

= From *Light Metals 2001*, Joseph L. Anjier, Editor =

ALUMINUM REDUCTION VIA NEAR ROOM TEMPERATURE ELECTROLYSIS IN IONIC LIQUIDS

Banqiu Wu¹, Ramana G. Reddy², and Robin D. Rogers¹
1 - Center for Green Manufacturing
2 - Department of Metallurgical and Materials Engineering
The University of Alabama, Tuscaloosa, AL 35487-0202

ABSTRACT

Study on aluminum reduction via electrolysis in ionic liquids at near room temperatures was carried out. Anhydrous aluminum chloride was used as raw material. The electrolyte was made from $AlCl_3$ and 1-butyl-3-methylimidazolium chloride (C_4 mimCl). X-ray diffractometer and micro-image analyzer were used for the product characterization. Aluminum was electrowinned at copper cathode and chlorine gas was released at graphite anode. Experimental temperatures were in the range of $100-140^{\circ}C$. Cathode current density was about 200-700 A/m². Dense aluminum deposition with thickness of 0.1-0.2 mm was obtained. Effects of temperature, cell voltage, and molar ratio of $AlCl_3$ to C_4 mimCl on the cathode current density and efficiency were also investigated.

INTRDUCTION

Aluminum is the most abundant metal element on the earth's crust (8%) and the third richest element exceeded only by oxygen (47%) and silicon (28%) [1]. Aluminum as well as copper is the most industrial important non-ferrous metal. Most important properties of aluminum for industrial use are the lightweight and corrosion resistance. Applications of aluminum alloy and its composites in automotive can significantly reduce the fuel consumption and pollutant emissions [2-3].

Because of the unique advantages of aluminum, the productions of primary and recycled aluminum are increasing. Unfortunately, aluminum production and recycling have severe environmental problems and are extremely energy intensive. High temperature electrolysis (900-1000°C) has been the only industrial method for primary aluminum production for the past century, although it has high production costs and pollutant emissions. Because of its very high negative reduction electrode potential, it cannot be electrolyzed in aqueous solutions. Not like many other non-ferrous metals (e.g. copper, zinc, and lead), aluminum cannot be easily reduced by carbon. The aluminum carbothermic reduction requires very high reaction temperature and has significant byproduct (aluminum carbide), limited its practical industrial applications.

Several alternative methods were proposed for the production of aluminum, but none of them were successful on an industrial scale. These methods include the carbothermic reduction of aluminum at about 2000°C [4-5], the ALCOA's electrolysis of aluminum chloride at about 700°C [6], and the electrolysis in organic solution at low temperatures [7-10]. The carbothermic process and ALCOA's method are carried out at high temperatures and have the intrinsic problems of all the high temperature processes, such as high energy consumption, severe environmental problem, corrosion, and high production costs. The electrolysis of aluminum in an organic solution had limited success. The main problems include the low electrochemical windows of the organic solutions, the low electrical conductivity, the volatility problem, and the inflammabilities.

The electrolysis of aluminum at near ambient temperature in ionic liquids was investigated [11-13]. The electrolyte used for the electrolysis was alkyl-pyridinium chloride-AlCl₃ system. The main problem of this electrolyte was the small electrochemical window, which resulted in the dissociation of electrolyte during the process of the electrolysis. The application of the ethylmethyl-imidazolium-AlCl₃ electrolyte was studied [14]. This electrolyte has a wider electrochemical window than the pyridinium ionic liquid system. Chloroaluminate ionic liquids formed from combination of AlCl₃ and organic salts such as 1ethyl-3-methylimidazolium chloride are promising electrolytes for aluminum electrolysis. Studies on aluminum electrodeposition in ionic liquids were reported [14-15]. But in these studies slow deposition rate (0.19 µm in 360 seconds) [14] limited its practical application. Rate process investigations at different ionic liquid composition, temperature and other kinetic parameters were not investigated. Therefore, optimization of electrolyte composition and kinetic data are needed for the feasibility study.

