

Conductivities of AlCl_3 /Ionic Liquid Systems and Their Application in Electrodeposition of Aluminium

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Abstract: Solubilities and conductivities of anhydrous AlCl_3 in six kinds of ionic liquids (ILs) were measured. Among the six kinds of ILs [bmim]Cl, [bmim]Br, [bmim]BF₄, [bmim]PF₆, [emim][EtSO₄] and [bmim][HSO₄], anhydrous AlCl_3 could be dissolved in the first five kinds but was hardly dissolved in [bmim][HSO₄]. The results showed that the nominal solubilities of AlCl_3 in ILs increased in the order of [bmim][HSO₄] < [bmim]PF₆ < [emim][EtSO₄] < [bmim]BF₄ < [bmim]Cl < [bmim]Br. Conductivities of the AlCl_3 /ILs systems depended apparently on the nominal molar ratio of AlCl_3 to ILs. The conductivities of AlCl_3 /[bmim]Cl, AlCl_3 /[bmim]Br and AlCl_3 /[bmim]PF₆ systems had a similar tendency as a function of the nominal molar ratio, that is, as the molar ratio was increased, conductivities increased first and then decreased, with the maximum conductivity obtained at approximately 0.9:1, 1.0:1 and 0.5:1, respectively. Conductivities of the AlCl_3 /[bmim]BF₄ exhibited a dentate change and decreased with the molar ratio of AlCl_3 to [bmim]BF₄ increasing in general. With the increasing of the anhydrous AlCl_3 amount in [emim][EtSO₄], conductivity of AlCl_3 /[emim][EtSO₄] monotonically decreased. AlCl_3 /[bmim]Cl system was chosen as the electrolyte for the electrodeposition of Al. Preliminary experimental results showed that dense, adherent and homogeneous Al coatings could be electrodeposited on stainless steel by means of constant potential technique and the surface coverage was quite satisfactory.

Key words: ionic liquid; AlCl_3 ; solubility; conductivity; electrodeposition of aluminium

CLC No.: O646

Document Code: A

Article ID: 1009-606X(2008)04-0814-06

1 INTRODUCTION

Coating of aluminium (Al) on steel is critically important due to its excellent corrosion resistance, decorativeness and physicochemical properties. However, aluminium cannot be electrodeposited from traditional electrolytes based on aqueous solutions because of its rather negative standard potential of Al/Al(III) couple (-1.67 V, vs. NHE). Thus, the electrodeposition process is restricted to non-aqueous aprotic electrolytes such as organic solvents^[1-4] and molten salts^[5-7]. But the flammability and volatility of organic solvents^[8] and the highly corrosive natures and relatively high temperature of inorganic molten salts^[9] make it necessary to find novel electrolytes for the electrodeposition of Al.

Over the last decades, employment of room temperature molten salts (usually called as room temperature ionic liquids, RTILs) in non-aqueous electrolytes has made it possible that the entire operation process was under mild conditions. RTILs are

regarded as a possible replacement due to their attractive properties^[10,11], such as good chemical and thermal stability, high electrical conductivity, ability to dissolve organic and inorganic materials, low molten point with insignificant vapor pressure and a large electrochemical window of about 4.0 V. The last property allows them to electrodeposit a wide variety of metals including transition, rare earth and refractory metals which are impossible to achieve with aqueous electrolytes. Recently, RTILs are receiving an upsurge in their utilization in the electrodeposition of Al, especially the AlCl_3 -based ILs^[12-15].

Electrical conductivity of the electrolytes is one of the most important properties for electrodeposition application. The electrolytes with higher conductivities will have lower Ohmic drop during electrolysis and lower cell voltage, and thus higher energy efficiency would be expected. Besides, in development of ILs for practical applications, despite the fact that the fundamental physical-chemical properties of ILs have been extensively studied, there are still little data on the

Received date: 2008-03-12; **Accepted date:** 2008-04-15

Foundation item: Supported by National Natural Science Foundation of China (No. 20776140); National Science Fund for Distinguished Young Scholars of China (No. 20625618); National 863 Program of China (No. 2006AA06Z317)

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solid-liquid equilibrium (SLE) reported in the literature and it will be necessary to accumulate more fundamental data on the solubility of metal compounds.

