

Low-temperature Electrolysis of Aluminium from 1-Butyl-3-methylimidazolium Chloroaluminate Ionic Liquids with Inert Anode

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To solve the inherent problems rooted in the traditional Hall-Héroult electrolytic process for aluminium production, it's necessary to develop low-temperature and low-energy technology. In this work, Lewis acidic 1-butyl-3-methylimidazolium chloroaluminate ionic liquids were chosen as electrolyte in the electrolysis of aluminium. Unlike previous research, glassy carbon was used as inert anode material in the study. On this basis, cyclic voltammetric and chronoamperometric measurements were performed to explore the micro-electrochemical reaction in ionic liquids. Scanning electron microscope graphs show that smooth, compact and well-adherent deposits could be obtained at 313.2~353.2 K, 5~15 mA/cm². The mass content of aluminium in all the products is higher than 99%. At the same time, systematical study on the release and adsorption of Cl₂ generated from inert anode was also carried out. According to experimental results, more than 96% efficiency has been achieved at -0.1 Mpa, 313.2~373.2 K and 5~25 mA/cm². It's expected that the present work may be useful for industrial application of ionic liquids in aluminium production.

Keywords: aluminium; electrolysis; inert anode; ionic liquids

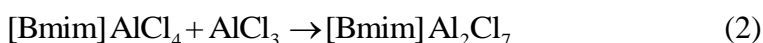
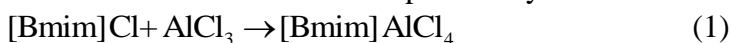
1. INTRODUCTION

As the most abundant metallic element in the earth's crust, aluminium plays an important role in the development of modern society. It's well known that aluminium has a variety of attractive properties, such as high strength, superior malleability, high corrosion resistance, good electrical and thermal conductivity [1]. This makes aluminium indispensable as the widely used metal material in the packaging, electronics, construction and transportation industry.

Since the end of 19th century, the production of aluminium has been mainly conducted by the Hall-Héroult electrolytic process. However, this method suffers from many problems, including high operating temperature, high energy consumption and high CO₂ emission [2]. Although the energy consumption of aluminium electrolysis decreases from the initial 40 kWh/kg to present 13 kWh/kg approximately, it's still much more than the theoretical value 6.32 kWh/kg according to Qiu et al.'s research [3]. Further efforts to reduce the energy consumption have been hindered by the high electrolysis temperature (900~950 °C). In fact, more than 50% of the electrical energy is consumed to compensate the heat loss of high-temperature molten cryolite-based salts. It's apparent that above problems are mainly rooted in the natural defects of traditional electrolytes. Therefore, it's necessary to develop more novel electrolytes for the low-temperature and low-energy electrolysis of aluminium [4].

Ionic liquids (ILs) are a new class of room-temperature molten salts, which are usually composed of organic cations and organic/inorganic anions. Owing to the unique structures, ILs exhibit relatively low melting points and a number of excellent physicochemical properties [5]. The research on ILs has attracted considerable interest and significant progress has been achieved in a wide range of research areas over the past two decades. Numerous studies show that ILs are promising electrolytes for the low-temperature electrodeposition of active metals [6].

In the early 1950s, Hurley et al. [7] first found that aluminium could be electrodeposited from the room-temperature molten salt based on *N*-ethylpyridinium halide/AlCl₃. Since the 1980s, extensive research on the electrodeposition of aluminium from ILs has been reported in literature [8-10]. It shows that the deposition process has lower operating temperature (<150 °C) and energy consumption (<11 kWh/kg). What's more attracting, improved quality of aluminium and higher current efficiency can also be expected. The most frequently studied electrolytes are the chloroaluminate ILs generated by the combination of imidazolium chloride with AlCl₃. Aluminium can be electrodeposited from Lewis acidic chloroaluminate ILs in which the molar fraction of AlCl₃ is higher than 0.5 and only [Al₂Cl₇]⁻ is the reducible Al-containing species [11,12]. Markiewicz et al. [13] made an economical and ecological assessment for the potential application of ILs in low-temperature aluminium production. Rogers and Lu [14,15] described a method of producing aluminium from ILs, respectively. The main chemical reactions can be expressed by



in which inert anodes are indispensable. However, our literature survey reveals that aluminium was used as insoluble anode in most of the previous work. No systematic researches have been reported on the electrolysis of aluminium from ILs with inert anodes yet.

The goal of this work is to explore the possibility of using ILs as potential electrolytes for aluminium production. Motivated by this aim, we focus on the studies of low-temperature aluminium electrolysis process, in which glassy carbon (GC) electrode was first employed as the novel inert anode material. The electrolytes used were Lewis acidic 1-butyl-3-methylimidazolium chloroaluminate ILs ([Bmim]Cl/AlCl₃) owing to their favorable physicochemical properties and good performance in the electrodeposition according to the literature and our previous work [8,12]. By means of electrochemical measurements, the aluminium electrodeposition and Cl₂ release on the electrodes were

both studied in detail. The effects of experimental parameters, including temperature, current density, vacuum degree and molar compositions of [Bmim]Cl/AlCl₃ on the electrolysis process have also been investigated. The results were analyzed from the perspective of microcrystalline nucleation/growth and ILs' structure. According to above research, the optimum conditions for aluminium electrolysis were finally obtained.

2. EXPERIMENTAL

2.1 Chemicals

All the chemicals used in this work were purchased commercially with analytic grade (mass fraction purity $\geq 99\%$) from Alfa Aesar and Sinopharm Chemical Reagent Co., Ltd. *N*-methylimidazolium, 1-chlorobutane, acetone, ethyl acetate and absolute alcohol were purified by distillation. Prior to the experiments, sodium hydrate and sodium thiosulfate were recrystallized twice. Anhydrous aluminium chloride and inorganic acids were used without further purification.