Ionic liquids are salts with wide temperature range for liquid, including room temperature. The main advantages compared with organic solution are the wide electrochemical windows, the stable

chemical properties, the extreme low volatility, and the non-inflammability. Applications on aluminum refining and recycling were reported [16, 17], which displays many advantages such as low consumption of energy and electrode materials, low pollutant emissions, and low operating costs.

In this study, aluminum was reduced by electrolysis at near room temperature in ionic liquids of 1-butyl-3-methylimidazolium chloride (C_4 mimCl) and AlCl₃. The products were characterized and electrolysis kinetics and thermodynamics were discussed.

EXPERIMENTAL

The experimental setup is shown in Figure 1. The anode is made of graphite and the cathode is made of copper. The electrode distance is about 2 cm. The electrolysis was carried out in ionic liquids made from C_4 mimCl and anhydrous aluminum chloride by mixing the tow powders. The molar ratio of AlCl₃ to C_4 mimCl is 1.5-2.0. The experimental temperatures were 100-140°C. The experiments were carried out in a 50 mL beaker.

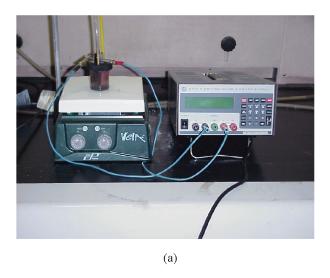
Before the experiments, the anode and cathode were weighed and roughly polished with sandpaper. The anode area is almost the same as the cathode one (about 4.5 cm²). The initial experiments were performed in a glove box protected with pure nitrogen to avoid moisture, but later experiments were carried out in a ventilated hood, in which the electrolysis cell was covered with nitrogen with a very slow flow rate to prevent moisture. The anhydrous AlCl₃ and C₄mimCl were weighed and mixed in the beaker on a hot plate stirrer. Because of the heat release, the temperature of the ionic liquid increased to 150-160°C and then decreased. The hot plate was used to heat the electrolyte as the temperature fell below the predetermined value. When the temperature was stable, electrolysis was started. The cell voltage was set at a constant value between 2.7-3.4 volts and the current changed with time at the beginning of the experiments. After about 5 minutes of electrolysis, the current became stable. The electrolysis lasted up to four hours.

During the electrolysis, chlorine was electrochemically released on the anode and aluminum was deposited on the cathode. After the electrolysis, the anode and cathode were taken out of the cell, washed with water, and weight changes were determined. The cathode was characterized using a micro-image analyzer and X-ray diffractometer.

The C_4 mimCl was synthesized in our laboratory. 1-methyl imidazole and 1-chlorobutane was put in a glass container with argon atmosphere for 4 days at 70° C with magnetic agitation. After the reaction, the product and un-reacted raw materials were in two liquid phases. The top one was impurities and was poured out. The product was washed with athylacetate for several times. Vacuum was used for the deep removal of un-reacted materials and washing liquid.

EXPERIMENTAL RESULTS

The morphologies of deposited aluminum on the cathode depend on the experimental conditions. Three main deposition structures are the dendrite deposition (Figure 2), porous deposition (Figure 3), and dense deposition (Figure 4). The X-ray diffraction of the deposited aluminum is shown in Figure 5, indicating only aluminum peaks and no impure peaks.



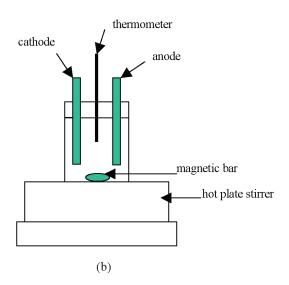


Figure 1. Experimental setup for electrolysis, (a) photograph of the setup, (b) sketch of the electrolysis cell

