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Ionic liquid electrolytes composed of AlCl₃ and primary/secondary alkylamine hydrochlorides with varying alkyl chain lengths for Al electrodeposition

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Keywords: Chloroaluminate ionic liquid Al electrodeposition Alkylamine hydrochloride Alkylammonium chloride	The electrodeposition of Al is essential for applications such as electroplating, electrorefining, and rechargeable Al batteries. However, the standard electrolyte currently used for Al electrodeposition, viz., 1-ethyl-3-methylimi- dazolium chloride–AlCl ₃ ionic liquid, is prohibitively expensive for widespread industrial application. This study explored alternative ionic liquid electrolytes composed of AlCl ₃ and primary or secondary alkylamine hydro- chlorides (RNH ₃ Cl and R ₂ NH ₂ Cl) with varying alkyl chain lengths (R = methyl (Me), ethyl (Et), <i>n</i> -propyl (<i>n</i> -Pr), <i>n</i> -butyl (<i>n</i> -Bu)) for Al electrodeposition. The phase states of a series of mixtures of alkylamine hydrochlorides and AlCl ₃ at different molar ratios were examined to identify the conditions required for forming a single liquid phase. Notably, a single liquid phase was obtained at room temperature (30°C) for <i>n</i> -PrNH ₃ Cl–AlCl ₃ , <i>n</i> - BuNH ₃ Cl–AlCl ₃ , and <i>n</i> -Bu ₂ NH ₂ Cl–AlCl ₃ ionic liquids. These ionic liquids exhibit conductivities of approximately 10 mS cm ⁻¹ at 30 °C. Galvanostatic electrodeposition studies using these electrolytes confirmed that Al elec- trodeposition occurs with current efficiencies exceeding 90 % at current densities of 5–12 mA cm ⁻² . This study demonstrates that alkylamine hydrochloride–AlCl ₃ ionic liquids with an appropriate alkyl chain length of the amine can serve as promising low-cost electrolytes for Al electrodeposition.			

1. Introduction

Aluminum (Al) electrodeposition is a critical process in various technologies, including Al electroplating [1], electrorefining [2], and as a reaction at the negative electrode in rechargeable aluminum batteries [3,4]. Owing to the significantly lower standard electrode potential of Al compared to that of hydrogen evolution, the electrodeposition of Al in aqueous electrolytes faces substantial challenges. As a result, nonaqueous electrolytes have been adopted for Al electrodeposition.

Numerous electrolytes capable of enabling Al electrodeposition near room temperature have been developed. The chemistry and classification of these electrolytes have been comprehensively reviewed in the literature [4,5]. Among these, chloroaluminate ionic liquids, created by mixing AlCl₃ with organic chlorides, have garnered the most attention. Specifically, chloroaluminate ionic liquids using 1-ethyl-3-methylimidazolium chloride (EMIC) as the cation source (EMIC–AlCl₃) have been extensively studied [6] owing to their high ionic conductivity, low viscosity, and minimal reactivity of the imidazolium cation. Despite these advantages, the high cost and limited scalability of EMIC hinder its economic feasibility for industrial applications.

To address these limitations, researchers have explored alternative electrolytes, including ionic-liquid analogs [7-12]. These analogs are derived by mixing AlCl₃ with polar organic solvents or non-ionizing organic compounds, such as urea [13–16] and acetamide [17–19]). Although electrolytes based on these organic compounds are more affordable than EMIC–AlCl₃, they typically suffer from higher viscosities and significantly lower ionic conductivities, which lead to reduced Al electrodeposition rates.

Within the scope of ionic liquids, various cost-effective organic chlorides and hydrochlorides have been proposed as substitutes for the expensive EMIC. Examples include guanidinium hydrochloride [13,20], acetamidine hydrochloride [13,21], and alkylamine hydrochlorides [3, 22–25]. In particular, tertiary alkylamine hydrochlorides (R₃NHCl)-based electrolytes, such as trimethylamine hydrochloride (Me₃NHCl)-AlCl₃ [3,23,24] and triethylamine hydrochloride (Et₃NHCl)-AlCl₃ [3,23,25], exhibit relatively high ionic conductivities at room temperature, making them strong candidates for further exploration. However, unpleasant odor of tertiary alkylamine

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hydrochlorides presents a challenge for practical applications.