2.2 Synthesis and characterization of ILs

[Bmim]Cl. According to Huddleston et al.'s work [16], *N*-methylimidazolium and 1-chlorobutane with molar ratio of 1:1.15 were added to a flask and stirred for 48 h at 343 K. Then the mixture was washed by ether acetate, recrystallized from acetone and dried under vacuum. The final product was obtained as a white wax-like solid at room temperature. ¹H NMR (DMSO-*d*₆): $\delta = 9.446$ (s, 1H), 7.840 (d, 1H), 7.765 (d, 1H), 4.177 (t, 2H), 3.856 (s, 3H), 1.747 (m, 2H), 1.233 (m, 2H), and 0.873 (m, 3H) ppm.

Lewis acidic [Bmim]Cl/AlCl₃. The preparation and subsequent purification processes were all conducted under the dry argon atmosphere in a glove box (Universal, MIKROUNA Co., China) where water and oxygen content was both kept below 1 ppm. Lewis acidic [Bmim]Cl/AlCl₃ with the molar ratio of 1:1.5, 1:1.8 and 1:2 were synthesized by mixing precise molar quantities of [Bmim]Cl with anhydrous AlCl₃ at room temperature. The resulting liquids were filtered through glass frit and purified by electrolysis before use. The final products were obtained as colorless liquids at room temperature. ¹H NMR of 1:1.5 [Bmim]Cl/AlCl₃: $\delta = 8.237$ (s, 1H), 7.252 (d, 1H), 7.215 (d, 1H), 4.050 (t, 2H), 3.804 (s, 3H), 1.748 (m, 2H), 1.239 (m, 2H), and 0.780 (m, 3H) ppm. ¹H NMR of 1:1.8 [Bmim]Cl/AlCl₃: $\delta = 8.096$ (s, 1H), 7.138 (d, 1H), 7.108 (d, 1H), 3.972 (t, 2H), 3.722 (s, 3H), 1.683 (m, 2H), 1.184 (m, 2H), and 0.746 (m, 3H) ppm. ¹H NMR of 1:2 [Bmim]Cl/AlCl₃: $\delta = 7.931$ (s, 1H), 6.997 (d, 1H), 6.969 (d, 1H), 3.858 (t, 2H), 3.610 (s, 3H), 1.599 (m, 2H), 1.118 (m, 2H), and 0.697 (m, 3H) ppm. ²⁷Al NMR of 1:2 [Bmim]Cl/AlCl₃: $\delta = 106.626$ ppm.

The NMR measurements of ILs were performed on a spectrometer (av-400 MHz, Bruker, Switzerland) at 298 K. In the measurement of NMR for Lewis acidic [Bmim]Cl/AlCl₃, acetone-*d*₆ was used as an external standard to suppress the interference from other solvents. All the peaks and corresponding chemical shifts obtained confirmed the structure of these ILs, and no impurity peaks were found in the NMR spectra.

The mass fraction of water in ILs was determined by Karl Fisher titration (751 GPD Titrino, Metrohm, Switzerland). For Lewis acidic [Bmim]Cl/AlCl₃, the results of measurement showed that the water content was below 50 ppm. The mass fraction purity of all the ILs was determined to be >99%.

2.3 The measurement of physicochemical properties

An electrospray ionisation mass spectrometry (ESI-MS) (Micromass Q-TOF, UK) was used to identify the structure of ions. The data of electrical conductivities were obtained through a conductivity meter (FE30, Mettler Toledo Int. Inc., Switzerland) from 303.2 to 373.2 K. The surface morphology and compositional analysis of aluminium deposits were examined with emission scanning electron microscope (SEM) (JSM-6700F, JEOL, Japan) and energy dispersive X-ray (EDAX) (XL30 S-FEG, FEI, USA), respectively.

2.4 Electrochemical experiments

All the electrochemical experiments were conducted in the argon-filled glove box mentioned above. Experiments were performed with an electrochemical workstation (CHI660D, Shanghai Chenhua Instrument Co., Ltd., China) controlled by CHI660D software in a three-electrode cell. Graphite (G347, Dalian Tokai-Jinqi-Fuji Carbon Co., Ltd.), Ru-Ti (2 mm radius, Suzhou Borui Industrial Material Co., Ltd.) and GC electrodes were investigated as inert anodes. Copper disc working electrode (1 mm radius, Tianjin Aidahengchen Co., Ltd.) and GC disc counter electrode (1 mm radius, Tianjin Aidahengchen Co., Ltd.) were used in the cyclic voltammetric measurement of aluminium electrodeposition. In the determination of cyclic voltammograms for Cl₂ evolution, the working and counter electrodes were GC disc and Cu disc electrodes, respectively. As for the experiments of electrolysis, the working and counter electrodes were copper (99.999%, Alfa Aesar) and GC plates (SA-2, Dalian Tokai-Jinqi-Fuji Carbon Co., Ltd.) with the same geometric area. In all these experiments, the reference electrode used was a high-purity aluminium wire (99.999%, Alfa Aesar) sealed with a fritted glass tube containing pure 1:2 [Bmim]Cl/AlCl₃. Prior to use, all the electrodes were polished with emery paper, cleaned with acetone, treated with a dilute hydrochloric acid/sulfuric acid mixture and dried. After each electrolysis experiment finished, the aluminium deposits were washed by absolute alcohol, deionized water and finally dried in air, while the stirring and pumping were kept for 30 min to ensure the fully absorption of Cl₂.

2.5 Calculation of current efficiency in the electrolysis

The cathode current efficiency (E_c) in the electrolysis was calculated by

$$E_c(\%) = \frac{3 \times 96485 \times m}{27 \times I \times t} \times 100 \quad (4)$$

where the yield of aluminium (m) was determined from the weight difference of cathode before and after deposition.

