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Electrodeposition of Nanocrystalline Aluminium from 1-Ethyl-3-methylimidazolium Chloroaluminate with Niacinamide as an Efficient Additive

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Nanocrystalline aluminium has been used as a promising energetic material due to its unique properties. However, the traditional methods for nanocrystalline aluminium production suffer from many inherent problems, which restrict the large-scale industrial application. In this paper, a systematic study was carried out on the nucleation mechanism and electrodeposition behaviour of nanocrystalline aluminium in Lewis acidic 1-ethyl-3-methylimidazolium chloroaluminate ionic liquid. It was found that niacinamide could be used as an effective additive in the preparation of nanocrystalline aluminium. According to electrochemical measurements and computational calculations, niacinamide was highly electroactive and polarized, which is probably attributed to non-uniform distributions of positive and negative charges on niacinamide. Its strong interaction with the electrode and subsequent adsorption onto the surface of aluminium nuclei prevented the further growth of crystals. Consequently, nanocrystalline aluminium was obtained at 313.2−333.2 K and 3−6 mA/cm^2 from 1-ethyl-3-methylimidazolium chloroaluminate that contained 8−12 mmol/kg niacinamide. Smooth and compact aluminium crystals with a minimum grain size of 20−30 nm could be electrodeposited at 313.2 K and 6 mA/cm^2 with 8−12 mmol/kg niacinamide. The molar concentration of additive, temperature and current density were confirmed as the major influencing factors in the electrodeposition of nanocrystalline aluminium from the chloroaluminate ionic liquid. It is expected that this work may be useful for the future preparation and application of nanocrystalline aluminium.

Keywords: nanocrystalline aluminium; ionic liquid; electrodeposition; niacinamide

1. INTRODUCTION

Aluminium is the most widely used non-ferrous metal, which is primarily due to its low density, high corrosion resistance, and superior thermal and electrical conductivities. However, aluminium becomes highly active and flammable in air when the size of crystals decreases to the nanoscale [1]. These unique properties make nanocrystalline aluminium attractive as a novel energetic material. In recent years, nanocrystalline aluminium has been employed in many scientific fields, such as military industry, aerospace engineering and electronics [2,3].

The traditional methods for nanocrystalline aluminium production can be divided into physical and chemical processes. The physical methods mainly include nitrogen atomization and mechanical attrition processes [4,5]. On the other hand, the chemical processes are usually performed via the reduction of aluminium compounds in organic solutions [6]. Although these methods have already been used in the preparation of nanocrystalline aluminium, some inherent problems still exist. For example, the nitrogen atomization process needs to be conducted above the melting point of aluminium, which always leads to higher operating temperatures and excessive energy consumption. By contrast, the mechanical attrition treatment performed by high energy ball milling is unsafe and environmentally unfriendly. Although the chemical process is easy to operate at low temperature, the organic solvents used are quite flammable and volatile. Accordingly, the drawbacks of these methods restrict the large-scale preparation of nanocrystalline aluminium. From the perspective of scientific research and industrial production, more work should be done in developing more processing technologies.

Ionic liquids, the so-called room-temperature molten salts, are generally composed of organic cations and inorganic/organic anions. The excellent properties of ionic liquids, such as nonflammability, negligible volatility, high conductivity and wide electrochemical windows have attracted worldwide attention over the past decades [7]. Numerous studies reported that Lewis acidic chloroaluminate ionic liquids could be used as promising electrolytes in the low-temperature electrodeposition of aluminium [8-11]. The electrodeposition process is more efficient and environmentally friendly and can be conducted around room temperature. However, the grain size of aluminium prepared by this method is usually more than 1 μm [12,13]. In 2003, Endres et al. [14] first found that nanocrystalline aluminium could be electrodeposited from imidazolium chloroaluminate ionic liquids with nicotinic acid as an organic additive. The resulting average crystal size was determined to be 14 nm. On this basis, Abbott et al. [15] investigated the effect of some organic and inorganic compounds on the surface morphology of aluminium deposits from chloroaluminate based ionic liquids. It was shown that the progressive addition of toluene decreased the crystal grain size of aluminium deposits to nanoscale. In addition, some pyridine-based compounds were also used as additives in the electrodeposition of nanocrystalline aluminium [16-18]. Although some progress has been achieved, the role of organic additives in the electrochemical process and corresponding reaction mechanisms are still little understood. Further, the effect of different experimental conditions on the growth of nanocrystalline aluminium should also be investigated in detail. To promote the industrial preparation and application of nanocrystalline aluminium, further research needs to be conducted on this novel technology.

