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Effect of Li Ions on Al Electrodeposition from Dimethylsulfone

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Abstract

The influence of LiCl coexistence with Al electrodeposition was investigated in a dimethyl sulfone, $DMSO_2$, bath containing $AlCl_3$ at 403 K. The electrochemical behaviors of Li and Al ions were examined using Pt electrodes in the bath and the deposition mechanism was analyzed by cyclic voltammetry, CV, with an Al reference electrode in the bath. The coexistence of LiCl in the $AlCl_3$-$DMSO_2$ bath inhibited the cathodic current corresponding to Al deposition in the CV experiment. The amount of ca. 500 μmol Al deposits was obtained in constant potential electrolysis for 1 h at −2 V in the bath with 10 mol% $AlCl_3$. However, it decreased to 140 μmol Al in the bath with 10 mol% $AlCl_3$ and 5 mol% LiCl. It was clarified that LiCl addition led to the formation of $Li(DMSO_2)^+$ more than the formation of $Al(DMSO_2)_3^{3+}$ from NMR measurement for the baths. This results in the suppression of Al deposition because LiCl inhibits the formation of $Al(DMSO_2)_3^{3+}$ complex ions, which is said to be necessary for Al electrodeposition.

Keywords

Electrodeposition, Aluminum, Lithium, Nuclear Magnetic Resonance, Dimethylsulfone

1. Introduction

Plating technology in surface treatment using aqueous solutions is one of the useful techniques for prolonging the life of metal products. Although aluminum, Al, is a less noble metal, Al reacts with O_2 in the air to form a dense oxide film, a passive state, so it is excellent in corrosion resistance. Because Al is also lightweight and has good features such as a glossy and beautiful surface, it is ap-

propriate for use as a plating material. Indeed, galvanized Al plating, *i.e.*, hot dipping, has been applied to a variety of pipes, heat exchange tubes, boilers, bolts, and nuts. Although galvanized and electroplated Zn films have been widely used as anticorrosive plating, Al is attracting attention as an alternative material to Zn because of concerns about exhaustion of Zn resources. It is, therefore, considered that progress in the Al plating processing technique is very important.

Several surface treatment methods, such as ionic liquids [1]-[9], molten salts [10] [11] [12], physical vapor deposition [13] [14], chemical vapor deposition, spray coating [15] [16], cementation [17] [18], sputtering [19] [20], hot dipping [21] [22], and electroplating [23] [24] [25], have been proposed to protect substrate against corrosion and to improve its other properties.

In the cases of vacuum plating using chemical or physical vapor depositions, the difficulty of mass production leads to a higher unit production cost, and a thin coating film may result in a stain on the basic material upon postprocessing. Moreover, hot dipping cannot provide a fair-quality coating film. It is also known that unlike other commercialized coating methods, Al metal cannot be obtained from aqueous solution because hydrogen evolution is dominant [26] [27]. The electrolyte must be aprotic. Essentially, two types of electrolytes are suitable: molten salts or electrolytes based on organic aprotic solvents. Both types are sensitive to moisture and air, and avoidance of these factors is essential for the bath life [23]. Accordingly, coating methods using organic compounds such as nonaqueous solvent and ionic fluid have been examined. These compounds are the nonvolatile ionic solvents $AlCl_3$-*N*-ethylpyridinium bromide, $AlCl_3$-*N*-ethylpyridinium chloride, $AlCl_3$-1,3-dialkylimidazolium chloride, and $AlCl_3$-1-butyl-1-methylpyrolidinium [28] [29] [30].

These ionic liquids have been recently proposed as alternative electroplating solutions [31] [32] [33]. In comparison with an ionic liquid, a lower vapor pressure, a higher electric conductivity, a wider electrochemical window, and its high flammability hinder its widespread use in many applications. To solve these problems, $AlCl_3$/dimethyl sulfone has been employed for electroplating at low temperature [34]-[42]. Dimethyl sulfone, $(CH_3)_2SO_2$ (called $DMSO_2$), is a nontoxic white crystalline powder with high solubility in $AlCl_3$ and in organic solvents such as acetone and ethyl alcohol, and exhibits a low melting point of 382 K [43].