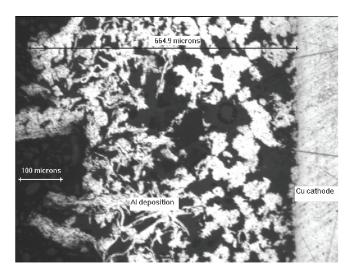


Figure 2. Dendrite aluminum deposition

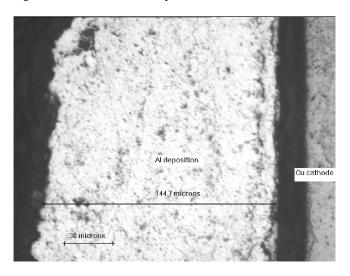


Figure 4. Dense aluminum deposition

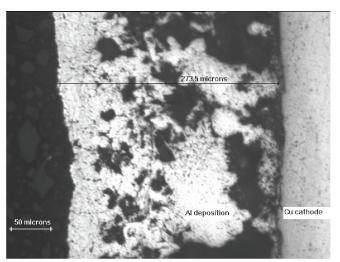


Figure 3. Porous aluminum deposition

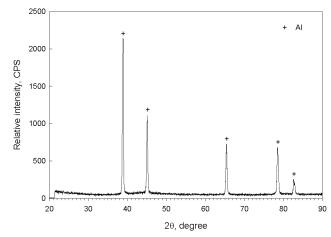


Figure 5. X-ray diffraction pattern of deposited aluminum



Systematical experiments were performed. Cathode current density and efficiency changes with temperature, cell voltage, and molar ratio of AlCl₃ to C₄mimCl were shown in Figures 6-8, respectively.

DISCUSSION

Thermodynamics

The electrolyte is an ionic liquid, consisting of AlCl₃ and MCl, where MCl is an organic chloride such as C_4 mimCl. The molar ratio of AlCl₃:MCl is greater than one (i.e. acidic) and the cathode reaction can be expressed as:

$$4Al_{2}Cl_{7}^{-} + 3e^{-} = Al + 7AlCl_{4}^{-} \tag{1}$$

The above electrode reaction occurs only in acidic liquid, because in basic liquid (ratio of AlCl₃:MCl is less than one), the concentration of Al₂Cl₇ is very small and the dominant chloroaluminate anion, AlCl₄ is not reducible [14].

Aluminum deposition from ionic liquid AlCl₃+MEIC (1-methyl-3-ethylimidazolium chloride) was reported [14]. With potential less than -0.2 V vs. an Al(III)/Al reference electrode in 1.1:1.0 AlCl₃:MEIC, aluminum deposition was obtained. The overall kinetic control step was considered to be the diffusion-controlled growth of the three-dimensional nuclei [18-20]. Tungsten and platinum were thought to be excellent electrode materials for aluminum deposition [14]. In current study, the cathode potential vs. Al(III)/Al electrode is in the range of -0.2 to -0.6, depending on the experimental conditions.

The reaction at anode occurs at electrode potential of +2.5 to 3.3 V. The anode reaction is shown in Eq.2.

$$4AlCl_{4}^{-} = 2Al_{2}Cl_{7}^{-} + Cl_{2} + 2e^{-}$$
 (2)

Combining Eq.1 and Eq.2, we have:

$$2Al_{2}Cl_{7}^{-} = 2Al + 2AlCl_{4}^{-} + 3Cl_{2}$$
 (3)

Acidity of the ionic liquid will change with the progress of electrolysis. By feeding raw material, AlCl₃, to the electrolysis cell, we have the reaction shown in Eq.4.

$$AlCl_3 + AlCl_4^- = Al_2Cl_7^- \tag{4}$$

The overall electrolysis cell reaction can be obtained combining Eq.3 and Eq.4, as shown in Eq.5.

$$2AlCl_3 = 2Al + 3Cl_2 \tag{5}$$

The thermodynamic properties and theoretical electrolysis based on ΔG° = nFE° of Eq.5 are shown in Table 1.