Before the calculation of anode current efficiency (E_A), the produced Cl_2 was pumped out and absorbed by the aqueous solution containing 5 wt% $\text{Na}_2\text{S}_2\text{O}_3$ and 2 wt% NaOH . Then, the total yield of Cl_2 (n) was measured as Cl^- using an ion chromatograph (ICS-900, Dionex, USA). The value of E_A was finally obtained by the following equation.

$$E_A(\%) = \frac{2 \times 96485 \times n}{71 \times I \times t} \times 100 \quad (5)$$

3. RESULTS AND DISCUSSION

3.1 Inert anode material

Searching for proper inert anode material is key to the low-temperature production of aluminium from chloroaluminate ILs. It's well known that graphite and Ru-Ti electrodes have been widely used as anode materials for Cl_2 evolution in the chlor-alkali industry. These electrodes have low resistivity and keep high chemical stability through the electrolytic process. Considering that the electrolysis of aluminium in ILs was also accompanied with Cl_2 release, graphite and Ru-Ti electrodes were first investigated in our work. However, experimental results showed that the graphite anode was quickly eroded in 1:2 [Bmim]Cl/ AlCl_3 when a constant cell voltage of 3 V was applied at 373.2 K. Meanwhile, the RuO_2 coating of Ru-Ti electrode was also eroded within 2 h at the same conditions. As Figure 1 shows, the dramatical fluctuation of current around 105 min reflects the erosion reaction of Ru-Ti electrode. Although both of these traditional anode materials were corroded in [Bmim]Cl/ AlCl_3 , the corrosion mechanism was distinct from each other. For graphite anode, it's probably the porous nature, layer structure and low mechanical strength that make it easy to swell by the slow release of Cl_2 in viscous ILs [17,18]. The chemical erosion of graphite may be excluded due to its high chemical stability. By contrast, the Ru-Ti anode was mainly eroded by chemical or electrochemical reaction. The high catalytic activity of RuO_2 for organic reaction may prompt the erosion of Ru-Ti anode in chloroaluminate ILs [19,20].

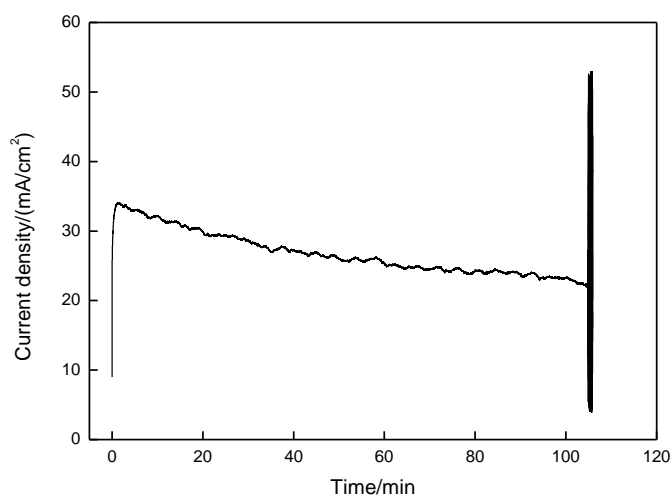


Figure 1. Current-time curve obtained on Ru-Ti anode electrode in 1:1.5 [Bmim]Cl/ AlCl_3 with constant cell voltage of 3 V at 373.2 K

GC is a kind of carbon material without pore and possesses higher mechanical strength than graphite. The excellent physicochemical stability makes GC popular as the novel working electrode in electrochemical research [17]. Therefore, GC may act as the novel inert anode in the low-temperature electrolysis of aluminium from ILs. For convenience, GC was employed as the electrode for Cl_2 evolution in the following experiments. The corresponding electrode for aluminium electrodeposition was copper plate from the perspective of industrial application.

3.2 Results of electrochemical measurement

In this work, cyclic voltammetry and chronoamperometry were used as main methods of electrochemical measurement. To facilitate the electrodeposition of aluminium, the performance of inert anode is very important. Thus, the Cl_2 evolution on GC electrode is first analyzed, following by the research into electrodeposition behavior of aluminium.

3.2.1 Cyclic voltammetry

Cyclic voltammetric measurements were carried out to investigate the reaction process on GC electrode. As Figure 2 shows, the initial potential of oxidation reaction is around 2.1 V and decreases when temperature rises in 1:2 [Bmim]Cl/ AlCl_3 . Obviously, experimental temperature has great effect on the formation of Cl_2 . In other words, Cl_2 is easier to be generated at higher temperature. It can be concluded that the anodic reaction is a typical endothermal process. Consequently, the electrochemical oxidation of $[\text{AlCl}_4]^-$ anion is prone to proceed with increasing temperature, which enhances the current density, charge and ion transfer on GC anode.

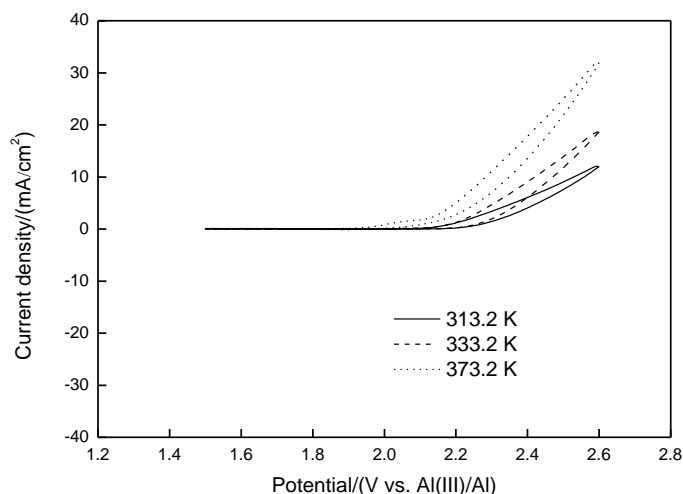
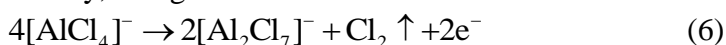
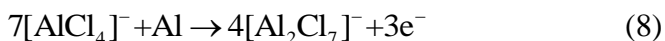


Figure 2. Cyclic voltammograms recorded on a GC disc electrode in 1:2 [Bmim]Cl/ AlCl_3 at different temperatures. The potential scan rate was 0.1 V/s.