In this work, six kinds of ILs (shown in Fig.1), 1-butyl-3-methylimidazolium chloride ([bmim]Cl), 1-butyl-3-methylimidazolium bromide ([bmim]Br), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆), 1-ethyl-3-methylimidazolium ethyl sulfate ([emim][EtSO₄]), and 1-butyl-3-methylimidazolium hydrogen sulphate ([bmim][HSO₄]), which could be easily and economically obtained on a large scale, were synthesized and attempted to research the feasibility whether they could be used as potential electrolytes for electrodepositing Al. Anhydrous AlCl₃ was used as the initial source of Al. Very few data is available for the solubility of anhydrous AlCl₃ in these ionic liquids and we cannot exclude that the real solubility of AlCl₃ is lower than the nominal concentrations added. Furthermore, up to our knowledge, no electrochemical or spectroscopic information exists concerning the electro-active species in this neutral melt. In view of these, nominal solubilities of anhydrous AlCl₃ in synthesized ILs were determined and the electrical conductivities were investigated as a function of the nominal molar ratio of AlCl₃/ILs. Electrodeposition of Al on stainless steel was performed to obtain appropriate system as electrolyte.

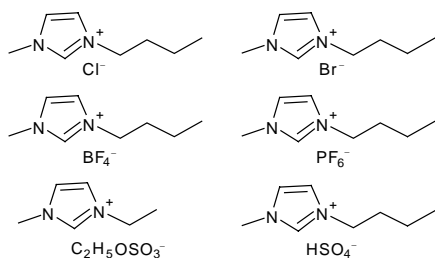


Fig.1 Structures of [bmim]Cl, [bmim]Br, [bmim]BF₄, [bmim]PF₆, [emim][EtSO₄] and [bmim][HSO₄]

2 EXPERIMENTAL

2.1 Materials

All the chemicals used in this study were of analytical grade. 1-Methylimidazole was distilled under reduced pressure. Deionized water was used in all experiments. [bmim]Cl^[16], [bmim]Br^[17], [bmim]BF₄^[18], [bmim]PF₆^[19], [emim][EtSO₄]^[20] and [bmim][HSO₄]^[21], were synthesized by the procedure described elsewhere. Anhydrous AlCl₃ (powder) was obtained from Beijing Chemical Reagents Company and used without further purification. Al plate (≥99.0%) and ultra-pure Al wire

(99.999%) were purchased from Beijing Chemical Reagents Company and Beijing Mountain Technical Development Center for Non-ferrous Metals, respectively.

2.2 Measurement of Solubilities and Conductivities of AlCl₃ in ILs

Solubility of anhydrous aluminium trichloride (AlCl₃) in synthesized ILs was measured in an electrolytic cell with a jacket under a dry nitrogen atmosphere (by introducing nitrogen into the cell at a constant flow rate), using continuous magnetic stirring. The conductivities were measured by a DDS-307 conductivity meter. Electrode constant of the meter was determined by calibration before and after measurement of each sample with 0.1 mol/L KCl solution at 298.15 K and was (1.021±0.002) cm⁻¹.

Precise quantities of anhydrous AlCl₃ were added to ILs placed in the cell at different molar ratio. Then the systems were thermostated at the predetermined temperature with an accuracy ±0.1 K, and continuously stirred (to ensure uniformity) until the conductivities of the formed AlCl₃/ILs systems did not change approximately (usually about 2~3 h). Then another feeding was started and repeated again. The criterion for the attainment of the maximum solubility was that the solid phase of AlCl₃ did not disappear for a period of about 8 h at given temperature and constant pressure.

