

1        **Aluminum electrodeposition in dry air atmosphere — comparative study of an**  
2        **acetamide–AlCl<sub>3</sub> deep eutectic solvent and a 1-ethyl-3-methylimidazolium**  
3        **chloride–AlCl<sub>3</sub> ionic liquid**

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12  
13  
14        **Abstract**

15        Aluminum electrodeposition using ionic liquids or deep eutectic solvents has  
16        attracted significant interest for coating applications. Although Al electrodeposition is  
17        usually carried out in a nitrogen- or argon-filled glove box, there may be a potential for  
18        process cost reduction if the Al electrodeposition process could be carried out in a dry  
19        atmosphere. In this study, we examined two commonly used baths, namely a 1-ethyl-3-  
20        methylimidazolium chloride (EMImCl)–AlCl<sub>3</sub> ionic liquid and an acetamide (AcAm)–  
21        AlCl<sub>3</sub> deep eutectic solvent, to determine their respective feasibilities for the  
22        electrodeposition of a uniform Al film in dry air. Electrodeposition in dry air using the  
23        AcAm–AlCl<sub>3</sub> bath produced uniform Al films even after the bath had been used for more  
24        than 10 weeks, whereas electrodeposition in dry air using the EMImCl–AlCl<sub>3</sub> bath failed  
25        to produce an Al film covering the entire substrate. The current efficiency was almost  
26        100% in the AcAm–AlCl<sub>3</sub> bath, whereas the value decreased to 50% in EMImCl–AlCl<sub>3</sub>  
27        bath in dry air. The findings of this study therefore reveal that AcAm–AlCl<sub>3</sub> is a suitable  
28        bath for Al electrodeposition in dry air.

29  
30        **Keywords**

31        electrodeposition, electroplating, deep eutectic solvent, ionic liquid

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## 1 **1. Introduction**

2 Metallic aluminum is a lightweight material that exhibits good workability, high  
3 specific strength, and excellent thermal and electrical conductivities. Al is also known to  
4 exhibit high resistance to corrosion and oxidation due to the formation of a dense oxide  
5 film on its surface. Owing to these properties, Al is used in various applications, such as  
6 in automotive bodies, heat exchangers, and cathode current collectors for lithium-ion  
7 batteries [1]. Al is also used as a coating material on material surfaces of products, since  
8 the formation of an Al film on the original material surface is expected to improve  
9 functionality of the product and extend its lifetime.

10 Primary methods for coating Al are hot-dip coating, vacuum evaporation, and  
11 electrodeposition. Among these, electrodeposition is advantageous due to its ability to  
12 produce a dense Al layer at a relatively high rate near room temperature on materials  
13 having complex shapes.

14 Since the standard electrode potential for Al in aqueous solutions is  $-1.66$  V vs. the  
15 standard hydrogen electrode (SHE), which is significantly lower than the potential for  
16 hydrogen evolution, Al electrodeposition using aqueous solutions is impossible.  
17 Therefore, Al electrodeposition is carried out in non-aqueous media such as inorganic  
18 molten salts [2,3], organic solvents [4–7], and ionic liquids [8,9]. Currently, the majority  
19 of electrolyte baths employed for Al electrodeposition use anhydrous aluminum chloride  
20 ( $\text{AlCl}_3$ ) as the Al ion source. In the past, baths based on triethyl aluminum [10] and lithium  
21 aluminum hydride [4,11] as the Al ion source have also been employed, but such baths  
22 have significant disadvantages in that they are more reactive, difficult to handle, and more  
23 hazardous than those based on  $\text{AlCl}_3$ .

24 While  $\text{AlCl}_3$  is widely preferred as the source of Al in electrodeposition baths, it is  
25 highly hygroscopic and easily hydrolyzed by the moisture present in the air. Once  
26 hydrolyzed, Al electrodeposition becomes impossible. Therefore, baths having  $\text{AlCl}_3$   
27 employed for Al electrodeposition must be handled in a dry atmosphere. Al  
28 electrodeposition is typically carried out in a nitrogen- or argon-filled glove box, which  
29 maintains the moisture and oxygen levels below 1 ppm. However, electrodeposition in a  
30 closed system, such as a glove box, is not suitable for industrial-scale production. This  
31 may be due to limitation in the size and number of substrates to be electrodeposited that  
32 can be handled simultaneously. In addition, since the processes carried out before and  
33 after electrodeposition, such as substrate pretreatment and washing of the  
34 electrodeposited material, are usually performed using aqueous solutions, it is unfeasible  
35 to conduct a series of processes continuously [8,12].

1           Several research groups have proposed that covering the bath with a hydrophobic  
2 liquid phase could prevent its hydrolysis so that the electrodeposition of Al under ambient  
3 air may be achieved [13,14]. However, even employing such a method, a marked decrease  
4 in the film quality of the electrodeposited Al has been observed after approximately one  
5 week [14], which may be due to seepage of the moisture present in the atmosphere. A  
6 method using hydrophobic ionic liquids as solvents has also been proposed [15,16], but  
7 since AlCl<sub>3</sub> is still used as the Al ion source in these liquids, gradual hydrolysis of the  
8 bath by moisture in the air is inevitable [17].