Table 1. Gibbs energy change in the electrolysis cell

Temperature, °C	ΔG°, kJ	E°, V
25	1260.041	2.177
50	1247.394	2.155
75	1234.813	2.133
100	1222.295	2.112
125	1209.844	2.090
150	1197.459	2.069

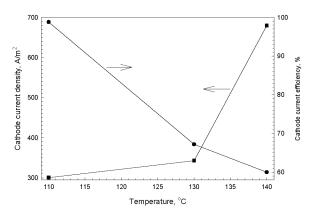


Figure 6. Temperature effect (V=3.4V, ratio=2:1)

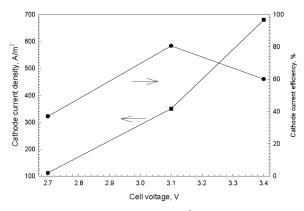


Figure 7. Cell voltage effect (T=140°C, ratio=2:1)

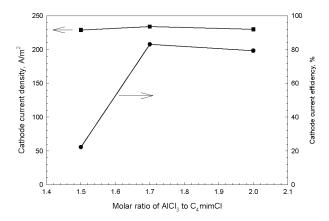


Figure 8. Molar ratio effect (T=105°C, V=3.1 V)



Kinetic Analysis

Polarization was reported for the aluminum deposition in ionic liquids [14]. In our current study, the current increased at the beginning of the experiment for a few minutes. Because the cathode is copper and a new aluminum crystal grows, current is small. When the aluminum layer was formed on the cathode, the cathode current became stable.

The cathode current density increased with temperature, but the current efficiency decreased, as shown in Figure 6. The significant increase of current density with temperature indicates that the activation polarization is the control step instead of the concentration polarization. The current efficiency decrease with temperature may be resulted from the side reaction of the impurities in the electrolyte. Because the C₄mimCl is newly developed, its accurate characterization is still in developing.

The cathode current density increases with the cell voltage, but does not affected much by the molar ratio of AlCl₃ to C₄mimCl, as shown in Figures 7 – 8. Figure 7 shows a maximum value of current efficiency at cell voltage of about 3.1 V. The higher cell voltage enhances the side reaction of the impurities, resulting in the lower current efficiency. High molar ratio increases the aluminum concentration, and then increases the current efficiency, but when it is greater than 1.7, further increase does not have effects on the current efficiency, as shown in Figure 8.

Different experimental conditions resulted in different morphologies of the aluminum deposition, as shown in Figures 2-4. In this electrolysis system, anion reduced to aluminum. It seems that high molar ratio, high voltage, and moderate temperature help the dense aluminum deposition be formed. The study on the morphology and its affects are in progress.

Production Process Consideration

The original aluminum-containing material is oxide (bauxite) and the aluminum chloride is the product of the chlorination of the aluminum oxide. For the chlorinating process, Gibbs energy minimization method is used to calculate stable temperature range of the products of the chlorinating process. When the input materials are carbon, chlorine, and aluminum oxide, the typical

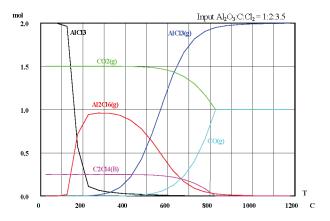


Figure 9. Equilibrium composition of the chlorinating process.

input condition and equilibrium composition in the system is shown in Figure 9.

Figure 9 shows that the chlorinating temperature can thermodynamically occur at ambient temperature, but the practical process mainly depends on the chlorinating kinetics. When the system is heated between 250-600°C, the equilibrium product is Al₂Cl₆ gas. When the system temperature is above 600°C, AlCl₃ gas is obtained. When the gaseous products are cooled below 150°C, gaseous aluminum chloride will be condensed and then solid aluminum chloride is obtained. In the chlorination, the alumina and carbon are solid particles and the product (aluminum chloride) is in the gas phase, which enhance the purification and the product separation from un-reacted raw materials. Chlorinating processes were investigated and published [21].

