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Abstract: Electrochemically active species in aluminum (Al) electrodeposition baths using AlCl3 and less volatile solvents i.e. glymes were investigated. Raman spectroscopy revealed that all the glyme baths contained AlCl4- anions and Al-Cl-glyme cations as ionic species. Room temperature conductivities were as high as the order of 10-3 S cm-1 for the diglyme (G2), triglyme (G3) and tetraglyme (G4) baths, whereas that for the butyl diglyme (butylG2) bath was only 10-4 S cm-1 due to a lower concentration of ionic species. Surprisingly, electrochemical measurements showed that, among the glyme baths, only the G2 bath enabled electrodeposition of Al. Consequently, despite the similar structures of Al-Cl-glyme complex cations, only the G2 complex cations are electrochemically active. This suggests that the desolvation of glymes from Al-Cl-glyme cations and their subsequent reduction is exceptionally easy for the G2 complexes. Dear Editor of Electrochimica Acta

We are submitting the revised version of the manuscript (ISE-15-07-04R1), titled "Electrochemically Active Species in Aluminum Electrodeposition Baths of AlCl<sub>3</sub>/Glyme Solutions". Labels of Graphs were amended to "Potential vs. Al (QRE) / V".

Our responses to the reviewer's suggestions are summarized as follows:

1. Introduction, Line 14: separate 'abovementioned' so it reads 'above mentioned'.

We corrected.

2.4 Bath characterization, Line 4: Were these measurements really performed in dry air or was an inert gas used?

We added the following sentence in lines 8-9 of 2.4: "The sample solutions were sealed under Ar with septum and then measured within an hour after taken out from a glove box."

3.5 Electrochemically active species, Lines 4-6: This text was taken word for word from my previous review. Since I am not listed as a co-author, I'd appreciate it if the authors used their own words.

In the revised manuscript we rewrote as "The sulfone-solvated  $Al^{3+}$  species are generated together with the formation of  $AlCl_4^-$ . Since the resource of  $Cl^-$  is  $AlCl_3$ , asymmetric cleavage of  $AlCl_3$  occurs to form  $AlCl_4^-$  and  $[Al(sulfone)_3]^{3+}$ .".

3.6 RT electrodeposition of Al, Lines 8-10: delete "essentially". Also, the way the sentence is written, it is not clear whether Al2O3 was present as an impurity in the -1.0 V electrodeposit.

We changed to "; in the case of potentiostatic electrodeposition at -1 V vs. Al QRE [47] the XRD profiles also show the deposits were crystalline Al.".

Sincerely yours,

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Electrochemically Active Species in Aluminum Electrodeposition Baths of AlCl<sub>3</sub>/Glyme Solutions

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#### Abstract

Electrochemically active species in aluminum (Al) electrodeposition baths using AlCl<sub>3</sub> and less volatile solvents *i.e.* glymes were investigated. Raman spectroscopy revealed that all the glyme baths contained AlCl<sub>4</sub><sup>-</sup> anions and Al-Cl-glyme cations as ionic species. Room temperature conductivities were as high as the order of  $10^{-3}$  S cm<sup>-1</sup> for the diglyme (G2), triglyme (G3) and tetraglyme (G4) baths, whereas that for the butyl diglyme (butylG2) bath was only  $10^{-4}$  S cm<sup>-1</sup> due to a lower concentration of ionic species. Surprisingly, electrochemical measurements showed that, among the glyme baths, only the G2 bath enabled electrodeposition of Al. Consequently, despite the similar structures of Al-Cl-glyme complex cations, only the G2 complex cations are electrochemically active. This suggests that the desolvation of glymes from Al-Cl-glyme cations and their subsequent reduction is exceptionally easy for the G2 complexes.

Keywords: Aluminum electrodeposition, Glyme, Raman spectroscopy, Electrochemically active species