The cyclic voltammograms of Lewis acidic [Bmim]Cl/ AlCl_3 with different molar ratios have also been studied (see Figure 3). As the apparent molar fraction of AlCl_3 decreases, the initial potential of Cl_2 evolution slightly increases. In such cases, the molar concentration of $[\text{AlCl}_4]^-$ is enhanced,

which promotes not only the formation of Cl₂, but also the current density, mass and ion transfer efficiency [21].

Compared with above results, Figure 4 and 5 represent the cyclic voltammograms recorded on Cu electrode at different conditions. It can be seen that a pair of peaks is obtained between -1.2 and 1 V in all the ILs. The reduction peaks below -0.1 V on the negative scan are ascribed to the bulk electrodeposition of aluminium, while the oxidation peaks around 0.6 V reflect the stripping process of deposited aluminium [8,22].



Similarly, temperature also has significant influence on the electrodeposition of Al. The initial reduction potential of Al(III) shifts more positive and reaction current is enhanced as temperature increases, indicating that Al is easier to be electrodeposited at higher temperatures. This phenomenon probably results from the increase of activated ions and mass charge transfer rate.

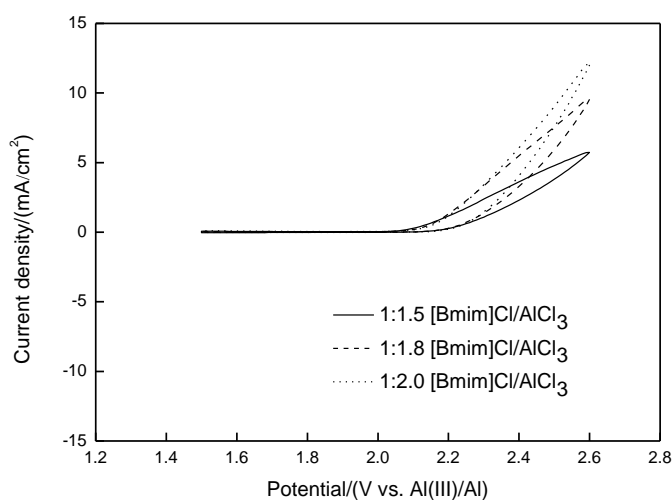


Figure 3. Cyclic voltammograms recorded on a GC disc electrode in Lewis acidic [Bmim]Cl/AlCl₃ at 313.2 K. The potential scan rate was 0.1 V/s.

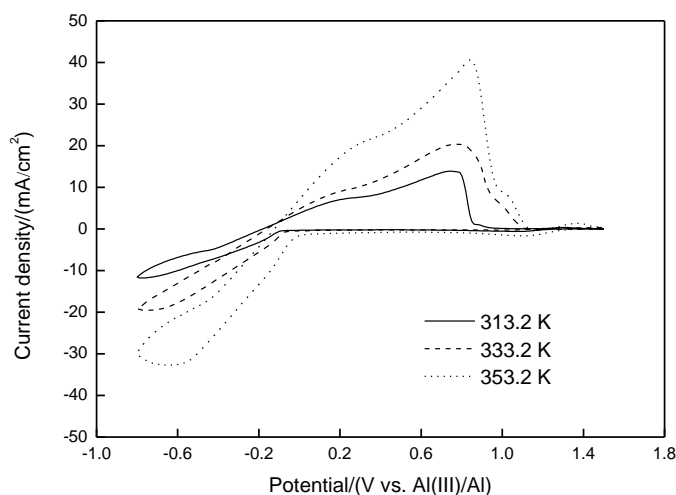


Figure 4. Cyclic voltammograms recorded on a Cu disc electrode in 1:2 [Bmim]Cl/AlCl₃ at different temperatures (cathodic potential regime). The potential scan rate was 0.1 V/s.

At the same temperature, the reduction potential of Al(III) decreases in the order: 1:2 [Bmim]Cl/AlCl₃ > 1:1.8 [Bmim]Cl/AlCl₃ > 1:1.5 [Bmim]Cl/AlCl₃. Based on above results, it's proper to state that the molar concentration of Al(III) and [Al₂Cl₇]⁻ in ILs increases when the apparent mole fraction of AlCl₃ rises. Based on our previous work, the weaker interaction between [Bmim]⁺ and [Al₂Cl₇]⁻ makes Al(III) more likely to be reduced [18] (see Figure 6). Accordingly, it promotes the electrodeposition process of Al and corresponding reaction current density.