The overall chlorinating reaction can be expressed in Eq.6.

$$Al_2O_3 + \frac{3}{2}C + 3Cl_{2(g)} = 2AlCl_{3(g)} + \frac{3}{2}CO_{2(g)}$$
 (6)

At various reaction temperatures, Gibbs energy change and enthalpy changes are shown in Table 2.

Table 2. Gibbs energy and enthalpy changes of the chlorination.

Temperature, °C	ΔG°, kJ	ΔH°, kJ
200	-188.620	-84.730
300	-210.471	-85.898
400	-232.078	-87.532
500	-253.411	-89.554
600	-274.463	-91.876
700	-295.239	-94.361
800	-315.753	-96.941

After the chlorinating process, gaseous product will be condensed into the solid phase. The condensing equation is shown in Eq.7. The ΔH for the condensing is about -114 kJ, indicating an exothermic process. Both chlorinating and condensing processes are exothermic, saving energy input for the chemical reaction.

$$Al_2Cl_{6(g)} = 2AlCl_{3(s)} \tag{7}$$

The chlorine gas released in the electrolysis cell can be recirculated to the chlorinating process. By combining Eq.5 and Eq.6, an overall reaction of the aluminum production process can be obtained, as shown in Eq.8.

$$Al_2O_3 + \frac{3}{2}C = 2Al + \frac{3}{2}CO_2 \tag{8}$$

Ionic Liquids

Ionic liquids are salts that are liquids over a wide temperature range, including room temperature. They are a big chemical group. Variations in cations and anions can produce many different kinds of ionic liquids, such as chiral, fluorinated, and antibacterial ionic liquids.

The properties of the ionic liquids depend on their structures. For room temperature ionic liquid, cations are typically big, bulky, and asymmetric, but most properties such as conductivity, viscosity, air and water stability are strongly dependent on the

anion structures. Important properties of ionic liquids include wide electrochemical windows, high ionic conductivity, almost non-volatile, non-flammable, high thermal stability, wide temperature range for liquid phase, and high solvating capability.

Typical ionic liquid cations include N-butylpyridimium (N-alkylpy), as shown in Figure 10(a), and 1-alkyl-3-methylimidazolium (alkylmin) or 1,3-dialkylimidazolium (RR'im), as shown in Figure 10(b). Common anions are [PF₆] and [BF₄]. The ionic liquid with [PF₆] is water immiscible and the ionic liquid with [BF₄] are water miscible, but both of them are moisture stable. Besides the above anions, there are many other anions, such as Triflate [TfO] CF₃SO₂, Nonaflate [NfO] CF₃(CF₂)₃SO₂, Bis(triflyl)amide [Tf₂N] (CF₃SO₂)₂N⁻, Trifluoroacetate [TA] CF₃CO₂, and Heptafluorobutanoate [HB], CF₃(CF₂)₃CO₂. Many investigations on ionic liquids, their properties and applications have been reported [22-25].

Figure 10. Typical ionic liquid cations

An important group of ionic liquids for metal production is the chloroaluminate ionic liquids. Room temperature chloroaluminate ionic liquids can be made from combination of AlCl₃ with organic salts such as N-butylpyridinium chloride (BuPyCl), 1-ethyl-3-methylimidazolium chloride (MEIC), and C_4 mimCl. Therefore, the ionic liquid mainly consists of $Al_2Cl_7^-$, $AlCl_4^-$, Cl^- and M^+ , where M^+ is the cation.

There is an acid-base reaction in the ionic liquid, as shown in Eq.9.

$$Al_{2}Cl_{7}^{-} + Cl^{-} = 2AlCl_{4}^{-}$$
acidic basic neutral (9)

Acidic or basic ionic liquid can be attainable through varying the concentration of acidic or basic ions, as shown in Eq.9, for the application in electrolysis of aluminum. Large electrochemical windows for the electrolysis of active metals can be obtained in both chloro and bromo ionic liquids.

In this experimental study, ionic liquid, C₄mimCl-AlCl₃, is moisture sensitive, the ionic liquid preparation and electrolysis were carried out under a protect gas.