Because of the hydrophilicity of the ILs and large effect of very small amounts of water on the solubility, the water content of ILs measured by a Karl Fischer titrator (Metrohm 787 KF Titrino, Switzerland) showed less than 10×10⁻⁶ before and after the experiments.

All data presented were measured three times in different samples to ensure its reproducibility within 5% in absolute value.

2.3 Electrodeposition in Ionic Liquid

Electrochemical measurements were performed using a CHI660C Electrochemical Workstation controlled with a personal computer. All the experiments were conducted using a three-electrode system: Al plate, stainless steel plate and ultra-pure Al wire were used as counter electrode, working electrode, and reference electrode, respectively. The distance between the cathode and the anode was about 2.0 cm. Al plate was dipped in NaOH, rinsed with deionized water, followed by acetone and then dried before use. Stainless steel plate was immersed in boiling NaOH, dipped in 20%~30% HCl (by volume), washed with deionized water and finally dried. Prior to use, the working electrodes were mechanically polished with sand paper, treated with a dilute mixture of hydrochloric acid (37%)

and sulfuric acid (98%), rinsed with deionized water, and finally immersed into dichloromethane for degreasing. After completing the pretreatments, the electrodes were assembled for immediate use. The depositions were carried out under a predetermined experimental temperature for 1 h with a constant stirring speed. Following each deposition experiment, excess electrolyte was removed from the sample by washing in absolute alcohol, then the sample was rinsed with deionized water and dried with cool air.

2.4 Analysis and Characterization of Aluminium Coatings

Surface morphology of the films was examined with emission scanning electron microscope (SEM, JSM-6301F). The compositional analysis of the deposits was confirmed by energy dispersive analysis with X-ray (EDAX, Oxford INCA300). The crystalline structure was studied on an X'Pert PRO (PANalytical) X-ray diffractometer with Cu $K\alpha$ radiation.

3 RESULTS AND DISCUSSION

3.1 Solubilities of Anhydrous AlCl_3 in ILs and Conductivities of AlCl_3 /ILs Solutions

3.1.1 AlCl_3 /[bmim]Cl system

At the very beginning of feeding, precise quantities of anhydrous AlCl_3 were mixed with [bmim]Cl in a dry electrolytic cell and the formed system turned to be liquid phase gradually, and then transparent yellowish liquid formed. Due to the highly exothermic reaction occurring between AlCl_3 and [bmim]Cl components, the adding should be slow and well proportioned. With the molar ratio of AlCl_3 to [bmim]Cl increasing, the color of the liquid turned from transparent yellowish to opaque white until the molar ratio of AlCl_3 to [bmim]Cl reached around 1.0:1, and the viscosity increased obviously. Along with continuous feeding, the color of the mixture turned to transparent dark brown and the viscosity decreased reversely until the molar ratio of AlCl_3 to [bmim]Cl got to 2.0:1. The maximum nominal molar ratio was 2.1:1, and with more addition, unsolvable AlCl_3 could be seen in the system.

Since anionic species of AlCl_3 /[bmim]Cl change with the molar ratio of AlCl_3 to [bmim]Cl, chemical and electrochemical properties of the melts change drastically with the composition. Conductivities of the AlCl_3 /[bmim]Cl system with different molar ratio at 298.15 K were shown in the Fig.2. It could be seen that the conductivity was markedly dependent upon the molar ratio of AlCl_3 to [bmim]Cl, as the molar ratio was increased, conductivities of the AlCl_3 /[bmim]Cl also increased before 1.0:1, then the conductivities decreased

and reduced to a steady level near 3 mS/cm from the molar ratio of 1.3:1. The maximum conductivity was obtained when the molar ratio of AlCl_3 to [bmim]Cl approached to approximately 0.9:1.