None of the less noble metals, such as aluminum and lithium, can be electrodeposited from a system using water as a solvent. Therefore, by dissolving chlorides such as aluminum chloride, $AlCl_3$, or lithium chloride, LiCl, using $DMSO_2$ instead of water and performing electrolysis, it is expected that the reduction reaction of metal ions occurs on the cathode electrode and electroplating can be performed.

^{27}Al NMR [33] and Raman analyses [38] of the $AlCl_3$-$DMSO_2$ mixtures indicate that there are two main soluble aluminum species, namely $AlCl_4^-$ and

$Al(DMSO_2)_3^{3+}$, formed according to the following reaction, although some researchers suggest the coexistence of $Al_2Cl_7^-$ [44]:

$$4AlCl_3 + 3DMSO_2 = Al(DMSO_2)_3^{3+} + 3AlCl_4^- \qquad (1)$$
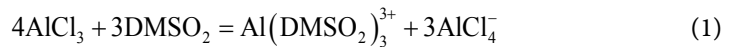
The electrodeposition of Al can occur from the solvated cation $Al(DMSO_2)_3^{3+}$, whereas the reduction of $AlCl_4^-$ is not observed within the electrochemical window of the electrolytes. It has been demonstrated that dense, uniform Al coatings with a high corrosion resistance can be electrodeposited from $AlCl_3$-$DMSO_2$ baths at 383 K [33] [43] [45] [46].

In this study, we investigated the electrochemical behavior in an $AlCl_3$-$DMSO_2$ bath with LiCl addition to obtain the effect of Li ions on the $Al(DMSO_2)_3^{3+}$ formation and Al deposition from NMR analysis for the bath and constant potential electrolysis, respectively. The possibility of Li electrodeposition was also examined in a LiCl-$DMSO_2$ bath.

2. Experimental

2.1. Electrode Preparation

Platinum plate and copper plate (>99% purity, Nilaco) were used as working electrodes for cyclic voltammetry, CV, measurement and electrolysis at a constant potential. They were masked with insulating tape, Nitoflon, leaving an exposed surface area of 1.0 cm². The Cu plate was wet-polished with 400 emery paper, and the Pt plate was also wet-polished, immersed in hydrochloric acid, washed with distilled water, and then washed with acetone for 20 min before tape masking. An Al rod (>99.99% purity, Nilaco) was immersed in the bath as a reference electrode, Al/Al^{3+}. Pt plate was also used as a counter electrode.

2.2. Bath Preparation

To remove moisture of ca. 300 ppm contained in $DMSO_2$ (99 mass%, Tokyo Chemical Industry, Japan), the $DMSO_2$ powder was maintained at 353 K for 72 h in a constant temperature drier (DO-450 A, AS ONE Corporation) and melted at 403 K. The amount of $DMSO_2$ used in each experiment corresponded to 0.2 mol.

A bath with 10 mol% or 20 mol% $AlCl_3$ was prepared by adding aluminum chloride, $AlCl_3$ (98 mass%, Nacalai Tesque, crystallized), to the melted $DMSO_2$. Further, a Li-Al bath was prepared by adding 0 - 20 mol% of lithium chloride, LiCl (98 mass%, Nacalai Tesque, crystallized) to each Al bath. Bath preparation was conducted in an Ar-filled glove box.

2.3. Electrochemical Measurements and Characterization of Deposits

Electrochemical properties were measured in the Ar-filled glovebox with a potentiostat/galvanostat (BioLogic, SP 150). Cyclic voltammograms were obtained at the potential region between –3.5 V and 3.5 V vs. Al/Al^{3+} at a scan rate of 100

mV·s^{-1}. Electrodeposition was attempted on the Cu plate by constant potential electrolysis under −2 V for 1 h. The temperature was maintained at 403 K using a hotplate. The electrolyte was agitated at 150 rpm during the experiment using a magnetic stirring device at the bottom of the beaker.