To address this issue, our group has focused on primary and secondary alkylamine hydrochlorides (RNH₃Cl and R₂NH₂Cl), which are nearly odorless. In contrast to EMIC, alkylamine hydrochlorides can be synthesized through simple and scalable processes using either synthetic precursors or natural fats and oils [26]. This makes them suitable for large-scale production and cost-effective. Pricing information for these compounds in Japan is provided in the Supporting Information. Additionally, safety data sheets (SDSs) suggest that these compounds have low hazards and toxicity, suggesting minimal risks when handled under standard conditions. In our previous study [27], we demonstrated that a ternary mixture of ethylamine hydrochloride (EtNH₃Cl), dimethylamine hydrochloride (Me₂NH₂Cl), and AlCl₃ (i.e., EtNH₃Cl-Me₂NH₂Cl-AlCl₃) can serve as a room-temperature ionic liquid electrolyte with conductivity comparable to that of R₃NHCl-AlCl₃. The EtNH₃Cl-Me₂NH₂Cl-AlCl₃ ionic liquid not only supports Al electrodeposition, but also functions effectively as an electrolyte for Al-ion batteries.

The physicochemical properties of ionic liquids can often be tailored by varying the alkyl chain lengths of their organic components [28,29]. However, this strategy has yet to be explored for alkylamine hydrochloride-based ionic liquids. In this study, we investigated the properties of ionic liquids derived from a range of primary and secondary alkylamine hydrochlorides (RNH₃Cl and R₂NH₂Cl, with R = methyl (Me), ethyl (Et), n-propyl (n-Pr), or n-butyl (n-Bu)) to identify promising low-cost alternatives to the currently used high-cost electrolytes. Specifically, we mixed each amine hydrochloride with AlCl₃ at different molar ratios to determine the conditions under which a single liquid phase forms. Electrolytes that exhibited a homogeneous liquid phase at room temperature were further examined for their conductivity and performance in Al electrodeposition. Additionally, the cathodic decomposition rates of the alkylammonium cations were assessed, as they could significantly influence the current efficiency of Al electrodeposition. The findings suggest that selecting alkylamines with appropriate alkyl chain lengths enables the development of low-cost alkylamine hydrochloride-AlCl3 ionic liquids as promising electrolytes for Al electrodeposition, fostering advancements in applications reliant on Al electrodeposition.

2. Experimental

2.1. Electrolytes

All alkylamine hydrochlorides, EMIC, and anhydrous AlCl₃ were purchased from Tokyo Chemical Industry Co., Ltd. Before use, the alkylamine hydrochlorides and EMIC were dried under vacuum at 80 °C for more than 72 h, while anhydrous AlCl₃ was purified by sublimation. All experiments involving the dried alkylamine hydrochlorides and purified anhydrous AlCl₃ were conducted in an argon-filled glove box (Miwa Manufacturing, DB0-1KH-HMK). The ionic liquid electrolytes were prepared by gradually mixing AlCl₃ with alkylamine hydrochloride at specified molar ratios. After being mixed, the liquids were stirred at 80 °C for more than 5 h to ensure homogeneity.

2.2. Electrochemical measurements

A typical three-electrode cell was used for electrochemical measurements. The current and voltage were controlled and measured using an electrochemical measurement system (Hokuto Denko, HZ-pro). A 25 mL cylindrical glass vessel (BAS) was used as the electrolysis cell, and approximately 15 mL of the electrolyte was used.

Cyclic voltammetry (CV) on electrolytes with an AlCl₃ molar ratio greater than 1 with respect to the organic amine component was conducted using a Pt disk electrode (BAS, φ 3 mm) as the working electrode, an Al plate (Nilaco, 99.99 %, 1.0 mm thickness) as the counter electrode, and an Al wire (Nilaco, 99.99 %, φ 1.0 mm) that was directly immersed

in the electrolyte as the reference electrode. The potential sweep rate was 10 mV $s^{\text{-1}}.$

In the linear sweep voltammetry (LSV) conducted on electrolytes with an AlCl₃ molar ratio below 1, an Al wire immersed in an EMIC–AlCl₃ ionic liquid with an EMIC:AlCl₃ molar ratio of 1:1.5 was used as the reference electrode. The electrolyte being evaluated was separated from the electrolyte in the reference electrode using an ionpermeable glass frit (BAS, sample holder: 6 mm φ). A Pt disk electrode and an Al plate were used as the working and counter electrodes, respectively.