# 1. Introduction

Aluminum (Al) metal is essential for structural materials because of its low weight, workability, and corrosion resistance. Smelting of Al has been industrialized as the Hall-Héroult process: Al is electrowon from alumina-dissolved cryolite molten salt at 1000 °C [1]. Compared to this high temperature process, medium-low temperature electrodeposition is also of interest because it can be employed as a new Al-coating process. Various kinds of medium-low temperature bath for Al and Al-alloy electroplating have been reported [2]: they include organic solvents (e.g. ethers [3,4], aromatic hydrocarbons [5–9], sulfones [10–18] and others [19,20]), and ionic liquids [21–29], to name only a few. Some of them are applied to improve the corrosion resistance of magnesium alloys and steel [30–33]. Such Al electroplating baths are also attractive as a negative electrode material for next-generation "Al-ion" batteries because Al has low redox potential (-1.68 V vs. SHE) and high theoretical capacity (8042 mAh cm<sup>-3</sup>). Reports on Al-ion batteries using various electrolytes including sulfones and ionic liquids have been presented [34-40]. However, the above-mentioned organic solvents are highly volatile at their electrodeposition temperatures including room temperature (RT). For example, there are RT sulfone baths to which toluene is added to make them liquid at RT and to improve the physical properties as Al electroplating baths [39, 40], but they become relatively volatile due to the addition of toluene. In addition, sulfur contamination of deposits has been reported in a sulfone system

[17]. RT Ionic liquids are attractive for electroplating baths because they are thermally and chemically stable, less volatile and less flammable [21-29]. What is disadvantageous for ionic liquids, compared with organic solvents, is the high cost of the chemicals required for the bath preparation.

Safe and cheap alternatives to Al electroplating baths are of special interest. Very recently, glymes, *i.e.* glycol ethers, have drawn attention as relatively safe solvents for lithium and magnesium ion batteries, because they have boiling points above 150 °C and relatively low volatilities at RT [41-46]. In 2014 we published a communication paper on RT electrodeposition of Al using AlCl<sub>3</sub> and glyme with the ratio AlCl<sub>3</sub>:diglyme (G2) = 1:5 by mol, which was the first report for Al electroplating glyme baths [47]. Since then some fluorine-containing Al electrolytes with glymes were reported for Al redox at RT [48,49]; however, anodic dissolution in these fluorine-containing baths was difficult [48] and the redox current density was one-order of magnitude smaller compared to the AlCl<sub>3</sub>-G2 bath [49]. Moreover, the electrochemically active species in the AlCl<sub>3</sub>-G2 bath are still unknown and systematic study using other glymes has not been reported yet. Therefore, detailed and systematic study on AlCl<sub>3</sub>/glyme baths is of interest. In this paper we discuss the electrochemical properties of AlCl<sub>3</sub>/glyme solutions using four kinds of glymes as shown in Fig. 1. Somewhat surprisingly, electrodeposition was only successful from G2 solutions. Bath characterization and Raman spectroscopy indicated that only G2 can form electrochemically active complex cations, which can then undergo easy desolvation of the glymes and subsequent reduction of  $Al^{3+}$ .

#### 2. Experimental

## 2.1 Reagents

Diglyme (G2; Diethyleneglycol dimethylether, electrochemistry grade, Kanto Chemical), triglyme (G3; triethyleneglycol dimethylether, 98.0% purity, Tokyo Chemical Industry), tetraglyme (G4; tetraethyleneglycol dimethylether, 98.0% purity, Tokyo Chemical Industry), and butyldiglyme (butylG2; diethyleneglycol dibutylether, 98.0% purity, Tokyo Chemical Industry) were dried to less than 40 ppm  $H_2O$  using 3A molecular sieves before bath preparation.

### 2.2 Bath preparation

Each glyme solvent and as-received AlCl<sub>3</sub> (Wako, 99.9% purity) were mixed with glyme:AlCl<sub>3</sub> at a 5:1 or 3:1 molar ratio with an agitation speed of 500 rpm. To dissolve AlCl<sub>3</sub>, the G2 mixture required heating at 65 °C for 12 h while the other glyme solutions were obtained at 35 °C for 1 h. The bath preparation was conducted in an Ar-filled glovebox. The as-prepared solution contained 200 - 300 ppm water determined by Karl Fischer titration, probably due to some residual water in the AlCl<sub>3</sub> reagent.