9           Although Al electrodeposition is usually conducted in a glove box filled with an  
10 inert gas, it may be possible to carry out this procedure in a dry air atmosphere, if the  
11 effect of oxygen on the bath and the electrodeposited Al is less damaging than that of  
12 moisture. Dry air rooms are typically used for semiconductor and lithium-ion battery  
13 production. If Al electrodeposition can also be carried out in dry air rooms, the process  
14 productivity can be greatly improved. The dissolution and electrochemical reduction of  
15 oxygen in many non-aqueous solutions have been studied [18]. Reports are available on  
16 the electrochemical behavior of oxygen in Lewis basic chloroaluminate ionic liquids [19],  
17 in which electrodeposition of Al does not occur. However, no studies in Lewis acidic ionic  
18 liquids used for Al electrodeposition are available in the literature, and the effects of  
19 oxygen on Al electrodeposition in terms of film morphology and current efficiency are  
20 not well understood.

21           Previously, we examined the electrodeposition of Al in dry air using a dimethyl  
22 sulfone (DMSO<sub>2</sub>)–AlCl<sub>3</sub> bath [20]. Although this bath produced a uniform Al film in an  
23 Ar atmosphere, electrodeposition in dry air yielded Al films with many holes and streaks,  
24 and uniform Al films were obtained only when a small amount of dimethylamine  
25 hydrochloride was added to the bath. These results indicated that oxygen adversely  
26 affected Al electrodeposition in the DMSO<sub>2</sub>–AlCl<sub>3</sub> bath, which resulted in poor film  
27 quality. However, the effect of oxygen on Al electrodeposition may differ depending on  
28 the type of bath employed. To the best of our knowledge, the DMSO<sub>2</sub>–AlCl<sub>3</sub> bath was the  
29 only one that has been previously examined.

30           To find a bath from which Al can be electrodeposited in dry air as well as in Ar, we  
31 explored various baths. We found that an acetamide (AcAm)–AlCl<sub>3</sub> deep eutectic solvent  
32 can yield Al films even in dry air, whereas many ionic liquids cannot. Herein, we report  
33 a comparative study of two electrolytes for the Al electrodeposition process in dry air: an  
34 AcAm–AlCl<sub>3</sub> deep eutectic solvent and a 1-ethyl-3-methylimidazolium chloride  
35 (EMImCl)–AlCl<sub>3</sub> ionic liquid, which is currently the most popular bath for Al  
36 electrodeposition. The electrochemical behaviors of Al in these two baths in dry air are

1 compared, and changes in the bath constituents in dry air are also investigated using  
2 Raman spectroscopy. Based on the results, the factors affecting the success or failure of  
3 Al electrodeposition in dry air are discussed.

## 6 **2. Experimental**

7 Acetamide (AcAm, Tokyo Chemical Industry, Japan, >98%) and anhydrous  
8 aluminum chloride ( $\text{AlCl}_3$ , Sigma-Aldrich, >98%) were used as received. 1-Ethyl-3-  
9 methylimidazolium chloride (EMImCl, Tokyo Chemical Industry, Japan, >98%) was  
10 dried under vacuum at 120 °C for three days prior to use. The water contents of the AcAm  
11 and the dried EMImCl were determined by Karl Fischer titrations (MKC-610, Kyoto  
12 Electronics Manufacturing, Japan) to be <30 ppm. Electrolyte baths were prepared by  
13 slowly mixing  $\text{AlCl}_3$  with AcAm or EMImCl at 25 °C in an Ar-filled glovebox. The molar  
14 ratios for the baths were  $\text{AlCl}_3/\text{AcAm} = 1.3$  and  $\text{AlCl}_3/\text{EMImCl} = 2$ . These molar ratios  
15 are commonly used for the electrodeposition of Al in an Ar atmosphere [21,22]. Baths  
16 with a volume of 13 mL were used for the electrochemical experiments.

17 The electrochemical experiments for the dry air environment were conducted in a  
18 dry chamber (SODA, Japan), where the air was kept dehumidified by an air-conditioning  
19 unit such that the dew point was maintained in the range of -65 to -75 °C. The  
20 experiments in Ar were performed in an Ar-filled glovebox (DBO-1KH-HMK, MIWA,  
21 Japan).

22 Cyclic voltammetry (CV) was carried out using a Pt disk electrode ( $\phi$  3 mm) as the  
23 working electrode at a scan rate of 10 mV s<sup>-1</sup> at 80 °C. An Al plate (thickness 1.0 mm,  
24 99.99%, Nilaco, Japan) was used as the counter electrode, and an Al wire ( $\phi$  1 mm,  
25 99.99%, Nilaco, Japan) directly immersed in the electrolyte bath was used as the reference  
26 electrode. Before the CV measurements, the Pt working electrode was polished with an  
27 alumina polishing agent (0.05  $\mu\text{m}$ ), rinsed with a 1 M NaOH aqueous solution and  
28 distilled water, and then dried under a flow of air. Galvanostatic electrodeposition was  
29 performed on a Cu plate (thickness 99.96%, Matsuo, Kyoto, Japan) at 80 °C. Prior to use,  
30 the Cu plate was ultrasonically cleaned with acetone and ethanol sequentially for 10 min  
31 each and then dried in air blow. A section of the Cu plate was covered with  
32 polytetrafluoroethylene tape to expose a defined area (5 mm  $\times$  5 mm). An Al plate was  
33 used as the counter electrode. The Cu and Al plates were placed vertically and parallel to  
34 each other at a distance of <10 mm. During the electrodeposition process, the bath was  
35 agitated at 100 rpm using a magnetic stirrer (PC-420D, CORNING, USA) and a magnetic  
36 flea (7 mm  $\times$  20 mm). The electrochemical experiments described above were carried out

1 using an electrochemical analyzer (HZ-7000, Hokuto Denko, Japan). After  
2 electrodeposition, the deposit was washed with ethanol and distilled water.