Galvanostatic electrodeposition was performed using a Cu plate as the cathode. Before use, the Cu substrate was ultrasonically cleaned in acetone and ethanol for 10 min each and then covered with polytetra-fluoroethylene (PTFE) tape (Chukoh Chemical Industries, ASF-110FR), exposing a 5 mm × 5 mm area for electrodeposition. Preliminary electrolysis was performed at 5 mA cm⁻² for 4800 s, after which the substrate was replaced with a fresh one for the main electrodeposition experiment. During electrodeposition, the electrolyte was magnetically stirred at 500 rpm using a hot stirrer and magnetic stir bar (ASONE, 7 mm × 20 mm). After electrodeposition, the Al deposits were washed with ethanol and distilled water.

2.3. Characterization

The ionic conductivity of the electrolyte was measured using a conductivity meter (DKK-TOA CM-41X). The surface morphology of the deposits was observed using a scanning electron microscopy (SEM; JEOL, JSM-6510LV). The compositions of the deposits were analyzed via energy-dispersive X-ray spectrometry (EDX; OXFORD INSTRUMENTS, INCAx-act) using the EDX instrument attached to the SEM instrument. The X-ray diffraction (XRD) analysis of the deposits was performed using an X-ray diffractometer (PANalytical X'Pert Pro-MPD PW3040/60) equipped with a Cu-Ka radiation source (tube voltage: 45 kV, current: 40 mA), and XRD measurements were conducted using the parallel beam method. The current efficiency of Al electrodeposition was calculated as follows: the entire Al deposit was dissolved in approximately 10 mL of hydrochloric acid (Wako Pure Chemical Industries, 35.0-37.0 %), and the Al-containing solution was then diluted with distilled water to 100 mL volume. The concentration of Al in the diluted solution was measured using inductively coupled plasma optical emission spectroscopy (ICP-AES; SII Nanotechnology, SPS7800) to determine the amount of electrodeposited Al. The current efficiency was calculated as the ratio of the measured quantity of electrodeposited Al to the theoretical amount of electrodeposited Al, which was calculated from the amount of electricity that passed through the set-up.

3. Results and discussion

3.1. Physical states of alkylamine hydrochloride /AlCl₃ mixtures

Each alkylamine hydrochloride (RNH₃Cl or R₂NH₂Cl) was mixed with AlCl₃ at different molar ratios (alkylamine hydrochloride:AlCl₃ = 1:*r*, where r = 1-2), and the compositions and temperature ranges over which the mixtures formed a single liquid phase were examined. Fig. 1 illustrates the states of the alkylamine hydrochloride/AlCl₃ mixtures, as observed visually after they were heated to 80 °C to form homogeneous liquids and then cooled to and maintained at specified temperatures. The states of the samples near the phase transition temperatures were observed and determined after maintaining them at the specified temperatures for more than 5 h.

When the primary amine hydrochloride (RNH₃Cl) with R = methyl was mixed with AlCl₃ (Fig. 1a), no liquid phase was observed at temperatures below 60 °C across the entire composition range. In contrast, when R was changed to ethyl (Fig. 1b), a single liquid phase was observed at 60 °C for r = 1.5 and 1.6. At these AlCl₃ molar ratios, as the temperature of the EtNH₃Cl/AlCl₃ mixture was decreased from 80 °C, a



Fig. 1. Physical states of the mixtures of AlCl₃ with (a) MeNH₃Cl, (b) EtNH₃Cl, (c) *n*-PrNH₃Cl, (d) *n*-BuNH₃Cl, (e) Me₂NH₂Cl, (f) Et₂NH₂Cl, (g) *n*-Pr₂NH₂Cl, and (h) *n*-Bu₂NH₂Cl at different molar ratios (*r*) of AlCl₃ with respect to the alkyl amine hydrochloride and different temperatures. Blue circles indicate the single liquid phase, while gray squares and red triangles indicate the solid phase and solid–liquid dual phase, respectively.