In this work, the Lewis acidic 1-ethyl-3-methylimidazolium chloroaluminate ionic liquid ([Emim][Al_2Cl_7]) was used as a low-temperature electrolyte in the deposition of aluminium. The effect of niacinamide on the nucleation mechanism and growth process of aluminium has been analysed in detail by electrochemical measurements and computational calculations. On this basis, nanocrystalline aluminium was obtained with niacinamide as an efficient additive from [Emim][Al_2Cl_7] at a wide range of temperatures, current densities and molar concentrations. Finally, the optimal experimental conditions for nanocrystalline aluminium preparation was determined.

2. EXPERIMENTAL SECTION

2.1. Chemicals

Ionic liquids 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][NTf_2]) were obtained commercially from Tokyo Chemical Industry Co., Ltd. All the other chemicals, including acetone, absolute alcohol, acetonitrile, anhydrous aluminium chloride, silver nitrate, hydrochloric acid and sulfuric acid were purchased as analytic grade from Sinopharm Chemical Reagent Co., Ltd. The mass fraction purity of these reagents was higher than 0.99. Before use, [Emim]Cl, [Bmim][NTf_2] and niacinamide were dried under vacuum (DZF-6020, Jinghong, China) at 353.2 K for 24 h. Acetone, absolute alcohol and acetonitrile were purified by distillation. Anhydrous aluminium chloride, silver nitrate and inorganic acids were directly used without further purification.

2.2. Synthesis of [Emim][Al_2Cl_7]

All the subsequent synthesis and purification processes were conducted in an argon-filled glove box (Universal, Mikrouna, China), where the mass contents of oxygen and water were controlled below 1 mg/kg. Initially, 1 mole of [Emim]Cl was mixed with 2 moles of anhydrous aluminium chloride at room temperature. After the mixture changed into a transparent solution, the resulting liquid was filtrated through glass frit. Then, the final product was purified by potentiostatic electrolysis at 353.2 K and −1 V for 3 h in an electrochemical workstation (CHI660E, Chenhua, China).

2.3. Characterization of [Emim][Al_2Cl_7]

The chemical composition and structure of [Emim][Al_2Cl_7] were characterized by nuclear magnetic resonance (NMR) spectroscopy, elemental analysis and water content analysis. The NMR spectra were collected on a spectrometer (AV-400 MHz, Bruker, Switzerland) with acetone-d_6 as an external standard at 298 K. An elemental analyser (Vario El cube, Elementar, Germany) was applied in the determination of the chemical composition. The water content of the ionic liquid has been calculated by Karl Fisher titration (751 GPD Titrino, Metrohm, Switzerland). The results of these data are listed as follows [19]. ^{1}H NMR: $\delta\times10^6$ = 8.077 (s, 1H), 7.158 (d, 1H), 7.118 (d, 1H), 4.032 (m, 2H), 3.726 (s, 3H) and 1.351 (t, 3H). ^{27}Al NMR: $\delta\times10^6$ = 103.386. Elemental analysis: C (17.39 wt%), N (6.73 wt%), H (2.64 wt%) and Cl (59.89 wt%). All of these experimental results confirmed the molecular structure and chemical composition of [Emim][Al_2Cl_7]. As determined by Karl Fisher titration, the corresponding water content was less than 50 mg/kg. It could be inferred that the mass fraction purity of [Emim][Al_2Cl_7] was higher than 0.998.

2.4. Characterization of Aluminium Deposits

The surface morphology of aluminium deposits was measured by a field-emission scanning electron microscope (SEM) (JSM-6700F, JEOL, Japan) at room temperature. The chemical composition of aluminium was confirmed by energy dispersive X-ray (EDAX) (XL30 S-FEG, FEI, USA) and inductively coupled plasma mass spectrometry (ICP-MS) (ICAP-Qc, Thermo Fisher Scientific, USA). According to these measurements, the mass fraction purity of aluminium samples was higher than 0.995.