#### 2.3 Electrochemical measurements and characterization of deposits

Electrochemical properties were measured in the Ar-filled glovebox with a potentiostat/galvanostat (Hokuto Denko, HSV-110). Measurements at RT were performed using a glass cell of 20 cm<sup>3</sup> capacity where the planar dimension of WE was fixed to 7.5 mm $\phi$  (EC Frontier, VM-2A) was utilized as reported in ref. 45, while a glass cell of 30 cm<sup>3</sup>

capacity was used for CV at elevated temperature and potentiostatic electrolysis. Cu sheet (Nilaco, 99.9% purity, 0.080 mm thickness for CV, and Yamamoto-MS, B-60-P05, 0.30 mm thickness for electrolysis) and Al sheet (Nilaco, >99% purity, 0.5 mm thickness) of size  $1.0 \times 2.5 \text{ cm}^2$  were used as working electrodes (WE). Al sheets of size  $1.0 \times 2.0 \text{ cm}^2$  were also used as a counter electrode (CE) and a quasi-reference electrode (QRE). The QRE was directly immersed in the same electrolyte. These electrodes were used for CV measurements after washing with acetone for 20 min. Before the potentiostatic electrolysis, Cu WE was first washed with an alkaline soak cleaner (ACE CLEAN, Okuno Chemical), then with an aqueous etchant containing 100 g dm<sup>-3</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 18 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, and 0.5 g dm<sup>-3</sup> CuSO<sub>4</sub>·5H<sub>2</sub>O, and finally with an activator (TOP SAN, Okuno Chemical). During the potentiostatic electrolysis, WE and CE were set to be parallel.

#### 2.4 Bath characterization

Bath conductivity measurements were performed using Japan Machinery CDM230 and CDC749, and kinematic viscosity measurements were conducted using SEKONIC VM-10A calibrated using a standard solution (Nippon Grease Co., Ltd.). These measurements were performed in a dry-air-filled atmosphere at less than 40 ppm H<sub>2</sub>O. Raman spectroscopy measurements were performed at RT using an integrated Raman system (B&W Tek, innoRam 785) comprising a semiconductor laser light source (785 nm), a holographic probe head, an axial transmissive spectrograph, and a charge-coupled device (CCD) detector. The sample solutions were sealed under Ar with septum and then measured within an hour after taken out from a glove box. The spectral acquisition time, *i.e.*, exposure time of CCD and the

number of exposures was varied for each sample so as to improve the signal-to-noise ratio of each spectrum. In order to lessen the fluorescence as background intensity each glyme bath was measured after pre-electrolysis at -1.0 V *vs*. Al QRE for 1 or 2 days to obtain colorless solution. For the G3 and G4 baths the current densities during the pre-electrolysis were almost constant at approximately 0.1 mA cm<sup>-2</sup>.

### 2.5 Characterization of electrodeposits

After electrolysis the deposits were characterized by means of X-ray diffraction (XRD; Rigaku RINT2200; 40 kV–30 mA, 0.4 degree min<sup>-1</sup>) and scanning electron microscopy (SEM; Keyence VE-8800), in order to check the crystal orientation and surface morphology. Energy dispersive X-ray (EDX; EDAX Genesis 2000) and X-ray photoelectron spectroscopy (XPS; JEOL, JPS-9010TRX) were carried out to examine the contents and/or chemical states of Al and Cl. The XPS was performed using a Mg-K $\alpha$  X-ray source with Ar<sup>+</sup> ion etching at a rate of approximately 18 nm min<sup>-1</sup>, which was determined from a SiO<sub>2</sub> standard film. The XPS spectra were calibrated assuming that the C 1s peak position from hydrocarbons would be 285.0 eV. XPS, XRD and SEM observations were carried out for the deposits after washing with pure G2 and vacuum-drying.

## 3. Results and Discussion

#### 3.1 Cyclic voltammetry

Figure 2(a) shows the CVs for the glyme baths at RT, where Cu was used as WE. For the G2 bath, the onset potential of Al deposition was ca. -0.7 V vs. Al QRE, a reduction loop with the overpotential of ca. 0.2 V was observed, and the Coulombic efficiency was ca. 75%. In addition, the dissolution of Al took place at a negative potential of -0.2 V, suggesting that the Al QRE have surface oxides to show a positive potential compared to the freshly deposited Al on WE. Similar negative shifts have been observed when Al QRE was directly immersed to the baths [22–24]. While large reduction currents and the corresponding oxidation currents (order of mA cm<sup>-2</sup>) were observed for the G2 bath as reported previously [47], only small reduction currents of the order of 0.1 mA cm<sup>-2</sup> were observed from near +0.5 V for the other glyme baths. With an onset potential of +0.8 V a reversible but small oxidation and reduction current was observed in every glyme bath; this was attributed to Cu(I)Cl formation [47].