white precipitate appeared between 55 and 40 °C, and a single solid phase was observed below 40 °C. At both higher and lower concentrations of AlCl₃, the temperature at which the liquid phase formed was higher. For R = *n*-propyl (Fig. 1c), a single liquid phase was obtained at 30 °C over a broad composition range $(1.1 \le r \le 1.7)$. Additionally, for *r* values between 1.4 and 1.6, the single liquid phase was maintained even when the temperature was decreased to 15 °C. For other compositions, a white precipitate appeared at lower temperatures. For R = *n*-butyl (Fig. 1d), the composition and temperature ranges over which a single liquid phase was formed were narrower than those for the *n*-propyl case. At 30 °C, a homogeneous liquid phase was observed only at *r* = 1.7 for the *n*-butyl case.

For secondary amine hydrochlorides, when R = methyl (Fig. 1e), a single liquid phase was observed at 60 °C for $1.5 \le r \le 2$. As the temperature was decreased further, a solid began to precipitate, and only the sample with r = 1.9 maintained a single liquid phase down to 40°C. Similarly, for R = ethyl (Fig. 1f), a single liquid phase was observed at 60 °C for $1.5 \le r \le 2$. However, for all compositions, the single liquid phase was maintained only at temperatures above 50 °C, with solid precipitation occurring below 45 °C. For R = n-propyl (Fig. 1g), the composition range over which a single liquid phase was formed at 60 °C shifted slightly toward higher r values ($1.6 \le r \le 2$) compared with those for methyl and ethyl cases. For r = 1.8, the single liquid phase persisted down to 35 °C. In contrast, for R = n-butyl (Fig. 1h), a homogeneous liquid phase was observed over a wide composition range ($1.1 \le r \le 2$) at 60 °C. Moreover, in the range of $1.4 \le r \le 1.9$, the homogeneous liquid phase was maintained even at temperatures as low as 15 °C.

Fig. 2 shows the dependence of the melting points of pure alkylamine hydrochlorides reported in the literature [30-34] and the minimum liquidus temperatures of their mixtures with AlCl₃ on the number of carbon atoms in the alkylamine hydrochloride. The minimum liquidus temperature is the lowest temperature at which a single liquid phase is observed for the system. Excluding MeNH₃Cl, the melting points of the pure alkylamine hydrochlorides increase with increasing number of carbon atoms within the same class (primary or secondary amine hydrochloride). Between the primary and secondary amine hydrochlorides with the same number of carbon atoms, the secondary amine hydrochlorides tend to have higher melting points. In ionic crystals, an increase in the ionic radius tends to lower the melting point, because the Coulombic forces between the ions decrease. However, a longer alkyl chain is expected to increase the melting point owing to the enhanced van der Waals interactions between the alkyl groups. Excluding MeNH₃Cl, the latter effect is dominant for all others, and compounds with a greater number of carbon atoms exhibit higher melting points. In the case of MeNH₃Cl, the smallest molecule, the contribution of Coulombic interactions is significant, leading to its anomalously high melting point.



Fig. 2. Melting points of pure (•) primary and (•) secondary alkylamine hydrochlorides, and the minimum liquidus temperature of the mixtures of (\circ) primary and (□) secondary alkylamine hydrochlorides with AlCl₃ vs. the number of carbon atoms in the alkylamine hydrochloride. The minimum liquidus temperatures of the *n*-PrNH₃Cl–AlCl₃ and *n*-Bu₂NH₂Cl–AlCl₃ systems are expected to be below 15 °C. No clear correlation was observed between the melting points of the pure alkylamine hydrochlorides and the minimum liquidus temperature of their mixtures with AlCl₃.

Fig. 2 shows that there is no clear correlation between the melting points of the pure amine hydrochlorides and the minimum liquidus temperatures observed for their mixtures with AlCl₃. In other words, the higher melting point of the pure amine hydrochloride does not necessarily result in a higher minimum liquidus temperature of its mixture with AlCl₃. For example, although the melting point of pure *n*-Bu₂NH₂Cl is the highest (285 °C), its mixture with AlCl₃ could maintain a single liquid phase down to 15 °C. Moreover, no simple trend was observed between the alkyl chain length or number of alkyl groups in the alkylamine hydrochlorides and the minimum liquidus temperature, implying that various factors are intricately involved in determining the melting points of the mixtures, including the Coulombic and van der Waals interactions, hydrogen bonding, and entropy gain owing to the structural complexity of the ionic molecule [29].