3 The current efficiency for the Al electrodeposition process was measured using  
4 inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Optima 5300 DV,  
5 PerkinElmer, USA). The electrodeposited Al films were dissolved in a 1 M HCl aqueous  
6 solution (~10 mL), and the solution was diluted to 100 mL using distilled water. The  
7 current efficiency was calculated from the amount of Al measured by ICP-AES and the  
8 charge applied for electrodeposition.

9 Scanning electron microscopy (SEM, JEOL, JSM-6510LV, Japan) combined with  
10 energy dispersive X-ray spectroscopy (EDX, INCAx-act, Oxford Instruments, UK) was  
11 employed to observe the morphology and measure the elemental composition of the  
12 deposit, respectively. X-ray diffraction (XRD) patterns were obtained using an X-ray  
13 diffractometer (X'pertPRO-MPD, PANalytical, Nederland) with Cu K $\alpha$  radiation ( $\lambda =$   
14 0.15405 nm) at a scan rate of 0.1 degrees s<sup>-1</sup>. The mean crystallite size was calculated  
15 from the line broadening of the Al (220) diffraction using the Scherrer equation, with a  
16 shape factor of 0.9. The line broadening was measured from the full-width at half-  
17 maximum of the diffraction peak after subtracting the instrumental line broadening, the  
18 latter being determined from the diffraction peaks of a Si standard sample with a mean  
19 crystallite size of approximately 4  $\mu\text{m}$ .

20 Raman spectra of the electrolyte baths were measured at 25 °C (RAMAN touch,  
21 nano photon, Japan) using a semiconductor laser light source (785 nm). The electrolyte  
22 baths (volume = ~0.3 mL) were sealed in a 1  $\mu\text{m}$ -thick quartz cell in a glove box or a dry  
23 chamber.

### 26 **3. Results and discussion**

#### 27 **3.1 Electrochemical behavior of Al in dry air atmosphere**

28 CV was carried out for the AcAm–AlCl<sub>3</sub> and EMImCl–AlCl<sub>3</sub> baths in both Ar and  
29 dry air atmospheres (Fig. 1). The CV profiles in dry air were measured after the baths had  
30 been left in the dry air for three days. In the AcAm–AlCl<sub>3</sub> bath, a cathodic current for Al  
31 deposition was observed with an onset potential of approximately –0.1 V vs. Al/Al(III)  
32 during the cathodic scan in both atmospheres, and an anodic current for the dissolution of  
33 Al was observed during the anodic scan. The cathodic current reached ~20 mA cm<sup>-2</sup> at  
34 –0.5 V in both atmospheres, although the current was slightly smaller in dry air than in  
35 Ar. The coulombic efficiency for dissolution/deposition, which was determined from the  
36 ratio of the area of the oxidation wave to that of the reduction wave in the CV profile, was

1 94% in Ar and 76% in dry air. As described later, the current efficiency for Al  
2 electrodeposition in the AcAm–AlCl<sub>3</sub> bath was almost 100%, irrespective of the  
3 atmosphere. Therefore, the decrease in the Coulombic efficiency in dry air was ascribed  
4 to the partial oxidation of deposited Al by dissolved oxygen to give an insoluble  
5 aluminum oxide. The CV curve recorded in the EMImCl–AlCl<sub>3</sub> bath showed more  
6 significant differences upon variation in the atmosphere. More specifically, the onset  
7 potential of Al deposition was –0.1 V in Ar, while it decreased to –0.4 V in the dry air  
8 atmosphere, indicating that a larger overvoltage was required for Al deposition in dry air.  
9 In addition, the reduction current reached 60 mA cm<sup>–2</sup> in Ar, but only 10 mA cm<sup>–2</sup> in dry  
10 air, thereby indicating that the anodic current was significantly smaller in a dry air  
11 atmosphere. Furthermore, the Coulombic efficiency was 94% in Ar and 14% in dry air.  
12 The variation in the Coulombic efficiencies may indicate that in dry air, in addition to the  
13 deposited Al being oxidized by dissolved oxygen, as observed for the AcAm–AlCl<sub>3</sub> bath,  
14 other side reactions may also occur during the reduction process. Further, comparison of  
15 the CV curves for the AcAm–AlCl<sub>3</sub> bath in dry air atmosphere and Ar atmosphere  
16 indicated that the electrochemical deposition and dissolution of Al in the AcAm–AlCl<sub>3</sub>  
17 bath in a dry air atmosphere proceeded in a similar manner to when an Ar atmosphere  
18 was employed. In contrast, comparison of the CV curves for the EMImCl–AlCl<sub>3</sub> bath in  
19 dry air atmosphere and Ar atmosphere indicated that the electrochemical deposition and  
20 dissolution of Al in the EMImCl–AlCl<sub>3</sub> bath were significantly suppressed by changing  
21 the atmosphere from Ar to dry air.

