionic liquids, demonstrating the intercalation of the organic cation, [C$_2$ mim]$^+$, and [AlCl$_4$]$^{−}$ into a graphite rod.\textsuperscript{120} Accordingly, it seems
that the electrochemical intercalation of \([\text{AlCl}_4^-]\) is a strong candidate for the positive electrode reaction. But an earlier paper describing an AlCl\(_2\) cell implies the necessity of novel graphite materials to achieve sufficient intercalation storage capacity.\(^{50}\) More recent reports describe improvements in the graphite after it has been tailored by chemical processing. For example, Lin, et al.\(^{122}\) have succeeded in the fabrication of a novel ultrafast Al rechargeable battery using a graphitic foam positive electrode with an open frame structure (Fig. 15a, 15b). The unique graphitic foam material enables a charge-discharge process by the electrochemical intercalation of \([\text{AlCl}_4^-]\) at very high current densities up to 5,000 mA \(g^{-1}\) (Fig. 15c, 15d), which is comparable to capacitive discharge rates. It also has good long-term cycle stability (Fig. 15c). In contrast, other workers have proposed a positive electrode with high coulombic efficiency based on the adsorption of the ionic species produced by the oxidation of \([\text{AlX}_n^-]\) and/or \([\text{AlX}_x\text{Cl}_{4-x}^-]\) (X: Cl or Br) on an activated carbon fiber cloth (Fig. 16).\(^{125}\) The storage capacity of this carbon fiber cloth is better with chloroaluminates than with bromoaluminates. This novel aluminum rechargeable energy storage device has a larger theoretical capacity than current redox flow battery systems\(^{123,124}\) and could be a key technology for output smoothing, which is required when the electricity generated by renewable energy must be delivered continuously. Sheng Dai’s group at ORNL have proposed novel energy the electricity generated by renewable energy must be delivered continuously. Sheng Dai’s group at ORNL have proposed novel energy theory calculations carried out by Ouyang, et al.,\(^{124}\) gives a plausible method for handling these reactive materials. It is also important to remember that most members of the haloaluminate RTIL family show more favorable physicochemical properties than any of the “second generation” air or water stable ionic liquids reported to date. In view of the above, we believe that the haloaluminate RTIL and mixture-based electrochemical technologies will find wide applications in electrochemical technology in the near future.

References

1. Ionic Liquids in Synthesis, Second Edition, P. Wasserscheid and T. Welton, Eds., Wiley-VCH Verlag GmbH, Weinheim, (2008).
2. Electrodeposition from Ionic Liquids, F. Endres, A. P. Abbott, and D. R. MacFarlane, Eds., Wiley-VCH Verlag GmbH, Weinheim, (2008).
3. T. Tsuda and C. L. Hussey, “Electrochemistry of Non-Chloroaluminate Room-Temperature Ionic Liquids,” in: Modern Aspects of Electrochemistry, R. E. White and C. G. Vayenas, Eds., Vol. 45, pp. 63, Springer Science+Business Media, New York, (2009).
4. T. Tornmoto, T. Tsuda, K. Okazaki, and S. Kuwahata, Adv. Mater., 22, 1196 (2010).
5. J. P. Parakowitsch, J. Zhang, D. Su, A. Thomas, and M. Antonietti, Adv. Mater., 22, 87 (2010).
6. Z. Ma, J. Yu, and S. Dai, Adv. Mater., 22, 261 (2010).
7. S. Zhang, M. S. Miran, A. Ikoma, K. Dokko, and M. Watanabe, J. Am. Chem. Soc., 136, 1690 (2014).
8. G. R. Stafford and C. L. Hussey, in Advances in Electrochemical Science and Engineering, R. C. Alkire and D. M. Kolb, Eds., Vol. 7, pp. 275, Wiley-VCH Verlag (in Japanese), Weinheim, (2002).
9. K. Nakamura and T. Shikata, ChemPhysChem, 11, 285 (2010).
10. F. H. Hurley, US Pat., 2,446,331 (1948).
11. F. H. Hurley and T. P. Wier Jr., US Pat., 2,446,349 (1948).
12. K. Kim, US Pat., 2,446,350 (1944).
13. J. R. Sanders, E. H. Ward, and C. L. Hussey, J. Electrochem. Soc., 133, 325 and 1526 (1986).
14. A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, R. L. Vaughan, J. S. Wilkes, and J. L. Williams, J. Phys. Chem., 98, 2014 (2014).