Based on the results, subsequent measurements were conducted on the electrolytes of *n*-PrNH₃Cl–AlCl₃ (r = 1.5), *n*-BuNH₃Cl–AlCl₃ (r = 1.7), and *n*-Bu₂NH₂Cl–AlCl₃ (r = 1.6), which formed a single liquid phase at room temperature (30 °C).

3.2. Ionic conductivity

The ionic conductivities of the *n*-PrNH₃Cl–AlCl₃, *n*-BuNH₃Cl–AlCl₃, and *n*-Bu₂NH₂Cl–AlCl₃ ionic liquid electrolytes at 30 °C are listed in Table 1, along with those of several representative chloroaluminate electrolytes. Among the three electrolytes developed in this study, *n*-Bu₂NH₂Cl–AlCl₃ exhibited a slightly lower conductivity (7.6 mS cm⁻¹) while the other two exhibited conductivities of ~10 mS cm⁻¹. This value is comparable to those reported for most chloroaluminate ionic liquids, including tertiary alkylamine hydrochloride–AlCl₃, 1-butyl-3-methylimidazolium chloride (BMIC)–AlCl₃, and guanidine or acetamidine hydrochloride–AlCl₃ with similar *r* values. EMIC–AlCl₃ is the only exception, for which 1.5 to 2.5 times higher ionic conductivities have been reported. The conductivities of alkylamine hydrochloride–AlCl₃ are significantly higher than those of other ionic liquid analogs composed of AlCl₃ and organic compounds, such as urea.

3.3. Al electrodeposition

To investigate the electrochemical behaviors of the n-PrNH₃Cl-AlCl₃, n-BuNH₃Cl-AlCl₃, and n-Bu₂NH₂Cl-AlCl₃ electrolytes, particularly the possibility of Al electrodeposition, CV was conducted at 30 °C using a Pt working electrode (Fig. 3a). In all electrolytes, when the potential was swept in the cathodic direction, a reduction current was observed at potentials more negative than 0 V. Upon reversing the potential sweep in the anodic direction, an oxidation current was observed at potentials more positive than 0 V. As described later, the occurrence of galvanostatic electrodeposition confirmed that the reduction current was due to the electrodeposition of Al. Therefore, the oxidation current can be ascribed to the dissolution of Al. The Coulombic efficiency, defined as the ratio of the charge of the oxidation current to that of the reduction current during CV, was approximately 100 % for n-PrNH₃Cl-AlCl₃ and 90 % for *n*-BuNH₃Cl-AlCl₃ and *n*-Bu₂NH₂Cl-AlCl₃, indicating that the Al deposition and dissolution processes in these electrolytes are nearly reversible. The maximum reduction current in the

Table 1

Ionic conductivities (σ) of alkylamine hydrochloride–AlCl₃ and certain other chloroaluminate ionic liquids and ionic liquid analogs with r = 1.4–1.7 at ~25 °C.

Electrolyte	R	<i>T</i> (°C)	σ (mS m ⁻²)	Refs.
n-PrNH ₃ Cl–AlCl ₃	1.5	30	10.34	This
				study
n-BuNH ₃ Cl–AlCl ₃	1.7	30	10.01	This
				study
n-Bu ₂ NH ₂ Cl–AlCl ₃	1.6	30	7.59	This
				study
Me ₃ NHCl-AlCl ₃	1.6	25	7.59	[24]
	1.7	25	7.43	[24]
Et ₃ NHCl-AlCl ₃	1.6	25	9.72	[3]
	1.7	25	9.67	[3]
EMIC-AlCl ₃	1.5	25	24.3	[35]
	1.5	25	17.9	[36]
	1.5	25	17.2	[37]
	1.6	25	15.2	[37]
	1.7	25	16.4	[37]
	1.5	30	16.0	[38]
	1.5	32	20.29	[39]
BMIC-AlCl ₃	1.6	25	9.31	[40]
	1.5	32	11.39	[39]
Guanidine hydrochloride–AlCl ₃	1.65	30	9.24	[20]
Acetamidine hydrochloride-AlCl ₃	1.5	25	7.14	[13]
Urea–AlCl ₃	1.5	25	1.06	[13]
Acetamide–AlCl ₃	1.5	40	2.6	[13]
	1.5	40	2.49	[41]
Propionamide-AlCl ₃	1.5	40	3.03	[41]
Butyramide-AlCl ₃	1.5	40	2.54	[41]
4-Ethylpyridine–AlCl ₃	1.4	25	0.91	[12]
1,3-Dimethyl-2-	1.5	40	1.7	[<mark>9</mark>]
imidazolidinone-AlCl ₂				