2.5. Electrochemical Experiments

All of the electrochemical experiments were carried out in the argon-filled glove box as mentioned above. A three-electrode electrolytic cell, controlled by an electrochemical workstation, was used in the electrochemical measurements. The electrolytic cell was heated by a magnetic stirrer with ±0.5 K accuracy of experimental temperature (RET basic, IKA, Germany). The working electrode and counter electrode were a platinum plate (Pt254, Ida, China) and a platinum disc (Pt160, Ida, China), respectively. A non-aqueous Ag^+/Ag electrode (CHI112, Chenhua, China) was employed as the reference electrode, which contained 0.01 mol/kg solution of silver nitrate in [Bmim][NTf_2]/acetonitrile (313.2 K). Before use, all the electrodes were polished with emery paper, rinsed in dilute hydrochloric/sulfuric acid mixture, cleaned with absolute alcohol and dried. The cyclic voltammetry measurements were performed at 313.2 K and 100 mV/s scan rates in the cathodic potential region. Then, the impedance experiments were carried out at 313.2 K over a frequency range of $1-5\times10^4$ Hz. The electrodeposition of aluminium was conducted by a galvanostatic electrolysis method at 313.2−353.2 K and 3−9 mA/cm^2 for 0.5 h. The molar concentration of niacinamide in [Emim][Al_2Cl_7] was 4−16 mmol/kg. Finally, the resulting aluminium deposits were washed by absolute alcohol and acetone and dried in an argon-filled atmosphere.

2.6. Computational Methods

All the computational calculations for the molecular structure and properties of [Emim][Al_2Cl_7] and niacinamide were performed with Gaussian 09 software, which is based on the density functional theory (DFT). The optimized structure and geometries of all the studied molecules have been obtained through the Becke-three-parameter-Lee-Yang-Parr (B3LYP) with 6-31++G(d,p) basis set. Each optimized molecular structure was checked with minimum energy at the corresponding level. Basis set superposition errors have been considered in the calculations of interaction energy by the counterpoise method [19].

3. RESULTS AND DISCUSSION

3.1. Results of Electrochemical Measurements

3.1.1. Cyclic Voltammetry

To investigate the effect of niacinamide on aluminium electrodeposition in [Emim][Al_2Cl_7], cyclic voltammetry measurements were first performed under different experimental conditions. The potential scan was applied in cathodic potential region from the reduction of aluminium to the subsequent oxidation process.

As Figure 1 illustrates, a couple of peaks can be seen in all the cyclic voltammograms. The peaks obtained around −1.3 V reflect the reduction of Al(III) on the working electrode (see Equation 1). On the other hand, the peaks near 0 V indicate the following oxidation of aluminium deposits (see Equation 2) [20,21]. As the molar concentration of niacinamide increases, the onset potential V_{Re} of aluminium reduction becomes more negative. In this case, the absolute values of reduction and oxidation peak current also decrease. This reveals that the addition of niacinamide hinders the reduction and electrodeposition of aluminium on the electrode, resulting in lower reduction current at the same potential [22,23]. This phenomenon is probably attributed to the greater attractive interaction between niacinamide and the electrode, which results from the high electrochemical activity of niacinamide. In such a case, the presence of niacinamide may help to promote the electrodeposition of nanocrystalline aluminium in [Emim][Al_2Cl_7] according to the literature survey and our previous work [24,25].

$$4[\mathrm{Al_2Cl_7}]^- + 3e^- \rightarrow \mathrm{Al} + 7[\mathrm{AlCl_4}]^- \qquad (1)$$

$$7[\mathrm{AlCl_4}]^- + \mathrm{Al} \rightarrow 4[\mathrm{Al_2Cl_7}]^- + 3e^- \qquad (2)$$