Figure 2(b) displays CV results for Al WE at RT, where small cathodic overpotentials were anticipated and Al electrodeposition would occur even in the G3 and/or G4 baths. However, sizable reduction currents were observed only in the G2 bath. The onset potential was -0.7 V vs. Al QRE, similar to the case of Cu WE. The increase of potential in the G2 bath around 0 V is due to dissolution of deposited Al making an anodic wave that finished at about +0.3 V or +0.4 V, followed by a sharper increase due to dissolution of the Al substrate. In the G3 and G4 baths, the cathodic currents were even smaller than in the case of Cu WE: as a result, there was no evidence of Al electrodeposition from G3 or G4 baths with overpotentials of

approximately 0.3 V was due only to dissolution of the Al substrate. We speculate that the small reduction currents correspond to the decomposition of impurities, not deposition of Al.

At elevated temperature the G2 bath showed larger redox currents than those at RT. Especially, a cathodic current of about 15 mA cm<sup>-2</sup> was observed at 60 °C. Up to 60 °C the redox currents became larger as temperature increases, and the bath properties also improved (see Table I). At 70 °C, by contrast, the redox current was halved compared to that at 60 °C (see Fig. 2(c)). This may be related to the sample color being brown at 70 °C, implying that thermal decomposition affects redox properties. CV measurements were also performed in the G3 and G4 baths at 60 °C. Compared with those at RT (Fig. 2(a)), larger reduction currents were observed from a similar onset potential of +0.5 V *vs*. Al QRE, while corresponding stripping currents were not observed (see Fig. 2(d)), suggesting that these currents are not due to Al deposition. It should be noted that a similar reduction current loop with a similar onset potential of +0.5 V has been reported for AlCl<sub>3</sub>-containing organic baths, although it is not clear whether they have the same origin [51].

Consequently, electrodeposition from the G3 and G4 baths was not successful at this point. It seems that G3 and G4 have much stronger interactions with Al<sup>3+</sup> than G2, thereby preventing the complexes from being electrochemically reducible to metallic aluminum. A detailed discussion of electrochemically active species is presented below.

### 3.2 Stability of Al electrode in the glyme baths

Figure 3 shows the potential difference between two Al electrodes immersed in the glyme baths. For the G2 bath the potential difference was fairly small for 20 h, with an average

value of  $-1.355\pm0.009$  mV. The long-term stability of the Al electrode in the G2 bath indicates that the redox should be dominated by Al<sup>3+</sup> + 3e = Al and that the Al electrode can be utilized as a favorable 'reference electrode of the first kind' [52]. The potential differences for the other glyme baths were not so small as that for G2. Nonetheless, in the G3, G4, and butylG2 baths the Al electrodes worked as QRE in the CV experiments, since the potential difference seldom fluctuated in a short period. The origin of the fluctuation of the potential for G3, G4 and butylG2 is not clear at this point. It may be better to use another reference electrode instead of Al, which was directly immersed in the electrolytes. For example, Al immersed in a chloroaluminate ionic liquid, which is separated from the electrolytes by a liquid junction may cause less potential fluctuation, although contamination from the liquid junction could take place.

#### 3.3 Bath properties at room temperature

Table II lists the molar conductivities and viscosities of the four kinds of glyme solution at 28 °C. Among them the G2 bath has the highest conductivity and the lowest viscosity. Nevertheless, the physical properties for the G2, G3 and G4 baths have the same order of magnitude, indicating comparable concentrations of ionic species. In fact, a previous NMR study on G2 and G3 solutions indicated that the ionic species in the G2 bath are four-Cl-coordinated AlCl<sub>4</sub><sup>-</sup> and six-O/Cl-coordinated [AlCl<sub>2</sub>(G2)<sub>2</sub>]<sup>+</sup>, while those in the G3 bath are AlCl<sub>4</sub><sup>-</sup>, [AlCl<sub>2</sub>(G3)<sub>n</sub>]<sup>+</sup> and [AlCl(G3)<sub>n</sub>]<sup>2+</sup> [50]. Notably, the six-O/Cl coordination needs at least two G2 molecules because a G2 molecule has only three ether oxygens. The butylG2 bath conductivity is one order of magnitude lower compared to the other baths.

Because its viscosity is similar to the other values, the low conductivity should be caused by a low concentration of ionic species. Given a specie  $[AlCl_x(butylG2)_n]^{(3-x)+}$  with hexacoordination in the butylG2 bath, at least two molecules are required for complexation in addition to G2; however, the approach by the oxygen atoms to  $Al^{3+}$  could be hindered due to the terminal butyl chains of butylG2, likely resulting in the low ion concentration.

