

AlCl₃-dissolved Diglyme as Electrolyte for Room-Temperature Aluminum Electrodeposition

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ABSTRACT

We first report an AlCl₃-containing diglyme electrolyte for room temperature Al electrodeposition, which have relatively low volatilities and low cost. With the molar ratio of AlCl₃ : diglyme = 1:5, the diglyme solution enabled deposition and dissolution of Al, which required relatively small overpotentials at room temperature. The deposits were not dendritic, indicating potential applications for Al plating or Al ion batteries. (62 words)

Keywords: Aluminum Electrodeposition; Room Temperature; Electrolyte; Diglyme

1. Introduction

Aluminum (Al) metal is industrially important because of its lightweight property, workability, and corrosion resistance. This light element is also attractive as a negative electrode material due to its low redox potential (-1.68 V vs. SHE) and high theoretical capacity.¹ Electrodeposition of Al and/or Al alloys has been reported in many kinds of electrolytes using Aluminum halides and/or hydrides,² although they are water-sensitive. Besides, the media range from high temperature molten salts,³ organic solvents (e.g. ethers,^{4,5} aromatic hydrocarbons,⁶⁻⁹ and dimethylsulfone (DMSO₂),¹⁰⁻¹⁵ and ionic liquids (ILs).¹⁶⁻²¹ Although the high temperature baths have mainly been used for industrial Al electrorefining, medium-low and/or room temperature (RT) baths are anticipated as promising Al electroplating and/or Al battery electrolytes. However, the reported organic solvents such as diethyl ether, tetrahydrofuran (THF) and benzene are so volatile even at RT; DMSO₂ is solid at RT and thus the DMSO₂ has mainly been utilized at 110 °C or above.¹⁰⁻¹⁵ Notably, the use of DMSO₂ baths may cause sulfur contamination.¹⁴ By contrast, ILs are less volatile and available for RT Al deposition; however, some ILs are highly viscous and still expensive for practical use. To improve the physical properties of Al electroplating baths, ILs have often been mixed with organic solvents, resulting in the loss of non-volatility i.e. the merit of ILs.^{17,21,22} Consequently, alternation of Al deposition baths are desired for several decades in interests of both safety and cost. Very recently glycol ethers i.e. glymes receive attention as relatively safe solvents for lithium and magnesium ion batteries, because they have high boiling points above 150 °C and relatively low volatilities at RT in addition to their good chelating ability.²³⁻²⁶ Furthermore, previous

NMR studies have indicated sizable amount of *ionic* Al species in glyme solutions,²⁷ possibly giving good conductivities. To the best of our knowledge, however, there have been no reports on their electrochemical properties. Here we report RT electrodeposition of Al without dendritic formation from an AlCl₃-dissolved diglyme solution.

2. Experimental

2.1. Preparation of Bath

Diethyleneglycol dimethyl ether (diglyme, Electrochemistry Grade, Kanto Chemical), was dehydrated to contain less than 40ppm H₂O using 3A molecular sieves before bath preparation. As-received AlCl₃ (Wako, 99.9% purity) was added into four molar excess of the dehydrated diglyme little by little to avoid thermal degradation, and then heated at 65 °C for 12 h with the agitation speed of 500 rpm in an Ar-filled glovebox. The water content of the solution was 200–300ppm, determined by Karl Fischer titration.

2.2 Electrochemical measurements

Electrochemical measurements were performed without stirring in the Ar-filled glove box with a potentiostat (Hokuto Denko, HSV-110). An electrode cell of which planar dimension of WE was fixed to 7.5 mm ϕ (EC Frontier, VM-2A) was utilized for cyclic voltammetry (CV). A Cu sheet (Nilaco, 99.9% purity, 0.080 mm thickness) or an Al sheet (Nilaco, >99% purity, 0.5 mm thickness) with 1.0 \times 2.0 cm² was used as working electrode (WE). Other two pieces of Al sheets directly immersed in the same electrolyte was used as

counter electrode (CE) and quasi-reference electrode (QRE). All the electrodes were washed with acetone before use. Note that we have purified the diglyme bath through a pre-electrolysis on Cu WE at -1.0 V vs. Al QRE for 24 h, where we obtained black sponge Al deposits; after the pre-electrolysis the bath changed from orange to colorless solution, possibly indicating the elimination of any impurities like iron. In the potentiostatic electrolysis, WE and CE were set to be parallel. After deposition the WE was washed with THF.