Selection of ionic liquid is important, which includes selecting different cations and anions, different carbon chain length, the mixing electrolyte of different ionic liquids, additives, and ionic concentrations. For the electrolysis process, electrolyte conductivity is an important parameter. Usually, ionic liquid has a high electrical conductivity compared with organic solution because of the high ionic concentration in the ionic liquid. In order to reduce the consumption of energy, some additives may be needed for the improvement of the electrolyte conductivity and electrolysis.

Feasibility Analysis

Typical experimental conditions are shown in Table 3. It shows that the cell voltage and energy consumption for aluminum reduction in ionic liquids at near room temperature is much lower than current industrial method. The ionic liquid is not consumed during the electrolysis. There is not pollutant emission in this low temperature reduction process.

Table 3. Typical experimental condition

Parameters	Electrolysis in	Currently
	ionic liquid	industry
Cell voltage, V	3.1	4.5
Energy consumption, kWh/lb	4.2	6.4
Current density, A/m ²	200-700	7000
Electrode distance, mm	20	100
Temperature, °C	110	1000
Ratio of AlCl ₃ to C ₄ mimCl	2.0	
Al deposition thickness, mm	0.1 - 0.2	

The cell structure is typical vertical electrodes, like the cell for the production of copper and zinc. The main parameters in current study such as current density and electrode distance are in the same level as the electrolysis cell of copper and zinc. Because of the horizon electrode of high temperature electrolysis cell, its current density is not compatible with that in ionic liquid at room temperature. Compared with high temperature process, the low temperature reduction does not consume expensive refractory materials.

There are many pollutants emitted to the environment every year from aluminum production industry. The main pollutants include aluminum dross, spent potliner, and fluorides (e.g. CF₄).

High temperature process costs are usually higher than similar processes at lower temperatures. The main contribution for higher costs is from energy consumption, uses of refractory materials, and difficulties of operating control. For the aluminum high temperature electrolysis, good graphite is used as electrode material, which make the operating costs even higher. Many studies on high temperature processes have been reported [26-31], which shows that high over voltage of aluminum electrolysis results in a high energy consumption. Because of the extreme difficulties of the electrolyte purification at high temperature, current aluminum electrolysis requires high purity aluminum oxide. Its preparation is very expensive part of the aluminum production [32]. Besides, maintenance costs are also very high for the high temperature process. It is evident that decrease in raw material preparation costs and avoidance of high temperature operation are the best approach for the decrease in production costs of aluminum and for pollution prevention.

For the ionic liquid, the price for large industrial scale application of aluminum electrolysis is not available now. Based on the synthesis procedure of ionic liquid, its cost is not expected to be high. Therefore, it is expected that the aluminum reduction in ionic liquids will be cost effective. Due to the avoidance of high temperature and closed loop of the chlorine, the new process is environmentally benign and will prevent pollution from aluminum production.

CONCLUSIONS

Aluminum was electrowinned in ionic liquids at near room temperatures, with current density 200-700 A/m², cell voltage 2.7-



3.4 V, cathode current efficiency up to 99%, and aluminum deposition of 0.1-0.2 mm thick on copper cathode. Based on the experimental results, the aluminum production in ionic liquids has the advantages of low temperature, low energy and materials consumption, and low pollutant emissions.

ACKNOWLEDGEMENT

We express our sincere appreciation for the financial support from National Science Foundation and Center for Green Manufacturing, The University of Alabama.