### 3.4 Raman spectroscopy

In Raman spectroscopy the CH<sub>2</sub> rocking and C-O-C symmetric stretching vibration area ranged between 900 cm<sup>-1</sup> and 780 cm<sup>-1</sup>. Figure 4 displays the Raman spectra for the case of G2. It is known that C-O-C vibrations in ethers usually locate between 890–850 cm<sup>-1</sup>. For the case of free ethers, which are not coordinated by alkaline metal cations, the Raman band is observed at 852 cm<sup>-1</sup> [46, 53]. The Raman band for free G2 at 852 cm<sup>-1</sup> is also seen in the AlCl<sub>3</sub>-containing G2 bath, indicating that a sizable amount of free G2 is still present even in the 1:3 bath. In the case of ethers coordinated by alkaline metal and alkaline earth cations, the Raman band for C-O-C vibration is seen as a blue shift, at 880–890 cm<sup>-1</sup> [46,54,55]. A shoulder peak appears at around 870 cm<sup>-1</sup> by AlCl<sub>3</sub> addition, which should correspond to [AlCl<sub>2</sub>(G2)<sub>2</sub>]<sup>+</sup> species as reported from the previous NMR results [50]. The positions of the shoulder peaks are somewhat smaller than those for [Li(glyme)<sub>n</sub>]<sup>+</sup> or [Mg(glyme)<sub>n</sub>]<sup>2+</sup> in Li<sup>+</sup> and Mg<sup>2+</sup> amide-glyme solutions [46,54,55], which may be due to the presence of Cl atoms. Note that the peak at 835 cm<sup>-1</sup>, which appears by AlCl<sub>3</sub> addition, should be assigned as an Al-Cl-G2 complex.

The spectra for the G3 and G4 systems also show shoulder peaks at around 870 cm<sup>-1</sup> like

 the G2 system (see the left panel of Fig. 5), strongly indicating that similar Al-Cl-glyme complexes of  $[AlCl_2(glyme)_n]^+$  cations exist and supporting the previous NMR results [50]. For the case of butylG2, the strongest peak is located at 840 cm<sup>-1</sup>, which differs from those for the G2, G3, G4 centered at 850 cm<sup>-1</sup>, due to the different length of terminal alkyl chains. However, no additional peaks are clearly observed for the AlCl<sub>3</sub>-containing bath, probably due to the low ion concentration as suggested by the bath properties (see Table II).

In other spectrum regions, Raman spectra for haloaluminate anions are specifically seen between 100 and 400 cm<sup>-1</sup> [56]. In the right panel of Fig. 4 the Raman profiles of the G2 baths show a broad peak at 310 cm<sup>-1</sup> and three sharp peaks at 120 cm<sup>-1</sup>, 179 cm<sup>-1</sup>, and 347 cm<sup>-1</sup>. Although it is reported that  $Al_2Cl_7$  shows a peak at 310 cm<sup>-1</sup>, the observed broad peak is very similar to that in pure G2, strongly indicating the absence of  $Al_2Cl_7$  in the  $AlCl_3/G2$ bath. Note that the previous NMR results also suggest the absence of  $Al_2Cl_7$  [50]. In the right panel of Fig. 5, the spectra for the G3, G4, and butylG2 baths resemble those for the G2 bath in appearance, strongly suggesting that the only anion is  $AlCl_4$ . These results afford collateral evidence of the existence of cationic species in the butylG2 bath, even though peaks for cationic species were not clear in the Raman spectra.

#### 3.5 Electrochemically active species

It is known that  $AlCl_4^-$  is electrochemically inactive while  $Al_2Cl_7^-$  is active in the case of RT ionic liquids. Since the anionic species in the G2 bath are  $AlCl_4^-$ , we conclude that cationic species  $[AlCl_2(G2)_2]^+$  are electrochemically active. Similarly, in  $AlCl_3$ -sulfone systems the electrochemically active species are  $[Al(sulfone)_3]^{3+}$  cations [56]. The