potential range of 0--0.5 V was approximately 12 mA cm⁻² for all three electrolytes, with no significant differences in the magnitude of the reduction current between the systems with different electrolytes.

To verify Al electrodeposition, galvanostatic electrodeposition was performed on a Cu substrate at a current density of 10 mA cm⁻² for a total charge of 24 C cm⁻². This amount of charge corresponds to that required to deposit an 8.3 µm thick Al film, assuming 100 % current efficiency. During electrodeposition, the temperature of the electrolyte was maintained at 30 °C, and the electrolyte was stirred at 500 rpm. After electrodeposition, a silvery-white deposit was obtained over the entire active area of the Cu substrate from all three electrolytes. The SEM images of the electrodeposited films are shown in Fig. 3b. Granular crystal grains with sizes of approximately 5, 3, and 2 μ m are observed for the films obtained from n-PrNH3Cl-AlCl3, n-BuNH3Cl-AlCl3, and n-Bu₂NH₂Cl-AlCl₃ electrolytes, respectively. The crystal size of the deposit decreased with increasing cation size of the electrolyte. We speculate that the cations adsorbed on the substrate surface inhibit the crystal growth of Al; the larger the cation is, the stronger the inhibitory effect is, which leads to smaller Al crystal grain sizes. The EDX profiles of all the electrodeposited films (Fig. 3c) reveal only the peak corresponding to Al, indicating that the main component of the electrodeposited films was Al. Furthermore, XRD patterns showed only the diffraction peaks of FCC Al, apart from the diffraction peaks of the Cu substrate, confirming that the electrodeposited films obtained from each electrolyte consisted of metallic Al (Fig. 3d). These analyses confirmed that Al can be electrodeposited from the alkylamine hydrochloride-AlCl₃ electrolytes.

As observed for many other organic chloride–AlCl₃ systems, when an alkylamine hydrochloride (RNH₃Cl or R₂NH₂Cl) is mixed with AlCl₃, alkylammonium cation (RNH₃⁺ or R₂NH₂⁺) and AlCl₄⁻ anion are expected to form at $r \leq 1$, while Al₂Cl₇⁻ is also expected to form in addition to these at r > 1. Near room temperature, AlCl₄⁻ does not reduce to Al, and Al electrodeposition occurs from Al₂Cl₇⁻.

3.4. Side reaction

The experiments described above demonstrate that Al electrodeposition is possible using alkylamine hydrochloride–AlCl₃ ionic liquid electrolytes. However, there is a concern that, alongside Al electrodeposition, a side reaction may occur, in which the protons of the alkylammonium cations are reduced to form H_2 , according to the following reactions:

$$2RNH_3^+ + 2e^- \rightarrow 2RNH_2 + H_2 \tag{1}$$

$$2R_2NH_2^+ + 2e^- \rightarrow 2R_2NH + H_2 \tag{2}$$

This side reaction can compete with Al electrodeposition and affect the current efficiency of the electrodeposition process. The rate and potential at which this reaction occurs are expected to vary depending on the type of the alkylammonium ion. Our previous study [27] indicated that Me₂NH⁺₂ and EtNH⁺₃ cations undergo reductive decomposition at potentials more negative than -0.3 V vs. Al/Al(III). To investigate the reactivities of *n*-PrNH₃⁺, *n*-BuNH₃⁺, and *n*-Bu₂NH₂⁺ cations, we conducted LSV on the corresponding electrolytes, that is, mixtures of these alkylammonium chlorides (i.e., alkylamine hydrochlorides) and AlCl3 at an AlCl3 molar ratio of less than 1. Considering that the mixture of the alkylammonium chloride and AlCl₃ with r < 1does not form a liquid electrolyte at room temperature, the EMIC-AlCl₃ ionic liquid was used as the solvent. The imidazolium cation derived from EMIC is known to be electrochemically inert at potentials above -2.5 V. Moreover, as Al electrodeposition does not occur in ionic liquids with AlCl₃ molar ratios below 1 (r < 1), we expected to observe currents solely due to the reduction of the alkylammonium cations in these electrolytes. The specific composition of the electrolyte used in the experiments was alkylamine hydrochloride: EMIC: $AlCl_3 = 0.3: 0.7: 0.9$ (molar ratio).

The LSV curves obtained from the electrolyte (alkylamine



Fig. 3. (a) Cyclic voltammograms of electrochemical systems with *n*-PrNH₃Cl–AlCl₃, *n*-BuNH₃Cl–AlCl₃, and *n*-Bu₂NH₂Cl–AlCl₃ electrolytes, showing distinct reduction currents corresponding to aluminum deposition. (b) SEM images illustrating the morphology of the electrodeposits, (c) EDX profiles confirming elemental composition, and (d) XRD patterns of the electrodeposits obtained by galvanostatic electrodeposition at a current density of 10 mA cm⁻² for a total charge of 24 C cm⁻² from the three ionic liquid electrolytes. These analyses collectively confirm the successful electrodeposition of Al from the alkylamine hydrochloride–AlCl₃ electrolytes."

hydrochloride: EMIC: $AlCl_3 = 0.3: 0.7: 0.9$ in molar ratio) are shown in Fig. 4a. For comparison, the results obtained for Me₂NH₂Cl and EtNH₃Cl are also presented. In the electrolytes containing Me₂NH₂Cl or EtNH₃Cl, the reduction current began to increase at a potential of -0.3 V vs. Al/Al (III), and currents exceeding 10 mA cm^{-2} were observed before the potential reached -1.0 V. In contrast, in the electrolytes containing *n*-PrNH₃Cl, n-BuNH₃Cl, or n-Bu₂NH₂Cl, the reduction current increased gradually but insignificantly as the potential decreased; in other words, no significant increase in the reduction current was observed. Even at -1.0 V, the reduction current remained at ~ 1 mA cm⁻². As mentioned above, these reduction currents are ascribed to the reduction of protons from the alkylammonium cations. The lower reactivities of the *n*-PrNH₃⁺, *n*-BuNH₃⁺, and Bu₂NH₂⁺ cations compared to those of Me₂NH₂⁺ and EtNH₃⁺ are likely due to steric hindrance caused by the longer alkyl chains, which decrease the probability of direct electron transfer from the electrode to the protons coordinated to the N atom, thus mitigating decomposition.

The current efficiencies of Al electrodeposition in the n-PrNH₃Cl-, n-

BuNH₃Cl-, and *n*-Bu₂NH₂Cl-AlCl₃ electrolytes were measured at current densities ranging from 5 to 15 mA cm⁻² (Fig. 4b). The current efficiency was calculated based on the amount of electrodeposited Al, which was determined by dissolving the deposited film in hydrochloric acid and analyzing the Al content using ICP-AES. In both the n-PrNH₃Cl-AlCl₃ and n-BuNH₃Cl-AlCl₃ electrolytes, the current efficiency exceeded 90 %, regardless of the current density. These current efficiency values exceeding 90 % were generally consistent with the Coulombic efficiency values measured during the CV (Fig. 3a). The fluctuations in the current efficiency can largely be attributed to the physical detachment of a portion of the deposited Al grains during the washing process after electrodeposition. On the other hand, in the n-Bu₂NH₂Cl-AlCl₃ electrolyte, the current efficiency was ~ 90 % up to a current density of 12 mA cm⁻², but decreased to 65 % at 15 mA cm⁻². As the electrodeposited film obtained at higher current densities was brittle, significant detachment of the film occurred, which likely resulted in lower calculated current efficiencies. In all three electrolytes, electrodeposition at a current density higher than 18 mA $\rm cm^{-2}$ resulted in black powdery