REFERENCES

- D.R. Lide (Editor in Chief), <u>CRC Handbook of Physics and Chemistry</u>, 75th Edition, (CRC Press, Boca Raton, Florida, USA, 1995), page 1 in Section 4.
- V.M. Kevorkijan, "Aluminum Compostes for Automotive Applications: A Global Perspective", <u>Journal of Metals</u>, November (1999), 54-58.
- B. Maruyama and W.H. Hunt, Jr., "Discontinuously Reinforced Aluminum: Current Status and Future Direction", Journal of Metals, November (1999), 59-61.
- K. Motzfeldt and B. Sanberg, "Chemical Investigations Concerning Carbothermic Reduction of Alumina", <u>Light</u> <u>Metal 1979</u> (W.S. Peterson, ed., AIME, Warrendale, PA, 1979), 411-428.
- M.J. Bruno, "Overview of ALCOA Direct Reduction Proces Technology", <u>Light Metals 1984</u> (Ed. by J.P. McGeer, Met. Soc. AIME, 1984), 1571-1590.
- H.S. Ray, R. Sridhar, and K.P. Avraham, <u>Extraction of Nonferrous Metals</u>, (Affiliated East-West Press PVT Ltd, New Delhi, India, 1992), 261-310.
- S.A. Capuano and W.G. Davenport, "Electrodeposition of Aluminum from Alkylbenzene Electrolytes", <u>J. Electrochem.</u> Soc., 118(1971), 1688-1695.
- E. Peled and E. Gileadi, "The Electrodeposition of Aluminum from Aromatic Hydrocarbons", <u>J. Electrochem.</u> <u>Soc.</u>, 123(1976), 15-19.
- 9. C.J. Smit and T.P.J. Peters, "Electrodeposition of Aluminum at Near Ambient Temperature", <u>Light Metals 1986</u> (Ed. by R.E. Miller, TMS, 1986), 253-260.
- J.H. Conner and A. Brenner, "Electrodeposition of Metals from Organic Solutions", <u>J. Electrochem. Soc.</u>, 99(1952), 234-241.
- 11. F.H. Hurley, "Electrodeposition of Aluminum", US Patent 2,446,331 (1948).
- 12. T.P. Wier, Jr. and F.H. Hurley, "Electrodeposition of Aluminum", US Patent (1948), No.: 2,446,349.
- 13. T.P. Wier, Jr., "Electrodeposition of Aluminum", US Patent (1948), No.: 2,446,350.
- R.T. Carlin, W. Crawford and M. Bersch, "Nucleation and Morphology Studies of Aluminum Depositied from an Ambient-Temperature Chloroaluminate Molten Salt, <u>J.</u> <u>Electrochem. Soc.</u>, 139 (1992), 2720-2727.
- P.K. Lai, and M. Skyllas-Kazacos, "Electrodeposition of Aluminum in Aluminum Chloride/1-methyl-3ethylimidazolium Chloride", <u>J. Electroanal. Chem. Soc.</u>, 248 (1988), 431-440.