22 The galvanostatic electrodeposition of Al was performed on a Cu substrate under  
23 Ar and dry air atmospheres at 10 mA cm<sup>–2</sup> (Fig. 2). A uniform gray film covering the  
24 entire surface of the substrate was obtained from the AcAm–AlCl<sub>3</sub> bath, regardless of the  
25 atmosphere employed. The electrodeposition of Al was also performed in the AcAm–  
26 AlCl<sub>3</sub> bath in dry air at 2 and 15 mA cm<sup>–2</sup>, both of which yielded an Al film covering the  
27 substrate (Supplementary Fig. S1). In contrast, in the case of the EMImCl–AlCl<sub>3</sub> bath,  
28 although a uniform film was obtained in Ar atmosphere, deposition in dry air resulted in  
29 a film being obtained only on a small portion of the substrate. SEM imaging showed that  
30 the films obtained using the AcAm–AlCl<sub>3</sub> bath in both atmospheres were composed of  
31 grains having a size of ~2–5 μm, while those obtained using the EMImCl–AlCl<sub>3</sub> bath in  
32 Ar were slightly larger (i.e., ~5–10 μm). The SEM image of the deposited films obtained  
33 using the EMImCl–AlCl<sub>3</sub> bath in dry air shows nodular grains formed in isolation on the  
34 substrate. The current efficiency for Al deposition from the AcAm–AlCl<sub>3</sub> bath was  
35 determined to be 97% in both Ar and dry air atmospheres. In contrast, the efficiency in  
36 the EMImCl–AlCl<sub>3</sub> bath was determined to be 98% in Ar but decreased to 51% in dry air.

1 Electrodeposition in dry air using the EMImCl–AlCl<sub>3</sub> bath was also performed at different  
2 current densities (i.e., 10–40 mA cm<sup>-2</sup>), but it was not possible to obtain an Al film  
3 covering the entire substrate at any of the current densities employed, although the current  
4 efficiency increased upon increasing the current density (Fig. 3). The increase in the  
5 current efficiency may be because dissolved oxygen is involved in the side reactions. The  
6 rate of the side reactions is limited by the diffusion of oxygen, whereas that of Al  
7 deposition increases with increasing applied current.

8 The crystal structure of each of the deposited films was then analyzed using XRD  
9 (Fig. 4). For the deposited films obtained under the Ar and dry air atmospheres, only fcc  
10 Al diffraction peaks were observed, with the exception of the fcc Cu diffraction peaks  
11 originating from the substrate. This indicates that metallic Al was electrodeposited in both  
12 atmospheres, although the current efficiency was significantly lower using the EMImCl–  
13 AlCl<sub>3</sub> bath in dry air.

14 To examine the long-term stability of the AcAm–AlCl<sub>3</sub> bath in dry air, the  
15 electrodeposition in dry air was conducted every week for 10 weeks using an identical  
16 AcAm–AlCl<sub>3</sub> bath, which was stored in a dry air atmosphere throughout the study period  
17 (Fig. 5). The electrodeposition conditions were identical to those used in the experiment  
18 outlined in Fig. 2. Figure 5 shows that uniform Al films without holes or streaks were  
19 obtained from the AcAm–AlCl<sub>3</sub> bath over the period of 10 weeks. The grain size of the  
20 electrodeposited Al gradually decreased with time, and the surface of the resulting  
21 deposited film became smoother. Some areas near the edge of the film electrodeposited  
22 from the bath after four weeks had an especially smooth surface and exhibited a metallic  
23 luster. The XRD patterns of these films (Fig. 6) exhibit only the diffraction peaks of Al in  
24 addition to those of the Cu substrate, showing that Al metal can be electrodeposited in  
25 dry air from the AcAm–AlCl<sub>3</sub> bath over a period of 10 weeks. Table 1 lists the crystallite  
26 sizes of Al estimated from the width of the Al (220) peak using the Scherrer equation.  
27 The crystallite sizes determined by the Scherrer equation showed a decreasing trend over  
28 time, which is consistent with the trend in grain size observed in the SEM images. Such  
29 a change in the grain size was not observed in electrodeposition in an Ar atmosphere. It  
30 is inferred that, in dry air, AcAm is slightly and gradually decomposed, and the  
31 decomposition products may suppress grain growth, as mentioned later. The current  
32 efficiency after ten weeks was determined to still be as high as 95% by ICP-AES.

### 34 **3.2 Reactions of the baths with oxygen**

35 The key difference between the Ar and dry air atmospheres that affects the  
36 electrodeposition of Al is the presence of oxygen in the dry air atmosphere. When

1 electrodeposition was performed in dry air, both the AcAm–AlCl<sub>3</sub> and EMImCl–AlCl<sub>3</sub>  
2 baths exhibited a color change from pale brown to dark brown, which was not observed  
3 under Ar (Fig. 7). This color change indicates that the baths reacted with oxygen.