2.3 Characterization

The deposits were characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The cross-sectional SEM images were obtained using specimens split by hand without polishing the faces. For the bath characterization conductivity measurements were performed using Japan Machinery CDM230 and CDC749. Viscosity measurements were conducted using SEKONIC VM-10A calibrated using a standard solution (NIPPON GREASE Co., Ltd.). These bath characterization measurements were performed in a dry-air-filled box (DAIKIN HRG-50A) with less than 40 ppm H_2O .

3. Results and Discussion

Figure 1 shows the CVs for AlCl_3 -dissolved diglyme solutions. With the onsets for Al deposition at -0.3 V and Al dissolution at around 0 V, a relatively large reduction and the corresponding oxidation currents reaching 4 mA cm^{-2} were observed. The coulombic

efficiency for dissolution/deposition was 95% at the 10th cycle. Notably, the electrochemical window was +1.0 V vs. Al QRE for Cu WE due to the formation of solid Cu(I)Cl on WE, confirmed by XRD (not shown); instead, the use of a tungsten electrode showed that the electrochemical window was about +2 V vs. Al QRE, probably due to oxidative decomposition of diglyme.

Presented in Fig. 2a is a photograph of the Cu WE electrodeposited at -1.0 V, coated by black sponge deposits. The XRD profiles show very sharp peaks with very similar intensity ratio of standard Al, indicating less preferential orientation (see Fig. 2b). The current efficiency for deposition at -1.0 V for 24 h was calculated to be 100% within an experimental error from the mass change using an Al sheet as WE.

Figure 3 displays the current-time plots for the cathodic deposition at -1.0 V. The cathodic current density at the beginning was as large as about 3.2 mA cm^{-2} , suddenly increased to about 4 mA cm^{-2} within an hour and almost constant for the first 19 h, followed by about 10% increase in the last few hours. The increase in current density probably corresponds to the formation of rough surface with the enlarged effective surface area. In fact, porous surface was observed in the plan view of the deposits, but the cross-sectional view indicated that except the top the deposits were densely packed without dendritic formation underneath (see Fig. 4). In the SEM image the thickness was about 130–140 μm , similar to the average thickness of 126 μm calculated from the total charge passed; the difference should come from the nodules at the corner of WE (see Fig. 2a). Shorter deposition time (less than 19 h) may result in dense deposits without porous surface.

Without any supporting electrolytes the diglyme bath showed the conductivity of 4.06 mS cm⁻¹ or 2.91 S cm² mol⁻¹, comparable to those of reported organic solvent baths with supporting electrolytes.^{6,7,22} A previous spectroscopic study on 1.7 mol dm⁻³ diglyme solution of AlCl₃ (cf. 1.4 mol dm⁻³ in this study) showed that the system consists of molecular species (AlCl₃·diglyme) and ionic ones of four-Cl-coordinated AlCl₄⁻ and six-O/Cl-coordinated [AlCl₂(diglyme)₂]⁺.²⁷ Therefore the sufficient conductivity should result from the sizable amount of the ionic Al species. Although the conductivity was an order of magnitude smaller than that of a conventional imidazolium aluminate IL, the viscosity of the diglyme bath was 2.71 mPa s, an order of magnitude smaller than that of the IL and very similar to the case of 60vol%-benzene-added IL.²² At this point, however, it has not been excluded that the residual water of 300 ppm in the diglyme bath, which can cause H⁺, may also affect the bath properties.

4. Conclusion

The less volatile diglyme-AlCl₃ two-component bath showed Al deposition/ dissolution, where relatively small overpotentials were observed at RT, probably due to its relatively high conductivity and low viscosity. Although the deposit was not smooth enough to show metallic luster, they were densely grown without dendrites. Electrolysis at an elevated temperature would improve surface morphology. Effect of water content on the electrolyte properties is also of interest.