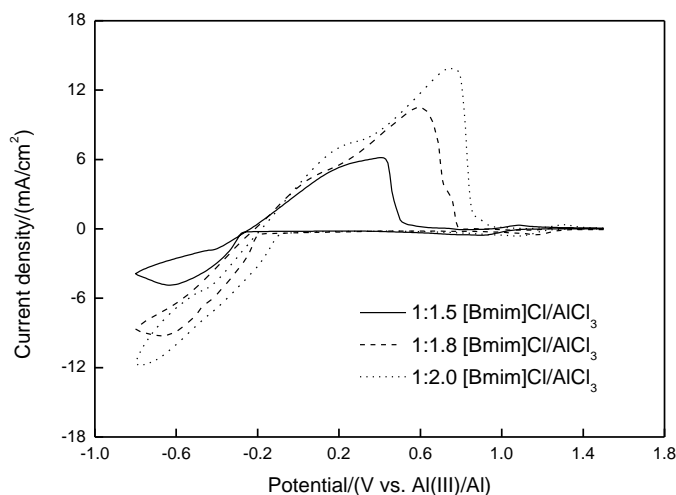


Figure 5. Cyclic voltammograms recorded on a Cu disc electrode in Lewis acidic [Bmim]Cl/AlCl₃ at 313.2 K (cathodic potential regime). The potential scan rate was 0.1 V/s.

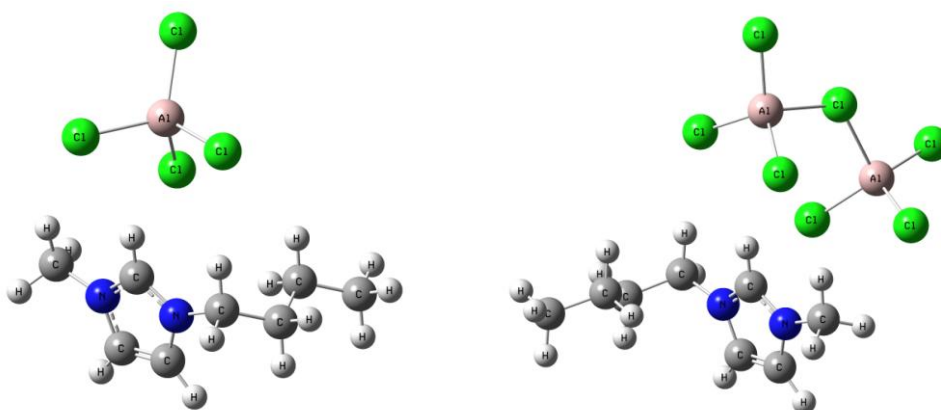


Figure 6. Optimized geometries of [Bmim][AlCl₄] and [Bmim][Al₂Cl₇] calculated by density functional theory. The cation-anion interaction energy of [Bmim][AlCl₄] and [Bmim][Al₂Cl₇] is 290.98 and 270.61 kJ/mol, respectively. This figure is reprinted with permission from American Chemical Society (Yong Zheng, Kun Dong, Qian Wang, Jianmin Zhang and Xingmei Lu. Density, viscosity, and conductivity of Lewis acidic 1-butyl- and 1-hydrogen-3-methylimidazolium chloroaluminate ionic liquids. *Journal of Chemical & Engineering Data*, 2013, 58(1): 32-42). Copyright (2012) American Chemical Society.

In summary, temperature and molar ratio of [Bmim]Cl/AlCl₃ are the main experimental parameters in electrolysis of aluminium. According to the results of cyclic voltammetric measurement,

electrochemical reactions on both cathode and anode are easier to take place when temperature increases. On the other hand, the enhanced molar concentration of Al(III) and $[\text{Al}_2\text{Cl}_7]^-$ can facilitate electrolysis process of aluminium.

3.2.2 Chronoamperometry

Chronoamperometric experiments have also been performed to study the nucleation process of aluminium. Figure 7 shows a group of current-time transients obtained at different potentials from Lewis acidic $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ at 313.2 K. It's apparent that a sharp decay of current occurs after the application of step potential, especially at higher potential. This probably results from the charging of electrode double layer between ions and cathode surface. The following increase in current is mainly attributed to the nucleation and growth of aluminium. As time goes by, the current curve finally reaches a maximum (i_m) at time (t_m), when the discrete diffusion zones of growing crystallites begin to overlap [23]. After that, the current transients decay as the deposited layer becomes thicker. It's obvious that the time needed to reach current maximum is shorten when the applied potential is more negative. Meanwhile, the increase of temperature and molar concentration of Al(III) could also reduce this time. These results show that the nucleation density and rate of aluminium are enhanced as the molar concentration of Al (III) increases in ILs.

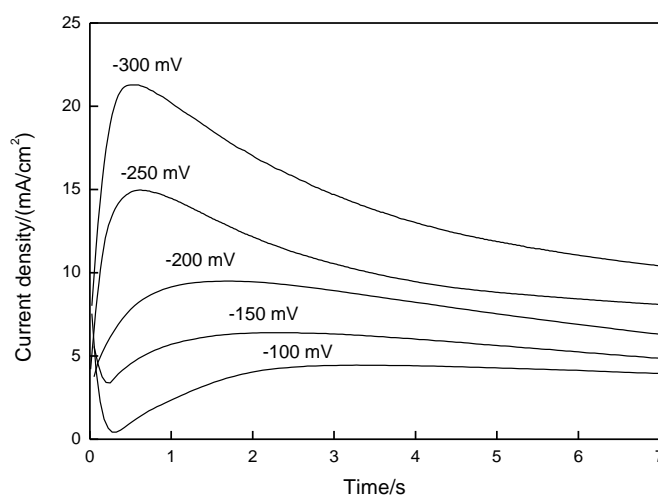


Figure 7. Current-time transients resulting from potential step experiments on Cu electrodes in 1:2 $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ at 313.2 K.

The bulk electrodeposition of aluminium on foreign substrates involves a three-dimensional nucleation/growth process. Hemispherical diffusion-controlled growth of the nuclei is a classic model proposed to describe this process [24]. This model has two limiting cases: instantaneous nucleation and progressive nucleation. To probe into the nucleation model in this study, the experimental time has been corrected for the potential-dependent induction time (t_0), by refining the time axis as $t' = t - t_0$ and $t'_m = t_m - t_0$. The dimensionless plots of $(i/i_m)^2$ vs. $(t'/t'_m)^2$ is presented with theoretical curves in Figure 8. As can be seen, the electrodeposition of aluminium fits well to the three-dimensional

instantaneous nucleation model. It indicates that all the nuclei are instantaneously formed at the beginning of chronoamperometric experiments with diffusion-controlled growth.