Fig. 4. (a) LSV curves for RNH₃Cl or R_2NH_2Cl in the EMIC–AlCl₃ electrolyte with a molar ratio of RNH₃Cl or R_2NH_2Cl :EMIC:AlCl₃ is 0.3:0.7:0.9. The observed reduction currents are attributed to the reduction of protons originating from the alkylammonium cations. (b) Current efficiency for Al electrodeposition and (c) cathode potential during electrodeposition in *n*-PrNH₃Cl–AlCl₃, *n*-BuNH₃Cl–AlCl₃, and *n*-Bu₂NH₂Cl-AlCl₃ electrolytes.

deposits only. The cathode potentials during the electrodeposition decreased as the current density increased (Fig. 4c); however, in all three electrolytes, the potentials were within -0.8 V, even at a current density of 15 mA cm⁻². From the cathode potential and LSV curves shown in Fig. 4a, it can be inferred that the reduction reactions of *n*-PrNH₃⁺, *n*-BuNH₃⁺, and *n*-Bu₂NH₂⁺ would also occur during Al electrodeposition. However, the fact that the current efficiency of Al electrodeposition is generally above 90 % indicates that the reaction rates of these alkylammonium cations are slower than those of Al electrodeposition.

4. Conclusions

We investigate the properties of ionic liquid electrolytes composed of AlCl₃ and primary or secondary alkylamine hydrochlorides (RNH₃Cl and R_2NH_2Cl , respectively) with varying alkyl chain lengths (R = Me, Et, *n*-Pr, and *n*-Bu). The mixtures of each alkylamine hydrochloride and AlCl₃ at different molar ratios were examined to determine the temperature and composition ranges over which a single liquid phase was formed. A single liquid phase was found near room temperature (30 °C) for the n-PrNH₃Cl-AlCl₃, n-BuNH₃Cl-AlCl₃, and n-Bu₂NH₂Cl-AlCl₃ ionic liquids. These electrolytes exhibited ionic conductivities of approximately 10 mS cm⁻¹ at 30 °C, which is comparable to the conductivity reported for most of the other chloroaluminate ionic liquids, except for EMIC-AlCl₃, but significantly higher than those of amide-AlCl₃ ionic liquid analogs. Galvanostatic electrodeposition confirmed that Al metal could be electrodeposited from these alkylamine hydrochloride-AlCl₃ ionic liquids. The sizes of the electrodeposited Al crystal grains decreased as the size of the cations (alkylammonium ions) in the electrolyte increased. In addition to Al electrodeposition, alkylammonium ions can undergo cathodic decomposition. However, the n-PrNH₃⁺, n-BuNH₃⁺, and n-Bu₂NH₂⁺ cations were more resistant to cathodic reduction than the

 $Me_2NH_2^+$ and $EtNH_3^+$ cations, probably because of the steric hindrance of the longer alkyl chains. Therefore, in the *n*-PrNH₃Cl–AlCl₃, *n*-BuNH₃Cl–AlCl₃, and *n*-Bu₂NH₂Cl–AlCl₃ electrolytes, the electrodeposition of Al could be generally accomplished with a current efficiency of more than 90 % at current densities of 5–12 mA cm⁻². The alkylamine hydrochloride–AlCl₃ ionic liquid electrolytes developed in this study can be cost-effective alternatives to the high-cost EMIC–AlCl₃ ionic liquids and are expected to contribute to the development of various applications, involving Al electrodeposition, such as Al electroplating for corrosion-resistant coatings, electrorefining for high-purity Al production, and rechargeable Al-ion batteries for energy storage solutions. However, further investigations are required to evaluate their long-term stability under extended usage conditions, particularly for industrial applications.

CRediT authorship contribution statement

Takashi Kubo: Writing – original draft, Investigation. Akihiro Tanaka: Writing – original draft, Investigation. Takumi Ikenoue: Validation. Tetsuji Hirato: Supervision. Masao Miyake: Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Masao Miyake reports financial support was provided by Japan Society for the Promotion of Science. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2025.145647.

Data availability

Data will be made available on request.

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