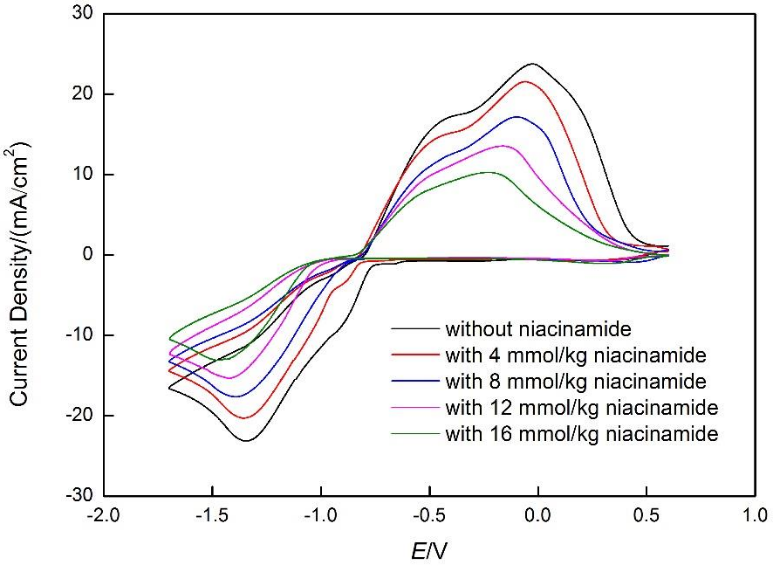


Figure 1. Cyclic voltammograms obtained on the platinum electrode in [Emim][Al_2Cl_7] with different molar concentrations of niacinamide at 313.2 K (cathodic potential regime). The potential scan rate was 100 mV/s.

It should be noted that temperature has a significant effect on the electrodeposition process. As shown in Figure 2, all the cyclic voltammograms obtained at different temperatures are similar in shape, involving the reduction and oxidation processes of aluminium. The onset potential and current density of aluminium deposition increase when the experimental temperature rises. As is well known, the electrodeposition of aluminium from chloroaluminate ionic liquids is significantly influenced by the electron transfer and mass diffusion [26]. It can be concluded that a higher temperature enhances the electrical conductivity and mass diffusion in ionic liquids, which facilitates the reduction of Al(III) and promotes the electrodeposition of bulk aluminium [26,27]. Consequently, more aluminium crystals have been obtained at the same experimental potential and time. As a result, the subsequent oxidation peak current of aluminium also increases.

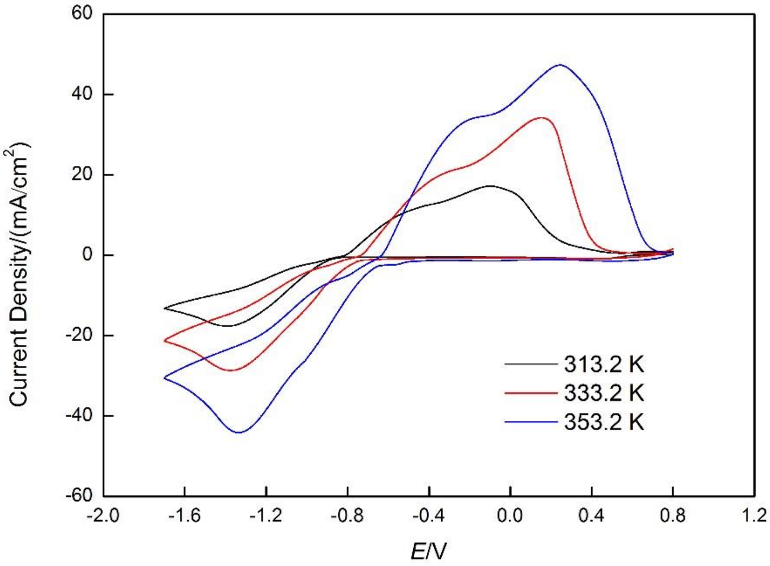


Figure 2. Cyclic voltammograms obtained on the platinum electrode in [Emim][Al_2Cl_7] with 8 mmol/kg of niacinamide at different temperatures (cathodic potential regime). The potential scan rate was 100 mV/s.

3.1.2. Differential Capacitance

According to the results of cyclic voltammograms, it is obvious that niacinamide has a stronger attractive interaction with the electrode, which is critical to the electrodeposition process and surface morphology of resulting aluminium. Apart from the cyclic voltammograms, it should also be pointed out that the corresponding electrical double layer formed on the electrode is usually considered as another fundamental issue and cannot be neglected in the electrodeposition of aluminium. The classical method of evaluating the double layer mainly involves impedance measurements at different potentials [28-30]. Consequently, impedance measurements were conducted to gain deeper insight into the influence of niacinamide on the electrical double layer at the ionic liquid/electrode interface and electrodeposition process.