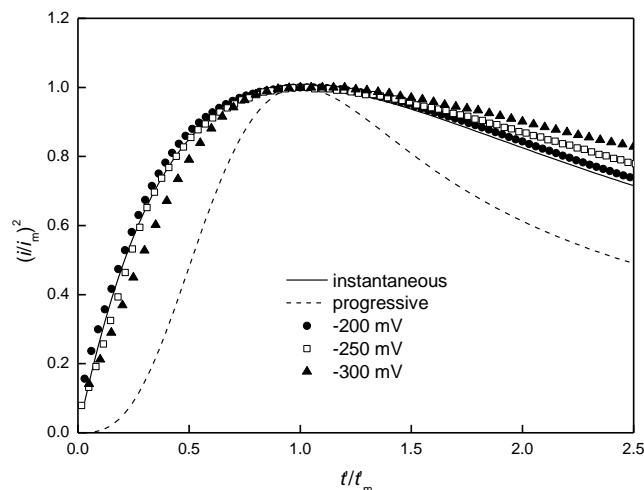


Figure 8. Comparison of the dimensionless experimental current-time transients, derived from the results in Figure 7, with the theoretical curves for instantaneous nucleation and progressive nucleation.

3.3 Characterization of products and current efficiency

On the basis of electrochemical measurement, it's necessary to characterize the products and current efficiency of electrolysis for industrial application. Accordingly, the following text presents relevant research results on this subject. Temperature, current density, molar concentration of $[\text{Al}_2\text{Cl}_7]^-$ and vacuum degree in electrolytic cell were investigated as main experimental parameters.

3.3.1 Cl_2 evolution

The performance of GC electrode is very important to electrolysis of aluminium, which can be evaluated by anode current efficiency. As discussed above, the values of anode current efficiency reflect the transformation rate from $[\text{AlCl}_4]^-$ to Cl_2 . In this section, the results of anode current efficiency obtained under different experimental conditions are presented and analyzed.

It's found that the vacuum degree in electrolytic cell is critical to superior anode current efficiency. The value of anode current efficiency can be remarkably improved when the vacuum degree increases, indicating that the evolution and of absorption Cl_2 is enhanced in this trend. Under the same temperature, current density and molar concentration of $[\text{Al}_2\text{Cl}_7]^-$, the highest efficiency can be obtained from $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ at -0.1 MPa according to our experimental results.

Figure 9 presents the anode current efficiency in aluminium electrolysis from 1:2 $[\text{Bmim}]\text{Cl}/\text{AlCl}_3$ at -0.1 Mpa and different temperatures. Apparently, the current efficiency decreases as temperature rises. Based on NMR and MS measurements, more organic by-products, such as alkanes and chlorides were formed at higher temperature. It indicates that more side reactions including the chlorination and decomposition of imidazolium cations are prone to take place at higher temperatures, which results in lower efficiency [25,26].

On the other hand, the increase of current density could improve anode current efficiency. According to our empirical research and literature survey [24], smaller quantity of Cl_2 is generated under lower current density. In such case, Cl_2 is easily lost during the capture and adsorption process. Accordingly, the corresponding anode current efficiency calculated by Eq.5 is always at a relatively low level. Therefore, appropriate current density is key to achieve higher efficiency.

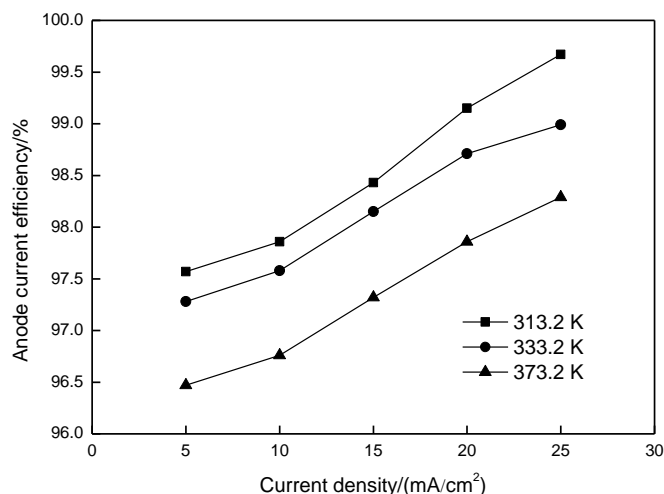


Figure 9. The anode current efficiency in the aluminium electrolysis from 1:2 [Bmim]Cl/AlCl₃ as a function of temperature at -0.1 Mpa.

As Figure 10 shows, the anode current efficiency measured from [Bmim]Cl/AlCl₃ follows the order, 1:2 [Bmim]Cl/AlCl₃ > 1:1.8 [Bmim]Cl/AlCl₃ > 1:1.5 [Bmim]Cl/AlCl₃. On the basis of cyclic voltammetry experiments, it can be inferred that Cl_2 is easier to release and side reactions are more difficult to occur when molar concentration of $[\text{Al}_2\text{Cl}_7]^-$ increases in ILs. The following adsorption rate of Cl_2 is enhanced. Consequently, the increase of molar fraction of AlCl₃ could improve anode current efficiency.