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Figure 1. CVs during ten cycles with sweep rate of 20 mV s^{-1} in the AlCl_3 -dissolved diglyme with $\text{AlCl}_3 : \text{diglyme} = 1:5$ by mol.

Figure 2. (Color online) (a) Photograph and (b) XRD profile of the Cu WE electrodeposited at -1.0 V vs. Al QRE for 24 h.

Figure 3. Current-time plots for electrodeposition at -1.0 V vs. Al QRE for 24 h.

Figure 4. SEM images in plan view (a,b) and cross-sectional view (c,d) of Al deposits obtained at -1.0 V vs. Al QRE from the diglyme bath.

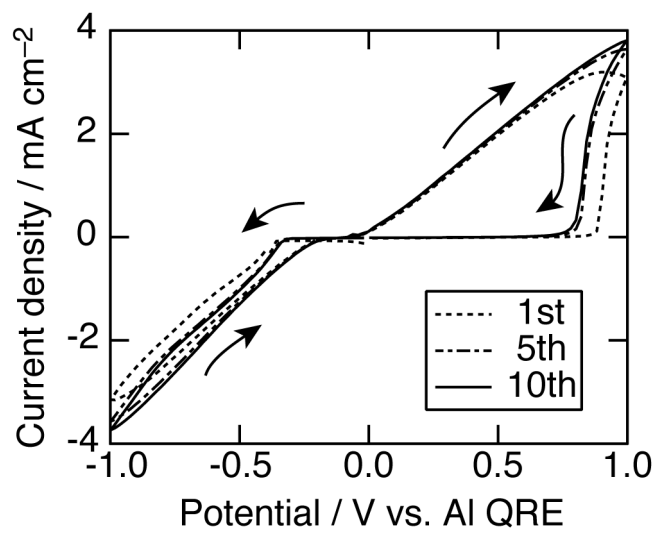


Fig.1 A. Kitada *et al.*

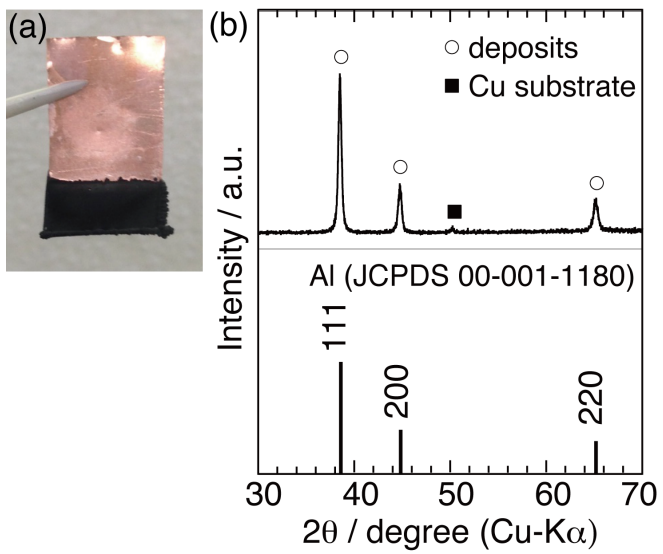


Fig. 2 A. Kitada *et al.*

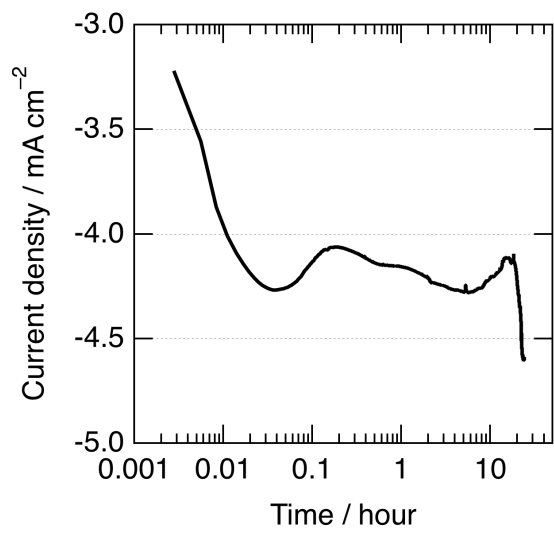


Fig. 3 A. Kitada *et al.*

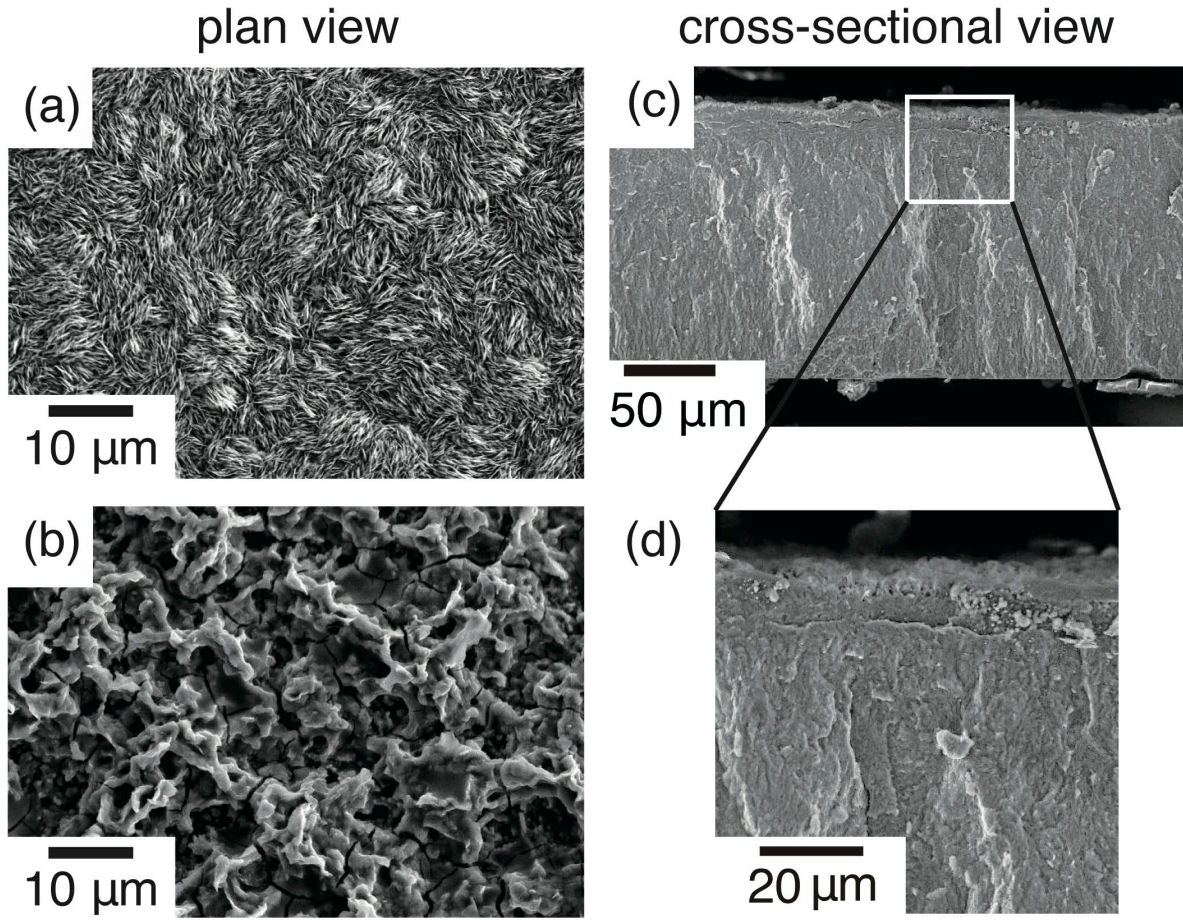


Fig. 4 A. Kitada *et al.*