4 Oxygen in dry air may react with Al ions and turn electrochemically active Al ions  
5 into inactive species such as Al-O-Cl ions, which are formed by the reaction of AlCl<sub>3</sub> with  
6 water [23]. The loss of the active Al ion species due to the reaction with oxygen may  
7 cause non-uniform Al deposition in the EMImCl–AlCl<sub>3</sub> bath in dry air. However, this  
8 hypothesis is denied by Raman spectroscopy for the baths. In the Raman spectra (Fig. 8),  
9 the AcAm–AlCl<sub>3</sub> bath exhibited peaks at 310 and 347 cm<sup>-1</sup>, which are attributed to AlCl<sub>4</sub><sup>-</sup>  
10 and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>, respectively [24]. The EMImCl–AlCl<sub>3</sub> bath exhibited two peaks at 310 and  
11 430 cm<sup>-1</sup>, both of which are attributed to Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> [24]. No clear AlCl<sub>4</sub><sup>-</sup> peak was observed  
12 from the EMImCl–AlCl<sub>3</sub> bath due to the higher AlCl<sub>3</sub> content (i.e., EMImCl:AlCl<sub>3</sub> = 1:2)  
13 compared to that of the AcAm–AlCl<sub>3</sub> bath (i.e. AcAm:AlCl<sub>3</sub> = 1:1.3) and the fact that the  
14 Al ions in the EMImCl–AlCl<sub>3</sub> bath exist almost exclusively as Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> at this AlCl<sub>3</sub>  
15 content [25]. Among the Al ion species, AlCl<sub>4</sub><sup>-</sup> is electrochemically inactive and Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>  
16 is reduced to metallic Al in both baths. In the AcAm–AlCl<sub>3</sub> bath, in addition to Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>,  
17 [AlCl<sub>2</sub>·nAcAm]<sup>+</sup> is also reduced to Al [14,25–27], although this species was not clearly  
18 detected in the Raman spectra. Comparison of the Raman spectra for the baths used in Ar  
19 and dry air show that the active Al ion, Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>, remained unchanged in both baths even  
20 after the use for more than four weeks in dry air. Although Al-O-Cl species may have  
21 been formed, their concentrations were negligibly small.

22 The presence of the active Al ions was further confirmed by the following  
23 experiment. The EMImCl–AlCl<sub>3</sub> bath that had been used for electrodeposition in dry air  
24 was transferred into the Ar atmosphere, and electrodeposition was carried out there. A  
25 uniform Al film was obtained as in the case of using the bath that had never been exposed  
26 to dry air. This result indicates that the major part of the bath components remained  
27 unchanged even upon exposure to dry air, suggesting that the failure of Al  
28 electrodeposition in dry air was caused by a local reaction on the cathode during the  
29 electrodeposition process.

30 In addition to the color change of the bath, a black gel-like substance was  
31 precipitated onto a part of the cathode near the surface of the bath after electrodeposition  
32 using the EMImCl–AlCl<sub>3</sub> bath in dry air for a prolonged duration of 4 h (Fig. 9(a)). This  
33 black substance was easily washed away from the cathode upon contact with the bath.  
34 Therefore, although this substance was observed only in the area near the surface of the  
35 bath, it is possible that the reaction producing this substance occurred over the entire  
36 surface of the cathode during electrodeposition. In contrast, no such substance was



1 observed on the anode, nor when the EMImCl–AlCl<sub>3</sub> bath was employed in Ar (Fig. 9(b)).  
2 The AcAm–AlCl<sub>3</sub> bath did not generate such a substance even when it was used in dry  
3 air. This black substance therefore may be a decomposition product of EMIm<sup>+</sup>. Since this  
4 substance precipitated only in dry air on the cathode and not on the anode, it was likely  
5 generated by the electrochemical reaction on the cathode in the presence of oxygen. This  
6 oxygen-involving cathodic decomposition of EMIm<sup>+</sup> may be responsible for the low  
7 current efficiency for Al electrodeposition in the EMImCl–AlCl<sub>3</sub> bath in dry air (Fig. 3).  
8 Further, it may be surmised that adsorption of a part of the decomposition products on the  
9 cathode surface prevents the electrodeposition of Al, resulting in failure to uniformly  
10 electrodeposit Al in dry air.

11 In the AcAm–AlCl<sub>3</sub> bath in dry air, AcAm may also have been decomposed slightly,  
12 as suggested by the color change of the bath. However, unlike in the case of EMImCl, the  
13 decomposition products of AcAm seemed not to have prevented Al deposition; instead,  
14 they only suppressed the crystal growth of deposited Al by surface adsorption, ultimately  
15 resulting in an Al film with a smooth surface comprising small grains, as shown in Fig. 5.  
16 The gradual grain refinement observed with time could be due to the accumulation of the  
17 decomposition products in the bath.

#### 19 **4. Conclusion**

20 The electrodeposition of aluminum using a 1-ethyl-3-methylimidazolium chloride  
21 (EMImCl)–AlCl<sub>3</sub> ionic liquid or an acetamide (AcAm)–AlCl<sub>3</sub> deep eutectic solvent was  
22 examined in both dry air and Ar atmospheres. CV profiles indicated that the  
23 electrochemical deposition/dissolution of Al in the AcAm–AlCl<sub>3</sub> bath was not  
24 substantially affected by the atmosphere, whereas Al deposition/dissolution in the  
25 EMImCl–AlCl<sub>3</sub> bath was significantly suppressed in the dry air atmosphere.  
26 Galvanostatic electrodeposition using the AcAm–AlCl<sub>3</sub> bath in both Ar and dry air  
27 produced uniform Al films, whereas electrodeposition using the EMImCl–AlCl<sub>3</sub> bath in  
28 dry air yielded Al films only on a small portion of the substrate surface. Both baths  
29 showed a color change after use in the electrodeposition process in dry air, which was not  
30 observed in Ar, thereby indicating that the baths may have reacted with oxygen present  
31 in the air. Raman spectroscopy showed that the electrochemically active Al ions, Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup>,  
32 remained unchanged in dry air for both baths. Electrodeposition using the EMImCl–AlCl<sub>3</sub>  
33 bath in dry air generated a black gel-like substance on the upper part of the cathode. It  
34 was inferred that the decomposition product, which was generated by the side reaction of  
35 Al electrodeposition in the presence of oxygen, was adsorbed on the cathode surface,  
36 preventing the deposition of a uniform Al film. In the AcAm–AlCl<sub>3</sub> bath, AcAm may also

1 have been decomposed by cathodic reaction in dry air; however, the decomposition  
2 product seemed not to inhibit Al nucleation, instead, only preventing Al crystal growth,  
3 thereby leading to the formation of uniform Al films even in a dry air atmosphere. Overall,  
4 our results suggested that the AcAm–AlCl<sub>3</sub> bath is more suitable for use in Al  
5 electrodeposition processes in dry air. Since the described electrodeposition process in  
6 dry air is more productive and less costly than the conventional process in an inert gas  
7 atmosphere, it will promote the utilization of Al electrodeposition process on an industrial  
8 scale.