The values of the differential capacitance C_d and potential of zero charge (PZC) were calculated from the experimental impedance data as described in our previous paper and the literature

[25,28,29]. As Figure 3 and Equation 3 illustrate, Z'' and f denote the imaginary part of the impedance and experimental frequency, respectively. It shows that the C_d of the electrical double layer formed at the ionic liquid/electrode interface is enhanced when the molar concentration of niacinamide increases in the range of 0−16 mmol/kg (see Table 1). This trend indicates that the structure and composition of the electrical double layer have been changed after the addition of niacinamide, which probably results from the specific interaction between niacinamide and the electrode [30]. On the other hand, the values of V_{Re} and PZC both decrease with increasing concentration of niacinamide. It can be concluded that the ions are prone to being adsorbed onto the surface of the electrode when aluminium is more easily reduced and electrodeposited at the same experimental conditions.

$$C_d = -\frac{1}{2\pi f Z''} \qquad (3)$$

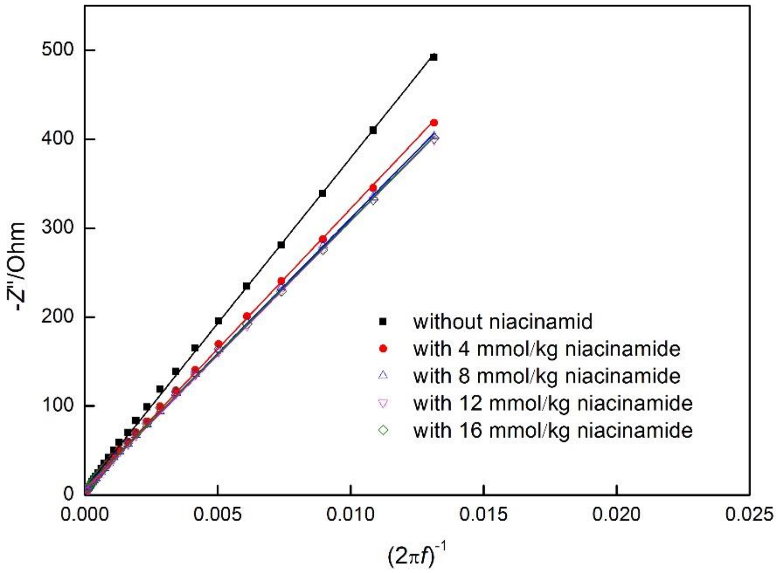


Figure 3. Nyquist plots for [Emim][Al_2Cl_7] with different molar concentrations of niacinamide on the platinum electrode at PZC and 313.2 K.

Table 1. Parameters of the electrical double layer formed on the platinum electrode in [Emim][Al_2Cl_7] with different molar concentrations of niacinamide at 313.2 K.

c/(mmol/kg)[a]	V_{Re}/V	PZC/V	C_d/(μF/cm^2)[b]
0	−0.75	~0.60	26.85
4	−0.82	~0.55	31.68
8	−0.88	~0.50	32.89
12	−0.93	~0.50	33.14
16	−0.96	~0.50	33.21

[a] molar concentration of niacinamide

[b] calculated from the experimental impedance data at PZC

To make further exploration of the deposition process, the molecular structure of ionic liquid and niacinamide has been studied by theoretical simulation. Based on the computational calculations, the dipole moments of the $[Emim]^+$ cation and niacinamide are 1.6659 and 5.5569 D, respectively. This reflects that the molecule of niacinamide is much more polarized, which is probably attributed to the non-uniform distributions of positive and negative charges on niacinamide (see Figure 4). Therefore, it can be inferred that niacinamide is more prone to interacting with the electrode and being absorbed onto the surface at the same experimental conditions. The strong electrostatic interaction between niacinamide and the electrode is confirmed as a major factor in the change in differential capacitance [31]. As calculated by computational methods, the average diameters of the $[Emim]^+$ cation and niacinamide are about 4.44 and 4.15 Å, respectively. This means that niacinamide has smaller molecular size than $[Emim]^+$, and the thickness of electrical double layer formed between niacinamide and electrode is smaller. Considering the above experimental results, it is appropriate to state that the smaller molecular volume and stronger absorption of niacinamide at the electrode make the structure of the electrical double layer denser and more compact [32]. Accordingly, the value of C_d increases as the molar concentration of niacinamide increases.