- B. Wu, R.G. Reddy and R.D. Rogers; "Production, Refining and Recycling of Lightweight and Reactive Metals in Ionic Liquids", U.S. patent pending (2000).
- 17. B. Wu, R.G. Reddy and R.D. Rogers, "Aluminum Recycling via Room Temperature Electrolysis in Ionic Liquids", Proceedings of Fourth International Symposium on Recycling of Metals and Engineered Materials (TMS, Pittsburgh, Pennsylvania, USA, October 22-25, 2000).
- S. I. Takahashi, I. K. Saeki, and M. Shoichiro, <u>Electrochemical Society Extended Abstracts</u>, (Montreal, Quebec, Canada, May 6-11, 1990), (Abstract No. 889), 1254.
- Auborn, J.J. and Y.L. Barberio, <u>J. Electrochem. Soc.</u>, 132(1985), 598-605.
- Chryssoulakis, Y.; J.-C. Poignet, and G. Manoli, <u>J. Appl. Electrochem.</u>, 17(1987), 857-864.
- S.C. Jacobs, L.K. King, and B.J. Racunas, "Control of Purity and Particle Size in Production of Aluminum Chloride", US Patent (1978), No.: 4,108,968.
- 22. R.D. Rogers, A.E. Visser, R.P. Swatloski, and D.H. Hartman, "Metal Ion Separations in Room Temperature Ionic Liquids: Potential Replacements for Volatile Organic Diluents," <u>Metal Separation Technologies Beyond 2000: Integrating Novel Chemistry with Processing</u>, (K.C Liddell and D.J. Chaiko Eds.; United Engineering Foundation, Washington, DC, 1999), 139.
- J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, and R.D. Rogers; "Room Temperature Ionic Liquids as Novel Media for 'Clean' Liquid-Liquid Extraction," <u>Chem.</u> Commun., (1998), 1765-1766.
- J.S. Wilkes, J.A. Lewisky, R.A. Wilson, and C.L. Hussey, Inorg. Chem., 21(1982), 1263-1264.
- Bonhote, P., A-P. Dias, N. Papageoorgiou, K. Kalyanasundaram and M. Gratzel, <u>Inorg. Chem.</u>, 35(1996), 1168-1178.
- N.A. Gokcen and R.G. Reddy, <u>Thermodynamics</u>, (Plenum Publ., New York, NY, USA, 1996), 247-280.
- R.G. Reddy and A. Narayan, "electrochemical Studies and Anode Reaction Mechanisms of Al-Li Alloys and L₂O-LiF-CaF₂ Melts," <u>Materials Science Forum</u>, 73-75(1991), 521-532
- R.G. Reddy, A.R. Narayan, and P.T. Velu, "Anode Over Voltage on Graphite in Li₂O-LiF-CaF₂ Melts," <u>Molten Salts</u>, ECS (1994), 385-391.
- P.T. Velu and R.G. Reddy, "Anodic Over Voltage on Graphite in Li2CO3-LiF-CaF2 Melts," <u>Light Metals 1996</u>, (TMS, 1996), 1139-1147.
- Reddy, R.G. and S.R. Reddy, "Thermodynamic Modeling of Molten Metal Systems, Emerging Separation Technologies in Minerals and Metals II," <u>Engineering Foundation</u> <u>Conferences</u>, (TMS, 1996), 17-34.
- 31. S. Wang and R.G. Reddy, "Low Melting Fluxes for Recycling of Al Scrap," Second International Symposium on Extraction and Processing for the Treatment and Minimization of Wastes, (TMS, 1996), 377-389.
- K.J. Driscoll, S. Saraf, and J.P. Martin, "An Assessment of the Avoidable Costs of Production for Western World Aluminum Smelters," <u>Light Metals</u> 1998, (TMS, 1998), 1273-1277

Recommended Reading

- Dokiya, M., et al. Blast furnace process for aluminum, calcium carbide, calcium hydride, and titanium (1986, pp. 241–252).
- Guzman, S.S., and G.C. D'Andrea. Thermodynamics of alumina chlorination (1987, pp. 417–427).
- Johansen, K., et al. Aluminum carbothermic technology Alcoa-Elkem advanced reactor processes (2003, pp. 401–406).
- Kibby, R.M., and A.F. Saavedra. Model studies in carbothermic reduction of alumina (1987, pp. 263–268).
- Murray, J.P. Aluminum-silicon carbothermal reduction using high-temperature solar process heat (1999, pp. 399–405).
- Myklebust, H., and P. Runde. Greenhouse gas emissions from aluminum carbothermic technology compared to Hall-Heroult technology (2005, pp. 519–522).
- Smit, C.J., and T.P.J. Peters. Electrodeposition of aluminium at near ambient temperatures (1986, pp. 253–260).
- Stevenson, D.T. Feasibility of an aluminum-silicon blast-arc process (1984, pp. 1613–1631).
- Troup, R.L. Feasibility of an aluminum-silicon blast furnace (1984, pp. 1591–1612).
- Zhang, M., V. Kamavaram, and R.G. Reddy. Aluminum electrowinning in ionic liquids at low temperature (2005, pp. 583–588).
- Zhang, M., and R.G. Reddy. Ionic liquid electrowinning of aluminum-modeling of batch reactor (2007, pp. 385–390).