3.1.2 AlCl_3 /[bmim]Br system

White [bmim]Br and anhydrous AlCl_3 (powder) were mixed together and the formed system became homogeneous phase slowly with the weight of anhydrous AlCl_3 in [bmim]Br increasing. The colors of the formed liquid were buff, milk white, buff, dark yellow and nut-brown in the different ranges of molar ratio of AlCl_3 to [bmim]Br, 0.1~0.7, 0.7~0.9, 0.9~1.0, 1.0~1.2 and 1.2~2.3, respectively. The variability of color of the system may be related to the molar ratio of AlCl_3 to [bmim]Br. Compared with AlCl_3 /[bmim]Cl, the maximum nominal molar ratio was 2.3:1, and with more addition, unsolvable AlCl_3 could be seen in the system.

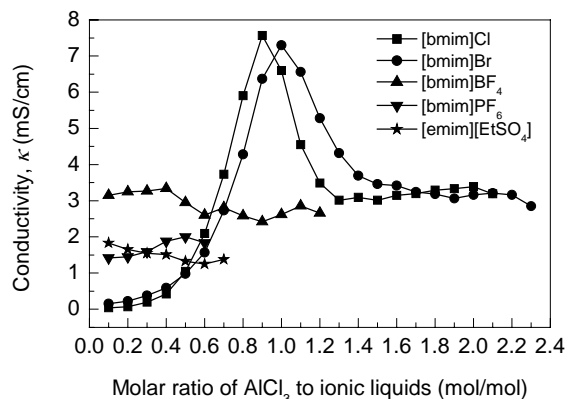


Fig.2 Electrical conductivities (κ) of the AlCl_3 /ILs systems at 298.15 K as a function of nominal molar ratio

It could be seen in Fig.2 that the conductivity was also markedly affected by the molar ratio of AlCl_3 to [bmim]Br at 298.15 K. The variation of conductivities of the formed AlCl_3 /[bmim]Br was similar to that of AlCl_3 /[bmim]Cl: as the molar ratio of AlCl_3 to [bmim]Br was increased, conductivities of the AlCl_3 /[bmim]Br also gradually increased before 1.0:1; then the conductivities decreased to a steady level from the molar ratio of 1.5:1. Conductivity of the system presented a maximum value at a molar ratio of 1.0:1.

3.1.3 AlCl_3 /[bmim]BF₄ system

As the molar ratio of AlCl_3 to [bmim]BF₄ was increased, the colors of the system were buff, milk white and buff in the different ranges of the molar ratio, 0~0.4, 0.4~0.9 and 0.9~1.1, respectively. The maximum nominal molar ratio was 1.1:1, which was smaller than those of AlCl_3 /[bmim]Cl and AlCl_3 /[bmim]Br.

In contrast to the conductivities of the AlCl_3 /[bmim]Cl and AlCl_3 /[bmim]Br, the conductivities

of AlCl₃/[bmim]BF₄ changed in a quite different rule as a function of the molar ratio of AlCl₃ to [bmim]BF₄ at 298.15 K. From Fig.2, the conductivities of AlCl₃/[bmim]BF₄ exhibited a dentate change and decreased with the molar ratio of AlCl₃ to [bmim]BF₄ increasing in general, which maybe resulted from variety of the anionic species of AlCl₃/[bmim]BF₄ system. With the molar ratio from 0.9 to 1.1, the viscosity of the system increased so much that it could not be stirred by magnetic stirrer. Interestingly, the conductivities also increased, which could not be specified well now. Elevating the temperature contributed little to improving the solubility and conductivity. Surprisingly, the system became solid at 358.15 K.

3.1.4 AlCl₃/[bmim]PF₆ system

The transparent white [bmim]PF₆ changed to be an opaque milk white one as long as the first quantity of anhydrous AlCl₃ was added to it. The greater the molar ratio of AlCl₃ to [bmim]PF₆, the larger viscosity of the system was. When the molar ratio reached about 0.6:1, the system transformed to be a solid phase with milk white. The maximum nominal molar ratio was 0.6:1, smaller than those of the above three systems. Temperature was also enhanced to improve the solubility and conductivity, and phenomena were quite the same as that of AlCl₃/[bmim]BF₄.