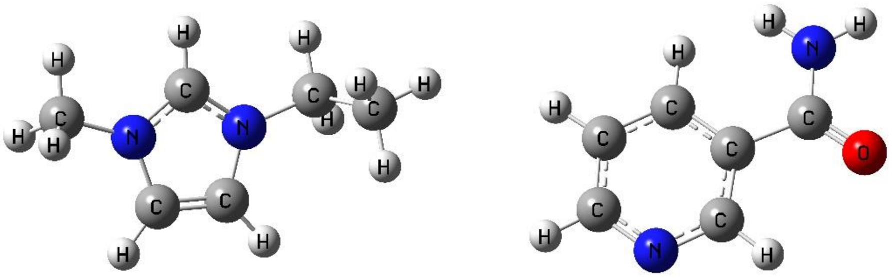
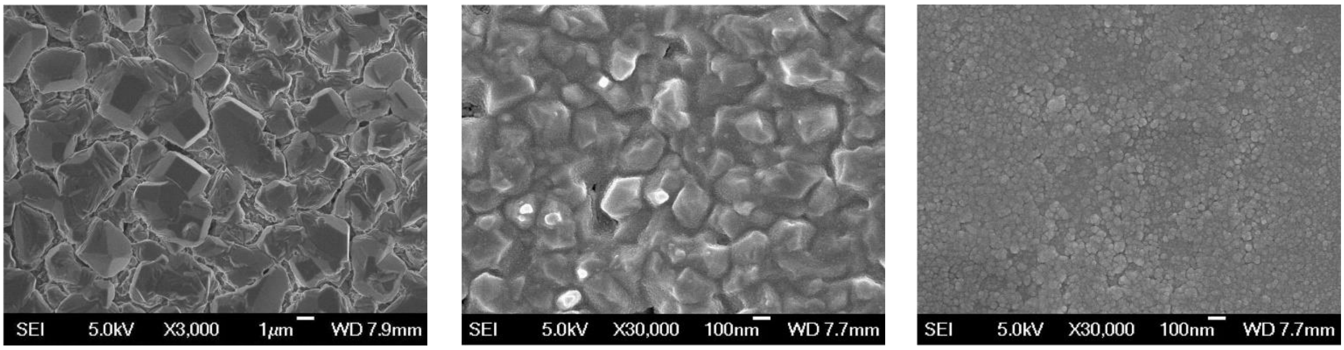


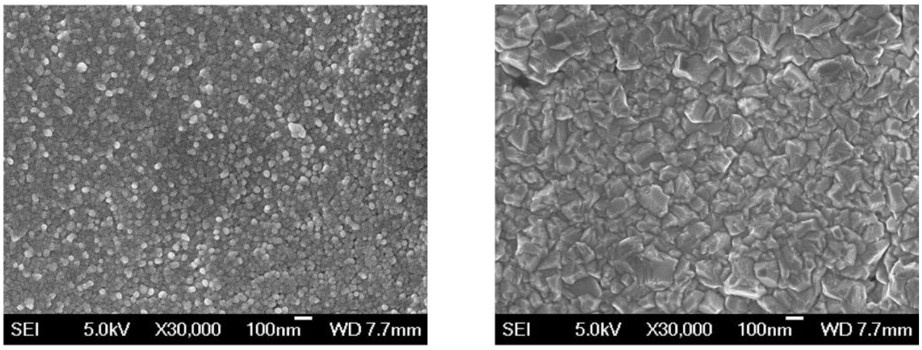
Figure 4. The optimized structure of the $[Emim]^+$ cation and niacinamide obtained by the DFT method.

3.2. Surface Morphology of Aluminium Deposits

On the basis of electrochemical measurements and computational calculations, aluminium was electrodeposited by electrolysis from $[Emim][Al_2Cl_7]$ under different experimental conditions. The influence of temperature, current density and molar concentration of niacinamide on the surface morphology and crystal size of aluminium deposits was analysed, in order to get the optimal experimental conditions and more information on the electrodeposition of nanocrystalline aluminium.



(a) without niacinamide (b) with 4 mmol/kg niacinamide (c) with 8 mmol/kg niacinamide



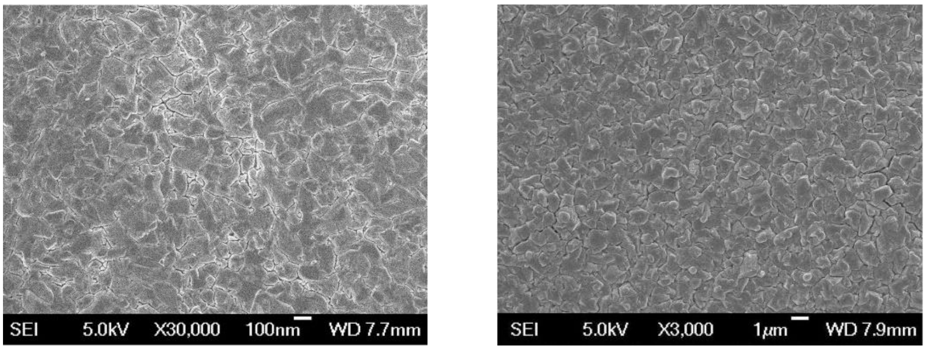
(d) with 12 mmol/kg niacinamide (e) with 16 mmol/kg niacinamide

Figure 5. SEM graphs of aluminium crystals electrodeposited from [Emim][Al_2Cl_7] with different molar concentration of niacinamide at 313.2 K and 6 mA/cm^2.