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1 **Figure captions**

2 **Figure 1.** CV profiles recorded for the (a) AcAm–AlCl<sub>3</sub> and (b) EMImCl–AlCl<sub>3</sub> baths in  
3 Ar and dry air atmospheres using a Pt working electrode at 80 °C.

4 **Figure 2.** Photographs and surface SEM images of deposits obtained from the AcAm–  
5 AlCl<sub>3</sub> and EMImCl–AlCl<sub>3</sub> baths in Ar and dry air atmospheres. All samples were  
6 deposited at 10 mA cm<sup>-2</sup> for 40 min at 80 °C.

7 **Figure 3.** Photographs of deposits obtained using the EMImCl–AlCl<sub>3</sub> bath in dry air with  
8 electrodeposition carried out at (a) 10 mA cm<sup>-2</sup>, (b) 20 mA cm<sup>-2</sup>, and (c) 40 mA cm<sup>-2</sup>.  
9 The deposition times were 40, 20, and 10 min, respectively. The current efficiency for the  
10 electrodeposition is shown in each image.

11 **Figure 4.** XRD patterns of deposits obtained on a Cu substrate by electrodeposition at 10  
12 mA cm<sup>-2</sup> for 40 min at 80 °C using the (a) AcAm–AlCl<sub>3</sub> and (b) EMImCl–AlCl<sub>3</sub> baths in  
13 Ar and dry air.

14 **Figure 5.** Photographs and surface SEM images of Al films electrodeposited from the  
15 AcAm–AlCl<sub>3</sub> bath that had been used (and stored) in a dry air atmosphere for up to 10  
16 weeks. All samples were deposited at 10 mA cm<sup>-2</sup> for 40 min at 80 °C.

17 **Figure 6.** XRD patterns of Al films electrodeposited from the AcAm–AlCl<sub>3</sub> bath that had  
18 been used (and stored) in a dry air atmosphere for up to 10 weeks. All samples were  
19 deposited at 10 mA cm<sup>-2</sup> for 40 min at 80 °C.

20 **Figure 7.** Photographs of the AcAm–AlCl<sub>3</sub> and EMImCl–AlCl<sub>3</sub> baths after use in Ar and  
21 dry air atmospheres.

22 **Figure 8.** Raman spectra of the (a) AcAm–AlCl<sub>3</sub> and (b) EMImCl–AlCl<sub>3</sub> baths after use  
23 in the electrodeposition process for more than four weeks under Ar and dry air  
24 atmospheres.

25 **Figure 9.** Photographs of the Cu cathode and the Al anode after electrodeposition using  
26 the EMImCl–AlCl<sub>3</sub> bath in (a) dry air and (b) Ar atmospheres. The black gel-like  
27 substance generated in the EMImCl–AlCl<sub>3</sub> bath in dry air is indicated by a white arrow.  
28 Electrodeposition was performed at 30 mA for 4 h.

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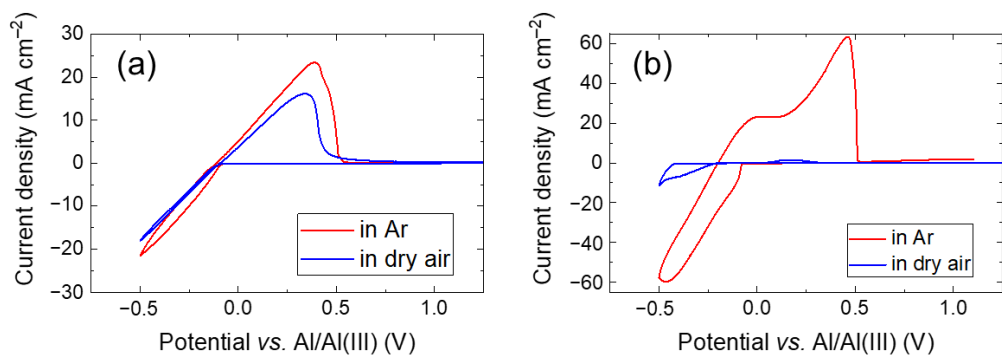
1 Table 1. Crystallite sizes determined by the Scherrer's equation for Al electrodeposits  
2 from the AcAm–AlCl<sub>3</sub> bath that had been used (and stored) in a dry air atmosphere for  
3 up to 10 weeks.