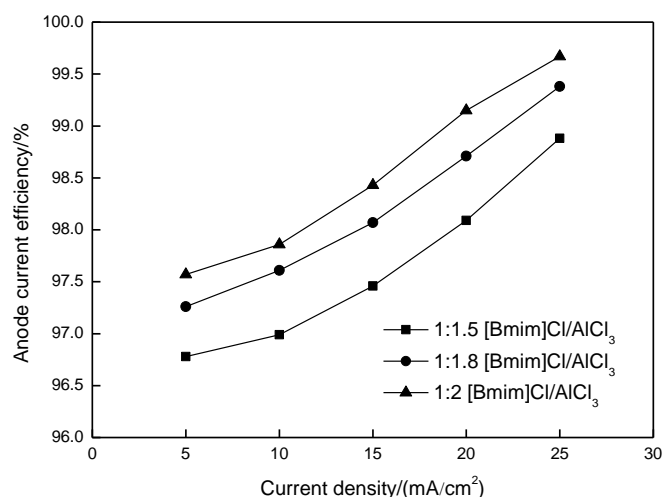


Figure 10. The anode current efficiency in the aluminium electrolysis from [Bmim]Cl/AlCl₃ as a function of molar ratios at -0.1 Mpa and 313.2 K.

In summary, the vacuum degree, temperature, current density and molar ratio of ILs have significant impact on the anode current efficiency. More than 96% efficiency has been achieved from 1:1.5~1:2 [Bmim]Cl/AlCl₃ at -0.1 Mpa, 313.2~373.2 K and 5~25 mA/cm². In these experimental conditions, the increase of current density, molar fraction of AlCl₃ and vacuum degree in electrolytic cell, as well as lower temperature could improve anode current efficiency. It indicates that fewer side reactions, higher release and absorption rate of Cl₂ make the electrolysis more efficient on GC anode.

3.3.2 Aluminium deposits

Different from Cl₂ evolution, our research reveals that the surface morphology of aluminium and cathode current efficiency is hardly affected by the vacuum degree in electrolytic cell. Therefore, the aluminium deposits prepared at -0.1 Mpa are chosen as examples in following discussion.

Experimental temperature is key to the electrodeposition of aluminium. It's found that smooth and well-adherent deposits could be obtained on copper substrates at 313.2~353.2 K. The grain size of crystallites increases as temperature rises (see Figure 11). However, the deposited coatings become rough and incompact at higher temperatures, especially above 373.2 K. The changes in microstructure of aluminium deposits may result from the variation of electrical conductivity and diffusion rate of ions at different temperatures [18,27]. In such case, the dendritic growth of aluminium probably is owing to the nonuniform distribution of ions and charge, as well as higher growth rate [23].

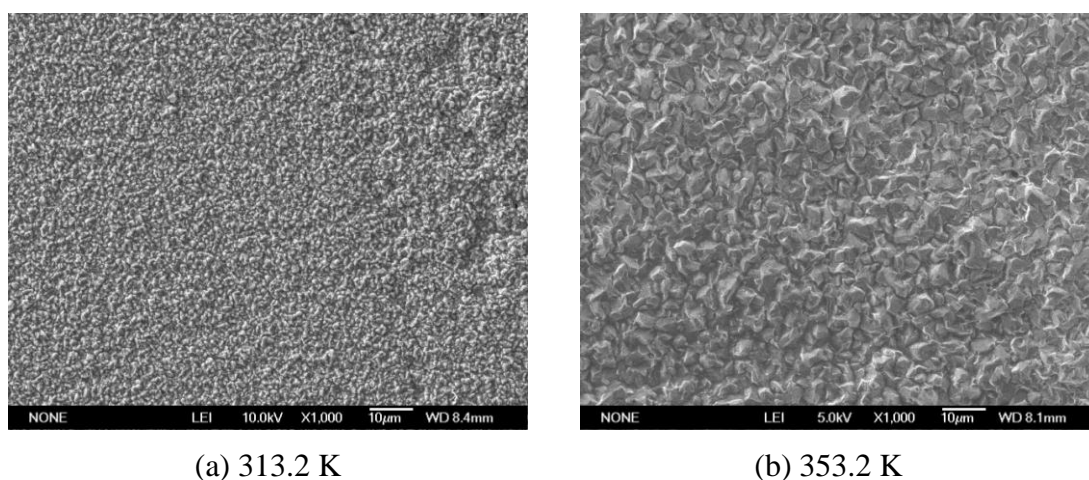


Figure 11. SEM micrographs of aluminium deposits obtained from 1:2 [Bmim]Cl/AlCl₃ at -0.1 Mpa, 15 mA/cm² and different deposition temperatures.

As Figure 12 and 11(a) illustrate, the average grain size of deposits decreases when current density rises from 5 to 15 mA/cm² at the same temperature. By contrast, the crystals enlarge in size with current density higher than 15 mA/cm². It shows that more nuclei can be obtained on substrate as current density increases in the range of 5~15 mA/cm², which promotes the smooth and compact growth of aluminium [23]. After reaching nucleation density maximum on the surface of copper

substrates, the excessive overlapping growth of crystallites leads to larger and rougher deposits [24,28]. Therefore, the grain size of aluminium crystals starts to increase when current density is more than 15 mA/cm².