The SEM measurement results demonstrate the significant role of niacinamide in aluminium electrodeposition. As Figure 5 shows, aluminium deposits are obtained with a grain size above 1 μm from [Emim][Al_2Cl_7] at 313.2 K and 6 mA/cm^2. The average grain size of aluminium deposits decreases appreciably as the molar concentration of niacinamide increases in [Emim][Al_2Cl_7]. Nanocrystalline aluminium has been electrodeposited with molar concentrations of niacinamide between 4 and 16 mmol/kg. The minimum grain size of aluminium deposits could attain 20−30 nm when [Emim][Al_2Cl_7] contained 8−12 mmol/kg niacinamide. However, the crystal size was found to increase with the molar concentration of niacinamide increasing over 12 mmol/kg. This trend reflects that aluminium has experienced a complicated growth process after the molar concentration of niacinamide increased.

It is evident that the addition of niacinamide has changed the electrodeposition and crystal growth of aluminium in [Emim][Al_2Cl_7]. Based on the above experimental results and analysis, niacinamide is more electroactive than [Emim]$^+$ cation owing to its particular structure, followed by the higher attractive interaction with the electrode. Therefore, niacinamide is prone to being adsorbed onto the surface of the electrode and growing nuclei, which prevents the further growth of aluminium crystals [23,33]. Thus, the aluminium deposits obtained are generally fine-grained with niacinamide as an additive. As the molar concentration of niacinamide increases in the range of 0−12 mmol/kg, the decrease in the average grain size of crystals is probably ascribed to the enhanced adsorption of niacinamide on the surface of the aluminium nuclei. Nevertheless, niacinamide might reach saturation at the electrode interface with molar concentrations higher than 12 mmol/kg, resulting in the overpotential deposition of aluminium and lower nucleation density [34]. In such a case, the subsequent excessive overlapping growth of deposits leads to larger aluminium crystals. As Figure 5e shows, the average grain size of aluminium increases to 100−200 nm at 313.2 K with 16 mmol/kg niaciamide in [Emim][Al_2Cl_7]. Consequently, the optimal molar concentration of niacinamide for the preparation of nanocrystalline aluminium is 8−12 mmol/kg. Compared to some previous reports, the deposits obtained in this work are more bright, compact and uniform with the addition of niacinamide [27,35].

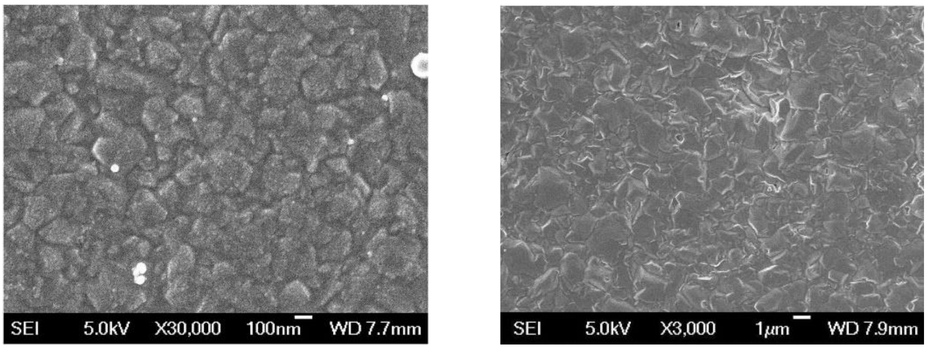
The SEM graphs of deposits show that experimental temperature also has significant influence on the preparation of nanocrystalline aluminium. According to Figures 6 and 5c, the crystal size of aluminium deposits increases substantially when the electrodeposition temperature rises from 313.2 to 353.2 K. For example, the average grain size of aluminium crystals reaches approximately 200 nm and 1 μm at 333.2 K and 353.2 K, respectively. According to the results of cyclic voltammograms, aluminium is prone to being electrodeposited at higher temperatures. In view of the three-dimensional nucleation/growth process, it can be stated that the increasing temperature leads to a higher mass diffusion and electron transfer on the electrode [25,35]. In such a case, the reduction and subsequent electrodeposition process of aluminium is accelerated with the increasing of temperature. As a result, larger and rough aluminium crystals have been obtained due to the higher growth rate of aluminium. Therefore, nanocrystalline aluminium is easier to prepare at the experimental temperature lower than 333.2 K.