sulfone-solvated  $Al^{3+}$  species are generated together with the formation of  $AlCl_4^{-}$ . Since the resource of Cl<sup>-</sup> is AlCl<sub>3</sub>, asymmetric cleavage of AlCl<sub>3</sub> occurs to form AlCl<sub>4</sub><sup>-</sup> and  $[Al(sulfone)_3]^{3+}$ . In the case of 4-propylpyridine (4-Pr-Py) bath, the asymmetric cleavage of AlCl<sub>3</sub> generates AlCl<sub>2</sub><sup>+</sup> and AlCl<sub>4</sub><sup>-</sup>, and the former is coordinated by 4-propylpyridine to produce the Al-containing cations ( $[AlCl_2(4-Pr-Py)_2]^+$ ) [19]. A similar solvation mechanism should occur with AlCl<sub>3</sub>-glyme. We also suggest that similar monovalent cationic species (*i.e.*  $[AlCl_2(G3)_n]^+$  and  $[AlCl_2(G4)_n]^+$ ) exist in the G3 and G4 baths, although they are not electrochemically active in marked contrast to  $[AlCl_2(G2)_2]^+$ . The coordination number is six where two chlorine atoms and four oxygen atoms coordinate to an  $Al^{3+}$  metal center for these monovalent cationic species. As we described above, because a G2 molecule has only three ether oxygens, two G2 molecules are needed to form the hexacoordinated complex (see Fig. 6); for the G3 and G4 complex, by contrast, even a single G3 or G4 molecule can form hexacoordination together with two chlorine atoms, which in turn cause a larger chelating effect or greater stabilization. Therefore, it is natural to consider that the G3 or G4 complex cations are hard to desolvate, resulting in electrochemical inactiveness. The fact that for bath preparation it is harder for G2 to dissolve AlCl<sub>3</sub> than for G3 and G4 may also suggest the weaker solvation of G2. Notably, the previous NMR results indicated that cationic species in the G3 bath include not only monovalent  $[AlCl_2(G3)_n]^+$  but also divalent  $[AlCl(G3)_n]^{2+}$ cations [50]. Similar divalent complexes could be present in the G4 bath, although no NMR studies for AlCl<sub>3</sub>/G4 have been presented so far. Such divalent G3 and/or G4 complexes would also have difficulty with desolvation, like the monovalent G3 and G4 complexes.

## 3.6 RT electrodeposition of Al

Cathodic deposition was performed potentiostatically at -2 V using the G2 bath for 55 C cm<sup>-2</sup>. The cathodic current during the deposition was approximately 8 mA cm<sup>-2</sup>, twice as large as that during the deposition at -1 V [47]. During electrolysis the G2 bath remained colorless and transparent, indicating that bath decomposition hardly occurred. As shown in Fig. 7(a), black deposits were obtained on Cu WE, like in the previous report [47]. It should be noted that when the deposits were peeled off using an adhesive tape, the surface contact to Cu WE substrate exhibited a metallic luster (see Fig. 7(b)).

The XRD measurements shown in Fig. 8 confirmed that the deposits consisted of crystalline Al metal without trace impurities such as  $Al_2O_3$ ; in the case of potentiostatic electrodeposition at -1 V *vs*. Al QRE [47] the XRD profiles also show the deposits were crystalline Al. No preferential orientation was observed. XPS analysis with  $Ar^+$  etching was conducted for the Al deposits to check the impurity contents and chemical state together with the depth profile. As a result O, C, and Cl were detected as the main impurities. Because the inclusion of Cl is characteristic of coatings electrodeposited from AlCl<sub>3</sub>-containing electrolytes [17], we focus on Cl. Fig. 9 shows the XPS spectra of the Cl 2p region, where a peak centered at ca. 200 eV was observed. This agrees with the Cl 2p<sub>3/2</sub> binding energies for many chlorides. The Cl content was about 4% before etching, and decreased with increasing  $Ar^+$  etching time, but did not become zero even after etching for 56 ks (ca. 1%). This confirms that the Cl was incorporated into the Al coating during the electrodeposition, and was not a surface contaminant. Notably, after etching the deposits showed a metallic luster.

Therefore we suggest that the black appearance was caused by the surface morphology *i.e.* rough surface.

Figure 10 shows SEM images of the deposits. A rough surface was also observed on the deposits obtained at -1 V [47]. Nonetheless, the deposits were almost flat and the thickness was 18–19 µm, in good agreement with the calculated one assuming 100% current efficiency (18.9 µm), indicating that the coatings were compact. EDX analysis for the area shown in Fig. 10(a) also indicated the presence of O, C, and Cl. While quantitative analysis of light elements such as O and C is difficult, the Cl content can be estimated; the value was approximately 2%, comparable to the XPS results.