Figure 2 shows the conductivities of the AlCl₃/[bmim]PF₆ with different molar ratios of AlCl₃ to [bmim]PF₆ at 298.15 K. Compared with those of AlCl₃/[bmim]BF₄, conductivities of AlCl₃/[bmim]PF₆ were relatively small and increased along with the molar ratio of AlCl₃ to [bmim]PF₆ increasing. The conductivity of the system reached the maximum when the molar ratio of AlCl₃ to [bmim]PF₆ approached to around 0.5:1.

3.1.5 AlCl₃/[emim][EtSO₄] system

The maximum nominal molar ratio of AlCl₃/[emim][EtSO₄] was 0.7:1, which was equal to that of AlCl₃/[bmim]PF₆. Fig.2 shows the conductivities of the AlCl₃/[emim][EtSO₄] with different molar ratio at 298.15 K. Electrical conductivity of the system was seen to monotonically decrease when AlCl₃ was added. When the molar ratio of AlCl₃ to [emim][EtSO₄] was 0.7:1, the color became darker and the viscosity increased so much that the magnetic stirrer could not work normally. Maybe it was possible to improve the solubility and conductivity if temperature was enhanced. However, the solubility and conductivity did not ascend as expected. The viscosity increased and the system turned to be solid, which could not be reverted to liquid

when cooled to room temperature. The cause of this phenomenon could not be identified at this time and more studies are necessary to elucidate it.

3.1.6 AlCl₃/[bmim][HSO₄] system

At 298.15 K, anhydrous AlCl₃ was hardly dissolved in [bmim][HSO₄]. When the molar ratio of AlCl₃ to [bmim][HSO₄] was just 0.1:1, conductivity was only 0.3 mS/cm and AlCl₃/[bmim][HSO₄] system became so viscous that it could not be effectively stirred by magnetic stirrer. Enhancing the temperature contributed little to increase the solubility and conductivity, which proved that the AlCl₃/[bmim][HSO₄] system was not appropriate as electrolyte for the electrodeposition of aluminium.

3.2 Electrodeposition of Aluminium on Stainless Steel

Among the six kinds of AlCl₃/ILs systems, AlCl₃/[bmim]Cl and AlCl₃/[bmim]Br are the most appropriate electrolytes for the electrodeposition of Al with the highest average conductivities (in the acid range where aluminium can be electrodeposited). Considering the stability, AlCl₃/[bmim]Cl system is chosen to be used as the electrolyte for the following experiments. Previous studies show that electrodeposition of Al can only be performed in acidic electrolytes, in which the electroactive Al₂Cl₇⁻, the only reducible aluminium containing species, are responsible for the electrodeposition according to the following reaction^[22]:



For ionic liquids with large halide concentrations the breakdown of metal oxides on electrode surfaces is prevalent, it is easier for ILs with chloride ions which can act as good ligands for the dissolving metal ions^[23]. Electrodeposition was performed on stainless steel.

3.2.1 SEM examination and microstructure

The study was performed by means of constant potential deposition on stainless steel. The 2.0:1 molar ratio of AlCl₃/[bmim]Cl was used for the electrodeposition of Al. Constant potential deposition was carried out on stainless steel substrate with potentials ranging from -0.5 to -1.5 V at 308 K for 1 h. All of the Al-deposited samples were dense, adherent and homogeneous and the surface coverage was quite satisfactory. Figure 3 shows the SEM micrograph of the deposits obtained in 2.0:1 AlCl₃/[bmim]Cl for 1 h under magnetic stirring on stainless steel at 308 K with potential $U = -1.0$ V. The deposits contain coarse cubic-shaped micro-crystallites with an average size at the order of 10~20 μm.