Period of time in dry air (weeks)	Crystallite size (nm)
<3	>200
4	103
5	64
10	56

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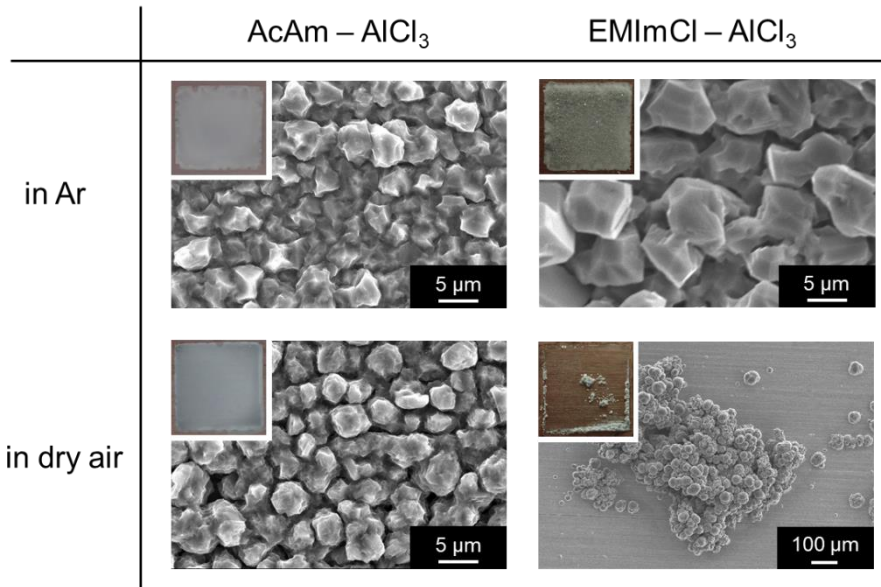
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**Figure 1.**

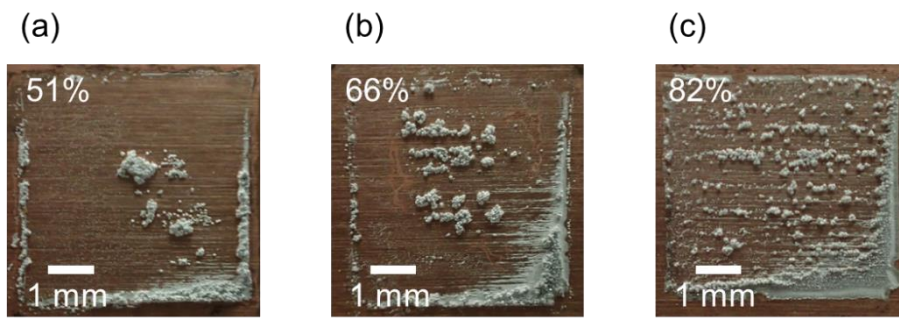
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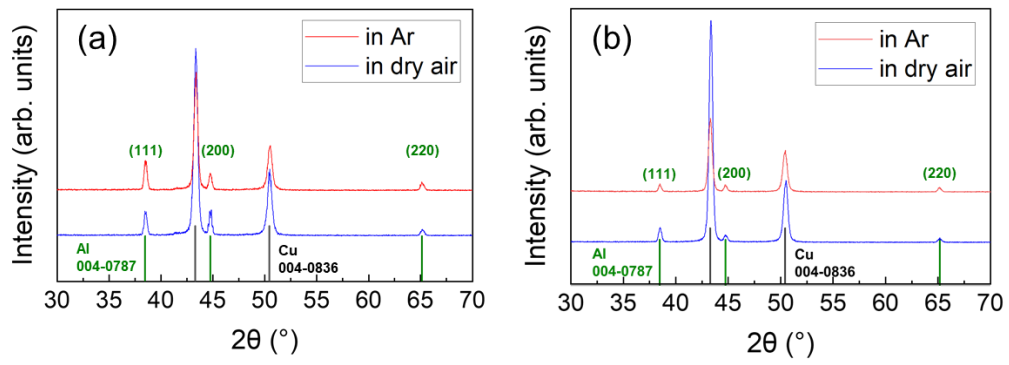
**Figure 2.**



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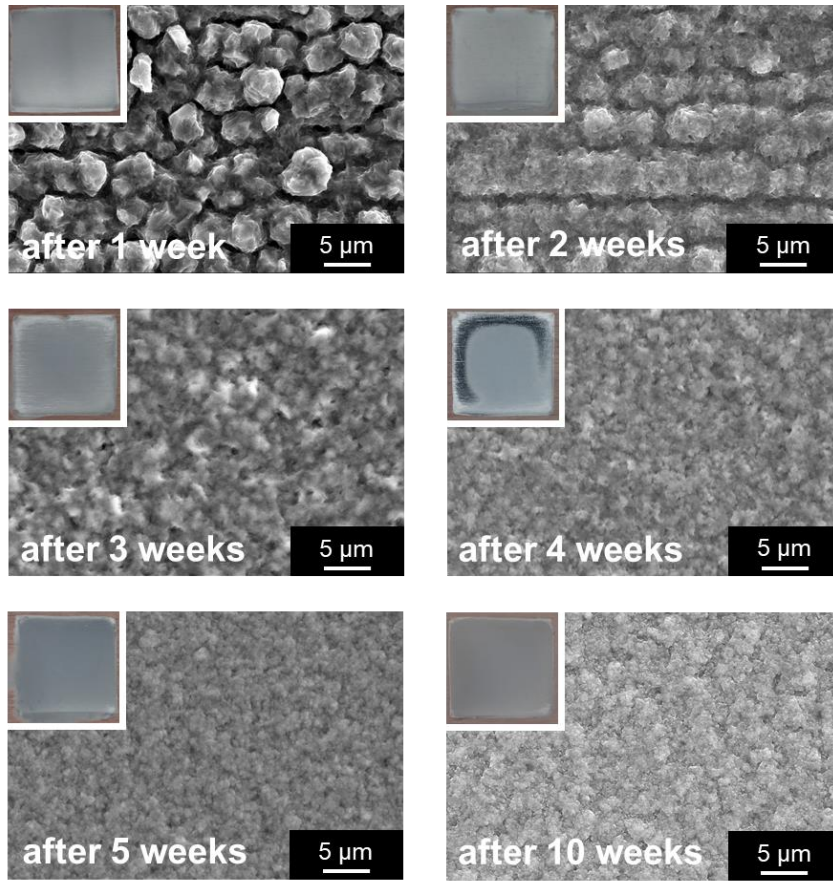
2 **Figure 3.**