#### 4. Conclusions

In order to develop relatively safe electrolytes for Al electrodeposition, a series of AlCl<sub>3</sub>-containing glyme baths were systematically studied. It was indicated that the ionic species in all glyme baths are AlCl<sub>4</sub><sup>-</sup> and [AlCl<sub>2</sub>(glyme)<sub>n</sub>]<sup>+</sup>, but only the G2 complex is electrochemically reducible to metallic aluminum due to the easy desolvation of G2. This strong dependence on the type of glymes seems specific to Al electroplating, and contrasts with lithium and magnesium electrodeposition [41–46]. Potentiostatic electrodeposition results using the G2 bath demonstrated that the coatings electrodeposited at as low as -2 V vs. Al QRE were essentially composed of a single phase of Al metal, although XPS indicated that Cl was incorporated in the states of chloride. However, the absence of a black appearance by Ar<sup>+</sup> etching suggests that the black appearance was caused by the surface

morphology, *i.e.*, a rough surface, and was not due to impurities. Further studies on AlCl<sub>3</sub>/glyme baths such as bright and/or flat electrodeposition using additives are of special interest.

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Table I. Bath properties of the G2 bath with the molar ratio of  $AlCl_3:G2 = 1:5$  at several temperatures.

Table II. Bath properties of the glyme baths at 28  $^{\circ}$ C with the molar ratio of AlCl<sub>3</sub>:glyme = 1:5.

Figure 1. Schematic structure of glymes used in this study.

**Figure 2.** CVs with sweep rate of 20 mV s<sup>-1</sup> in AlCl<sub>3</sub>-dissolved glyme solution with AlCl<sub>3</sub>:glyme = 1:5 by mol, under the condition of (a) Cu WE at RT, (b) Al WE at RT, (c) Cu WE at several temperatures, and (d) Cu WE at 60 °C.

**Figure 3.** Time change in potential difference between two Al electrodes immersed in the glyme at RT with molar ratio of  $AlCl_3$ :glyme = 1:5. Dashed line indicates zero line.

**Figure 4.** Raman spectra for the AlCl<sub>3</sub>:G2 = 1:3 and 1:5 by mol, and pure G2 obtained between 900 cm<sup>-1</sup> and 780 cm<sup>-1</sup> (left panel) and between 400 cm<sup>-1</sup> and 100 cm<sup>-1</sup> (right panel). Dashed lines emphasize specific peaks for Al<sup>3+</sup>-G2 complex, pure G2 and AlCl<sub>4</sub><sup>-</sup>.

**Figure 5.** Raman spectra for the AlCl<sub>3</sub>:glyme = 1:3 and pure glyme obtained between 900  $\text{cm}^{-1}$  and 780  $\text{cm}^{-1}$  (left panel) and between 400  $\text{cm}^{-1}$  and 100  $\text{cm}^{-1}$  (right panel). Dashed lines emphasize specific peaks for Al<sup>3+</sup>-glyme complex, pure glyme and AlCl<sub>4</sub><sup>-</sup>.

**Figure 6.** Possible schematic structures of  $[AlCl_2(glyme)_n]^+$  complexes for the case of G2 (top), G3 (middle), and G4 (bottom).

**Figure 7.** Photographs of the Cu WE electrodeposited from the G2 bath at -2 V *vs*. Al QRE: (a) obverse side and (b) reverse side, which appeared by peeling off the deposits with an adhesive tape.

**Figure 8.** XRD profiles of the electrodeposits obtained at -2 V vs. Al QRE.

Figure 9. XPS spectra of the Al electrodeposits obtained at -2 V vs. Al QRE.

**Figure 10.** (a) Top view and (b) cross-sectional view of the SEM images for the Al deposits obtained at -2 V *vs*. Al QRE.

Temperature	Conductivity (mS cm <sup>-1</sup> )	Viscosity (mPa s)
28 °C	4.08	2.92
40 °C	4.48	2.67
50 °C	5.53	2.35
60 °C	6.48	2.03

Table(s)

Electrolyte	Conductivity (mS cm <sup>-1</sup> )	Molar conductivity (S cm <sup>2</sup> mol <sup>-1</sup> )	Viscosity (mPa s)
G2	4.08	2.92	2.71
G3	2.07	1.88	4.54
G4	1.10	1.14	6.24
butyl G2	0.16	0.19	5.42







Time / hour









Figure(s)





Figure(s)





Binding energy / eV

Figure(s)