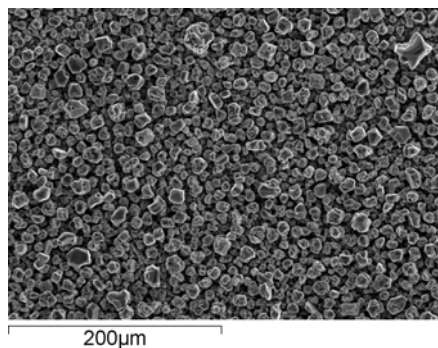


Fig.3 SEM micrograph of the aluminum coating on stainless steel obtained from 2.0:1 $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ at 308 K with $U=-1.0$ V for 1 h under magnetic stirring

3.2.2 Analysis of composition and crystal structure of electrodeposited aluminium coatings

The chemical compositions of the samples electrodeposited under different conditions were inspected with an EDAX and the results revealed similar spectrum. Fig.4 shows the EDAX analysis of the deposits obtained on the working electrodes after 1 h in 2.0:1 $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ at 308 K with potential $U=-1.0$ V. As expected, the deposits display a strong peak for aluminum, and relatively weak peaks of iron and oxygen. The Fe detected in the Al deposits may come from the substrate and the detected O may result from the oxidation of Al or Fe. Table 1 shows the components of the deposits clearly.

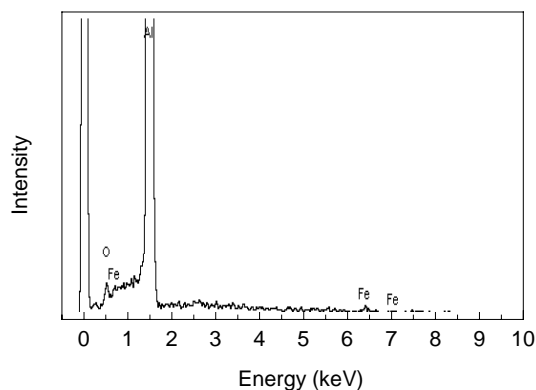


Fig.4 EDAX spectrum of the electrodeposit on cathode in 2.0:1 $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ at 308 K and $U=-1.0$ V for 1 h

Table 1 Components of the deposit on stainless steel in 2.0:1 $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ for 1 h at 308 K and $U=-1.0$ V

Element	Mass percentage (%)	Atomic percentage (%)
O	2.05	3.43
Al	96.86	96.05
Fe	1.10	0.53
Total	100.00	100.1

Crystalline structure analyses were also carried out using XRD, and the acquired diffraction pattern of the

obtained sample shows only the pattern of aluminum metal (Fig.5). The diffraction peaks attributed to pure Al with a face-centered cubic structure (fcc) were clearly detected from the sample. Similar results were observed for other samples.

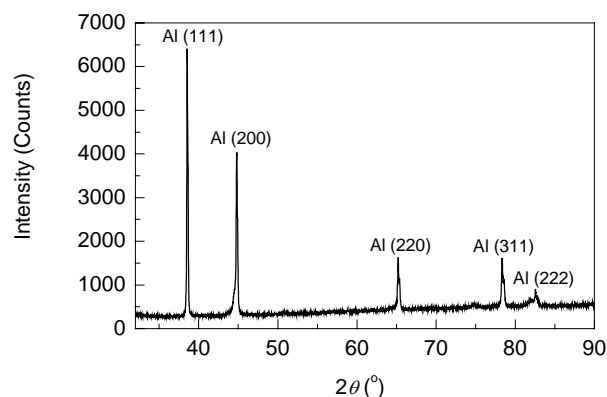


Fig.5 XRD pattern of the electrodeposit on stainless steel in 2.0:1 $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ at 308 K and $U=-1.0$ V for 1 h

4 CONCLUSIONS

Based on the above results, some conclusions may be drawn as follows:

(1) Among the six kinds of ILs $[\text{bmim}]\text{Cl}$, $[\text{bmim}]\text{Br}$, $[\text{bmim}]\text{BF}_4$, $[\text{bmim}]\text{PF}_6$, $[\text{emim}][\text{EtSO}_4]$ and $[\text{bmim}][\text{HSO}_4]$, anhydrous AlCl_3 could be dissolved in the first five kinds, but hardly dissolved in $[\text{bmim}][\text{HSO}_4]$. The nominal solubilities of AlCl_3 in ILs increased in the order of $[\text{bmim}][\text{HSO}_4] < [\text{bmim}]\text{PF}_6 < [\text{emim}][\text{EtSO}_4] < [\text{bmim}]\text{BF}_4 < [\text{bmim}]\text{Cl} < [\text{bmim}]\text{Br}$.

(2) Conductivities of the AlCl_3/ILs systems depended apparently on the nominal molar ratio of AlCl_3 to ILs. Variation in the conductivities of $\text{AlCl}_3/[\text{bmim}]\text{Cl}$, $\text{AlCl}_3/[\text{bmim}]\text{Br}$ and $\text{AlCl}_3/[\text{bmim}]\text{PF}_6$ had a similar tendency as a function of the nominal molar ratio, that is, as the molar ratio increased, conductivities increased first and then decreased, with the maximum conductivity obtained at approximately 0.9:1, 1.0:1 and 0.5:1, respectively. The conductivities of $\text{AlCl}_3/[\text{bmim}]\text{BF}_4$ exhibited a dentate change and decreased with the molar ratio of AlCl_3 to $[\text{bmim}]\text{BF}_4$ increasing in general. With increasing of the anhydrous AlCl_3 amount in $[\text{emim}][\text{EtSO}_4]$, conductivity of $\text{AlCl}_3/[\text{emim}][\text{EtSO}_4]$ monotonically decreased.

(3) From the analyses of the conductivities of AlCl_3/ILs systems and considering the stability of ILs, $\text{AlCl}_3/[\text{bmim}]\text{Cl}$ system was chosen as the electrolyte for the electrodeposition of Al. Preliminary experiments were performed by means of constant potential deposition on stainless steel. Results showed that dense,

adherent and homogeneous Al coating could be electrodeposited and the surface coverage was quite satisfactory. Further studies will be needed to optimize the operating conditions.

REFERENCE:

- [1] Ziegler K, Lehmkuhl H. Die Elektrolytische Abscheidung von Aluminium aus Organischen Komplexverbindungen [J]. *Z. Anorg. Allg. Chem.*, 1956, 283(1/6): 414–424.
- [2] Yoshio M, Ishibashi N. High-rate Plating of Aluminium from the Bath Containing Aluminium Chloride and Lithium Aluminium Hydride in Tetrahydrofuran [J]. *J. Appl. Electrochem.*, 1973, 3(4): 321–325.
- [3] Peled E, Gileadi E. Electroplating of Al from Aromatic Hydrocarbons [J]. *Plat. Surf. Finish.*, 1975, 62(4): 342–347.
- [4] Jiang T, Chollier Brym M J, Dube G, et al. Studies on the AlCl₃/Dimethylsulfone (DMSO₂) Electrolytes for the Aluminum Deposition Processes [J]. *Surf. Coat. Technol.*, 2007, 201(14): 6309–6317.
- [5] Godshall N. Molten Salt Metallizing of Nickel Alloys [J]. *J. Electrochem. Soc.*, 1976, 123(4): 137C–140C.
- [6] Li J C, Nan S H, Jiang Q. Study of the Electrodeposition of Al–Mn Amorphous Alloys from Molten Salts [J]. *Surf. Coat. Technol.*, 1998, 106(2/3): 135–139.
- [7] Jafarian M, Mahjani M G, Gopal F, et al. Electrodeposition of Aluminum from Molten AlCl₃–NaCl–KCl Mixture [J]. *J. Appl. Electrochem.*, 2006, 36(10): 1169–1173.
- [8] Zhao Y G, VanderNoot T J. Electrodeposition of Aluminium from Nonaqueous Organic Electrolytic Systems and Room Temperature Molten Salts [J]. *Electrochim. Acta*, 1997, 42(1): 3–13.
- [9] Endres F. Ionic Liquids: Solvents for the Electrodeposition of Metals and Semiconductors [J]. *Chem. Phys. Chem.*, 2002, 3(2): 144–154.
- [10] Welton T. Room-temperature Ionic Liquids: Solvents for Synthesis and Catalysis [J]. *Chem. Rev.*, 1999, 99(8): 2071–2083.
- [11] Brennecke J F, Maginn E J. Ionic Liquids: Innovative Fluids for Chemical Processing [J]. *AIChE J.*, 2001, 47(11): 2384–2389.
- [12] Carlin R T, Crawford W, Bersch M. Nucleation and Morphology Studies of Aluminum Deposited from an Ambient-temperature Chloroaluminate Molten Salt [J]. *J. Electrochem. Soc.*, 1992, 139(10): 2720–2727.
- [13] Yang C C. Electrodeposition of Aluminum in Molten AlCl₃–*n*-Butylpyridinium Chloride Electrolyte [J]. *Mater. Chem. Phys.*, 1994, 37(4): 355–361.
- [14] Abbott A P, Eardley C A, Farley N R S, et al. Novel Room Temperature Molten Salts for Aluminium Electrodeposition [J]. *Trans. Inst. Met. Finish.*, 1999, 77(1): 26–28.
- [15] Jiang T, Brym M J C, Dube G, et al. Electrodeposition of Aluminium from Ionic Liquids: Part I. Electrodeposition and Surface Morphology of Aluminium from Aluminium Chloride (AlCl₃)–1-Ethyl-3-methylimidazolium Chloride ([Emim]Cl) Ionic Liquids [J]. *Surf. Coat. Technol.*, 2006, 201(1/2): 1–9.
- [16] Huddleston J G, Visser A E, Reichert W M, et al. Characterization and Comparison of Hydrophilic and Hydrophobic Room Temperature Ionic Liquids Incorporating the Imidazolium Cation [J]. *Green Chem.*, 2001, 3(4): 156–164.
- [17] Nishida T, Tashiro Y, Yamamoto M. Physical and Electrochemical Properties of 1-Alkyl-3-methylimidazolium Tetrafluoroborate for Electrolyte [J]. *J. Fluorine Chem.*, 2003, 120(2): 135–141.
- [18] Holbrey J D, Seddon K R. The Phase Behavior of 1-Alkyl-3-methylimidazolium Tetrafluoroborates Ionic Liquids and Ionic Liquid Crystals [J]. *J. Chem. Soc. Dalton Trans.*, 1999, (13): 2133–2139.
- [19] Dzyuba S V, Bartsch R A. New Room-temperature Ionic Liquids with C₂-symmetrical Imidazolium Cations [J]. *Chem. Commun.*, 2001, (16): 1466–1467.
- [20] Holbrey J D, Reichert W M, Swatlosk R P, et al. Efficient Halide Free Synthesis of New, Low Cost Ionic Liquids: 1,3-Dialkylimidazolium Salts Containing Methyl- and Ethyl-sulfate Anions [J]. *Green Chem.*, 2002, 4(5): 407–413.
- [21] Fraga-Dubreuil J, Bourahla K, Rahmouni M, et al. Catalysed Esterifications in Room Temperature Ionic Liquids with Acidic Counteranion as Recyclable Reaction Media [J]. *Catal. Commun.*, 2002, 3(5): 185–190.
- [22] Carlin R T, Osteryoung R A. Aluminum Anodization in a Basic Ambient Temperature Molten Salt [J]. *J. Electrochem. Soc.*, 1989, 136(5): 1409–1415.
- [23] Abbott A P, McKenzie K J. Application of Ionic Liquids to the Electrodeposition of Metals [J]. *Phys. Chem. Chem. Phys.*, 2006, 8(37): 4265–4279.