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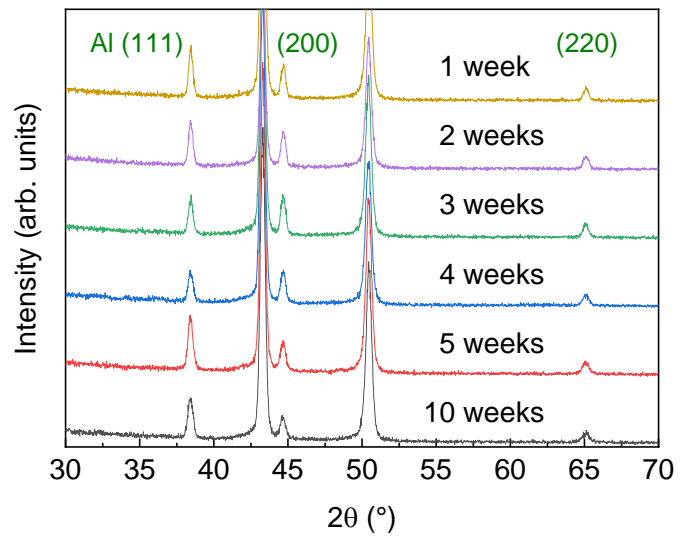


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Figure 4.



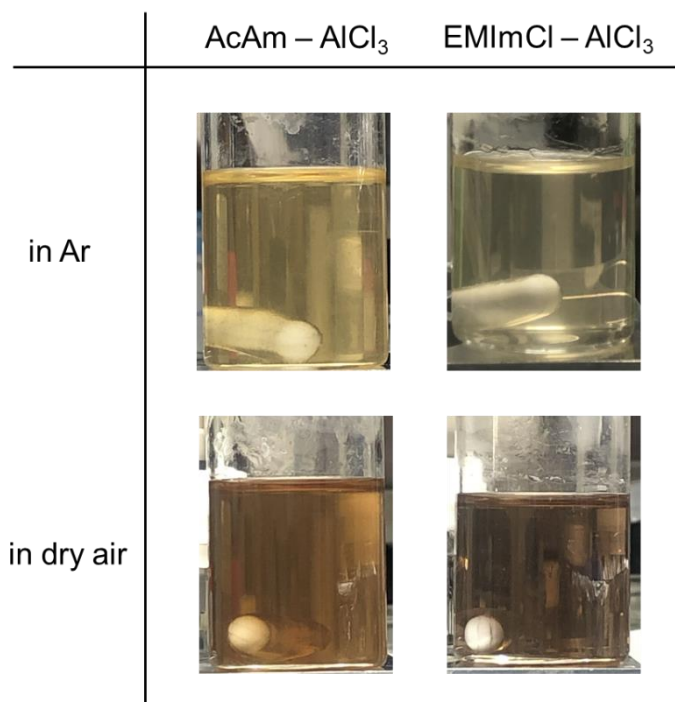
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2 **Figure 5.**  
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Figure 6.

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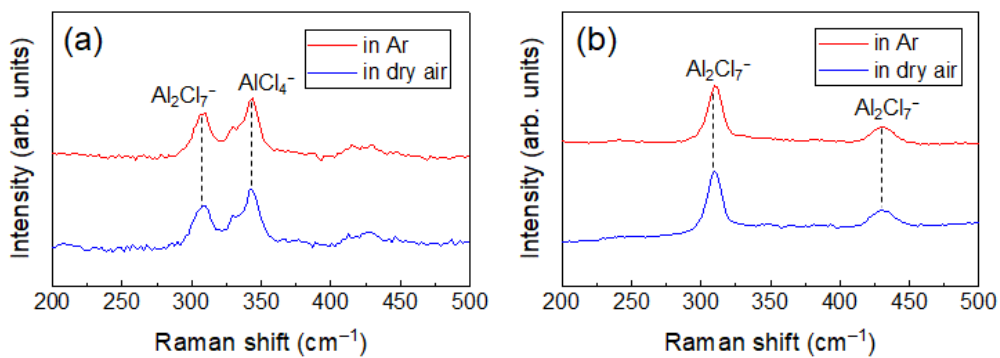
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**Figure 7.**

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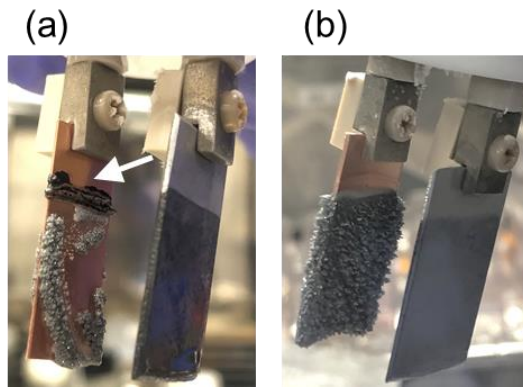
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3 **Figure 8.**

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2 **Figure 9.**