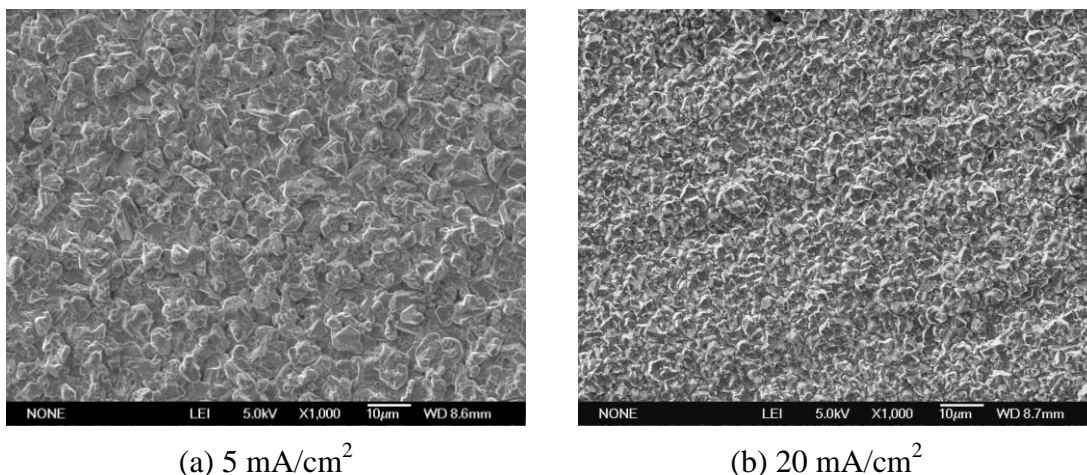


Figure 12. SEM micrographs of aluminium deposits prepared from 1:2 [Bmim]Cl/AlCl₃ at -0.1 Mpa, 313.2 K and different current density.

The molar concentration of [Al₂Cl₇]⁻ is also an important experimental parameter in the electrodeposition process. According to the SEM micrographs shown in Figure 13 and 11(a), smaller grain size of deposits is prone to be obtained when the molar fraction of [Bmim]Cl/AlCl₃ changes from 1:1.5 to 1:2. Based on above analysis and previous work [18,28], the molar concentration of reducible [Al₂Cl₇]⁻ anions and corresponding nucleation density of aluminium on copper substrates increase as the molar content of AlCl₃ rises. Consequently, it's easier to achieve compact, smooth and dense aluminium deposits from 1:2 [Bmim]Cl/AlCl₃ than 1:1.5 and 1:1.8 [Bmim]Cl/AlCl₃.

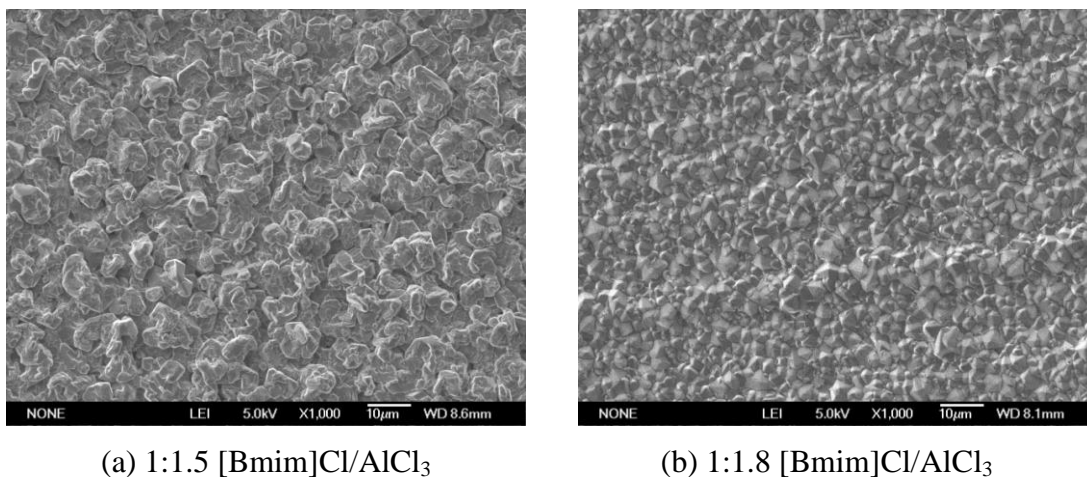


Figure 13. SEM micrographs of aluminium deposits obtained from [Bmim]Cl/AlCl₃ at -0.1 Mpa, 15 mA/cm² and 313.2 K.

In conclusion, compact, uniform and dense deposits can be obtained at 313.2~353.2 K, 5~15 mA/cm² from 1:1.5~1:2 [Bmim]Cl/AlCl₃. Appropriate experimental temperature, current density and molar concentration of [Al₂Cl₇]⁻ are essential to the preparation of deposits with optimum surface morphology. According to the results of EDAX spectra, the mass content of aluminium in all the samples is higher than 99%. On the other hand, more than 98% cathode current efficiency has been achieved for the electrodeposition process. From the perspective of current efficiency, the optimum condition for aluminium electrolysis is at 313.2 K, 15~25 mA/cm² and -0.1 Mpa from 1:2 [Bmim]Cl/AlCl₃.

4. CONCLUSIONS

In this work, GC was used as inert anode material in consideration of its higher chemical stability and mechanical strength. According to cyclic voltammetric and chronoamperometric measurements, the electrochemical behavior of Lewis acidic [Bmim]Cl/AlCl₃ at different experimental conditions has been analyzed. It shows that electrodeposition of aluminium fits well to the three-dimensional instantaneous nucleation model with diffusion-controlled growth. As for the Cl₂ generated on GC inert anode, more than 96% current efficiency was achieved at -0.1 Mpa, 313.2~373.2 K and 5~25 mA/cm². On this basis, the effect of temperature, current density, ILs' molar ratio and vacuum degree on the surface morphology of aluminium deposits was discussed systemically. Smooth, dense and well-adherent deposits could be prepared at 313.2~353.2 K, 5~15 mA/cm² from 1:1.5~1:2 [Bmim]Cl/AlCl₃. Compared with previous research on aluminium electrolysis, the purity of deposits and current efficiency has been improved. It can be concluded that the application of GC inert anode not only facilitates formation and release of Cl₂, but also reduces the incidence of side reactions. Accordingly, this work may provide a new method for the low-temperature aluminium electrolysis.

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