(a) 333.2 K (b) 353.2 K

Figure 6. SEM graphs of aluminium crystals electrodeposited from [Emim][Al_2Cl_7] with 8 mmol/kg niacinamide at 6 mA/cm^2 and different temperatures.

As Figure 7 shows, nanocrystalline aluminium with an average grain size of 100−200 nm can be electrodeposited from [Emim][Al_2Cl_7] with 8 mmol/kg niacinamide at 3 mA/cm^2 and 313.2 K. When the current density increases to 6 mA/cm^2, the average crystal size reaches the minimum value of 20−30 nm. However, micrometre-sized aluminium particles are obtained as the current density increases to 9 mA/cm^2. It is obvious that current density plays an important role in the morphology of aluminium deposits. Considering the instantaneous nucleation process of aluminium in ionic liquid, all the nuclei are generated at the beginning of the electrodeposition [34]. It can be inferred that the density of the aluminium nuclei is enhanced with current density rising from 3 to 6 mA/cm^2, which facilitates the smooth and uniform growth of crystals [12,27]. As a result, compact and bright nanocrystalline aluminium deposits have been obtained. After the density of nuclei exceeds the maximum, the excessive overlapping growth of aluminium generates larger crystals [35,36]. Subsequently, the average grain size of aluminium is generally over 1 μm when the current density is higher than 6 mA/cm^2 at the experimental conditions. Therefore, choosing the appropriate experimental temperature, current density and molar concentration of niacinamide is very important to the preparation of nanocrystalline aluminium.



(a) 3 mA/cm^2 (b) 9 mA/cm^2

Figure 7. SEM graphs of aluminium crystals electrodeposited from [Emim][Al_2Cl_7] with 8 mmol/kg niacinamide at 313.2 K and different current densities.

In conclusion, the molar concentration of niacinamide, temperature and current density have been confirmed as key experimental parameters in the electrodeposition of aluminium. Nanocrystalline aluminium can be obtained at 313.2−333.2 K and 3−6 mA/cm^2 from [Emim][Al_2Cl_7] with 8−12 mmol/kg niacinamide. The minimum average grain size of 20−30 nm was achieved at 313.2 K and 6 mA/cm^2 when the molar concentration of niacinamide was in the range of 8−12 mmol/kg. The results of surface morphology characterization are consistent with those of electrochemical measurements as mentioned above. Therefore, this work not only confirms niacinamide as an effective additive in the low-temperature electrodeposition of nanocrystalline aluminium from chloroaluminate ionic liquid, but also sheds light on the nucleation mechanism and growth process of nanocrystalline aluminium.

4. CONCLUSIONS

In this paper, we have shown that niacinamide could be used as an effective additive in the electrodeposition of nanocrystalline aluminium from chloroaluminate ionic liquid [Emim][Al_2Cl_7]. According to the systematic electrochemical measurements and computational calculations, it was found that niacinamide was highly electroactive and polarized, which is probably attributed to the non-uniform distributions of positive and negative charges on niacinamide. Therefore, niacinamide was more prone to interact with the electrode than [Emim]$^+$ cation under the same experimental conditions. The smaller molecular volume and stronger absorption of niacinamide at the ionic liquid/electrode interface rendered the structure of the electrical double layer denser and more compact. The subsequent extensive absorption of niacinamide on the surface of aluminium nuclei hindered the further growth of crystals. As a result, nanocrystalline aluminium was obtained at 313.2−333.2 K and 3−6 mA/cm^2 from [Emim][Al_2Cl_7], which contained 8−12 mmol/kg niacinamide. Smooth and bright aluminium crystals with a minimum average grain size of 20−30 nm have been electrodeposited at 313.2 K and 6 mA/cm^2 with 8−12 mmol/kg niacinamide. The molar concentration of niacinamide, experimental temperature and current density were confirmed as the major influencing factors in the preparation of nanocrystalline aluminium. It is expected that the results of this work could help to gain more insight into the electrodeposition mechanism and preparation process of nanocrystalline aluminium.

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