15. R. J. Gale, B. Gilbert, and R. A. Osteroyning, Inorg. Chem., 17, 2728 (1978).
16. J. C. Nardi, C. L. Hussey, and L. A. King, US Pat., 4,122,245 (1978).
17. J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., 21, 1263 (1982).
18. G. R. Stafford and G. M. Haarberg, Plasmas & Ions, 1, 35 (1999).
19. L. Legrand, A. Tranchant, and R. Messina, Electrochimica Acta, 39, 1427 (1994).
20. L. Legrand, M. Heintz, A. Tranchant, and R. Messina, Electrochimica Acta, 40, 1715 (1995).
21. Y. Nakayama, Y. Senda, H. Kawasaki, N. Koshitani, S. Hosoyi, K. Hubo, and M. Nagamine, Phys. Chem. Chem. Phys., 17, 5758 (2015).
22. T. Hirato, J. Fransaer, and J.-P. Celis, J. Electrochem. Soc., 148, C280 (2001).
23. T. Jiang, M. J. C. Brym, G. Dubé, A. Lasia, and G. M. Brisard, Surf. Coating Technol., 201, 6309 (2007).
24. A. Okamoto, M. Morita, and N. Yoshimoto, J. Surf. Finish. Soc. Jpn., 63, 641 (2012).
25. A. Okamoto, M. Morita, and N. Yoshimoto, J. Surf. Finish. Soc. Jpn., 65, 47 (2014).
26. H. M. A. Abood, A. P. Abbott, A. D. Ballantyne, and K. S. Ryder, Chem. Commun., 47, 3523 (2011).
27. A. Kitada, K. Nakamura, K. Fukami, and K. Murase, Electrochemistry, 82, 946 (2014).
28. A. Endo, M. Miyake, and T. Hirato, Electrochim. Acta, 137, 470 (2014).
29. Y. Fang, K. Yoshii, X. Jiang, X.-G. Sun, T. Tsuda, N. Mehio, and S. Dai, Electrochim. Acta, 160, 82 (2015).
30. Y. Zhao and T. J. VanderNoot, Electrochim. Acta, 42, 3 (1997).
31. H. L. Chum and R. A. Osteryoug, in Ionic Liquids, D. Inman and D. G. Lovering, Eds., pp. 407, Plenum Press, New York, (1981).
32. C. L. Hussey, in Advances in Molten Salt Chemistry, G. Mamantov, Ed., Vol. 5, pp. 185, Elsevier, New York, (1983).
33. C. L. Hussey, in Chemistry of Nonaqueous Solutions, Current Progress, G. Mamantov and A. I. Popov, Eds., pp. 227, VCH Publisher, New York, (1994).
34. R. T. Carlin and J. S. Wilkes, in Chemistry of Nonaqueous Solutions, Current Progress, G. Mamantov and A. I. Popov, Eds., pp. 277, VCH Publisher, New York, (1994).
35. S. Takahashi, N. Koura, S. Kohara, M.-L. Saboungi, and L. A. Curtiss, Plasmas & Ions, 2, 91 (1999).
36. K. Kim, C. Lang, R. Moulton, and P. A. Kohl, J. Electrochem. Soc., 151, A1168 (2004).
37. K. Kim, C. Lang, R. Moulton, and P. A. Kohl, J. Electrochem. Soc., 152, E56 (2005).
38. J. Vaughan and D. Dreisinger, J. Electrochem. Soc., 155, D68 (2008).
39. J. Fischer, K. Leadbetter, M. Mann, D. Larson, M. Kading, E. Nagel, B. Prout, and H. Kassaw, Advanced Engineered Material Center, University of North Dakota, Report Number JF 130828, (2014). (http://engineering.und.edu/research/aemc/aluminum-plating-report-01-15-2014.pdf).
40. Q. Liu, W. R. Pinter, G. Stewart, C. L. Hussey, and R. G. Stafford, J. Electrochem. Soc., 144, 936 (1997).
41. K. Ui, T. Yatsushiro, M. Futamura, Y. Idemoto, and N. Koura, J. Surf. Finish. Soc. Jpn., 55, 409 (2004). (in Japanese)
42. Q. Liao and C. L. Hussey, Aust. J. Chem., 65, 1262 (2012).
43. M. Ueda, S. Hayama, and T. Ohtsuka, J. Solid State Electrochem., 16, 3423 (2012).
44. T. Tsuda, T. Nohira, and Y. Ito, Electrochim. Acta, 47, 2817 (2002).
45. L. Liu, X. Lu, Y. Cai, Y. Zheng, and S. Zhang, Aust. J. Chem., 65, 1523 (2012).
46. Q. Zhang, Q. Wang, S. Zhang, and X. Lu, J. Solid State Electrochem., 18, 257 (2014).