2.4. Bath Characterization

^{7}Li and ^{27}Al NMR spectra were obtained at 130.3 MHz using a 500 MHz NMR spectrometer (Agilent Technology). All chemical shifts were referenced to D_2O containing 1.5 M Al(NO$_3$)$_3$, which was used as an external reference. Samples were placed in 10 mm NMR tubes with a 5-mm coaxial tube filled with DMSO-d$_6$ as a lock solvent. Spectra were gathered at 403 K, as in the electrochemical measurements.

2.5. Characterization of Electrodeposits

After electrolysis, deposits were washed with an AlCl$_3$–DMSO$_2$ solution and vacuum-dried prior to characterization. Crystal orientation and surface morphology of the deposits were characterized by X-ray diffraction, XRD (Rigaku Ultima IV; 40 kV, −30 mA, 0.4 deg·min^{-1}), and the nitric acid solution was collected by suction and analyzed for Al and Li by inductively coupled plasma-atomic emission spectrometry, ICP-AES (Seiko Instruments, SPS 7800).

3. Results and Discussion

3.1. Electrochemical Behavior in DMSO$_2$ Bath Containing LiCl Only

The possible cathodic reactions on Pt electrode were examined, initially, by CV measurements in a DMSO$_2$ electrolyte containing LiCl at concentrations between 5 and 20 mol% at 403 K. The electrode potential was scanned from the open-circuit potential near 1 V in the negative direction to −3.5 V followed by scanning in the positive direction to 3.5 V and then cycled.

Figure 1 shows the voltammograms recorded after 20 cycles. The shapes of the curves did not change after five cycles. Several peaks of redox reactions were obtained. Compared with the result in the bath with AlCl$_3$ only as described later in Figure 5(a), Figure 5(f), anodic and cathodic currents at potentials between −2 V and +2 V may not clearly depend on LiCl concentration. They may correspond to the redox reactions by moisture in the bath. The cathodic current seems to increase with LiCl concentration at a potential less than −2 V. These currents are considered to be Li deposition concerning the complex ion accompanied with the DMSO$_2$ ligand. The cathodic current density at −3.5 V is smallest for the bath containing 5 mol% LiCl and largest for 15 mol% LiCl.

^{7}Li NMR spectroscopy was next employed as this technique allows the environment of Li atoms to be unambiguously determined in most cases. For consideration of the reaction mechanism of Li electrodeposition, NMR analysis was conducted as a state investigation of ions in the bath. The NMR analysis results for ^{7}Li and ^{7}Li chemical shift are shown in Figure 2. A peak was detected in the

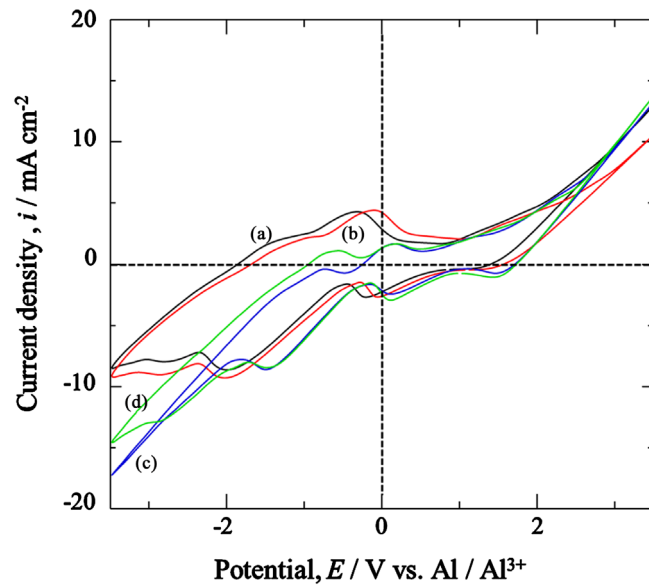**Figure 1.** Cyclic voltammograms of Pt electrode in DMSO₂ baths with various LiCl concentrations at 403 K. (a) 5; (b) 10; (c) 15; and (d) 20 mol%.
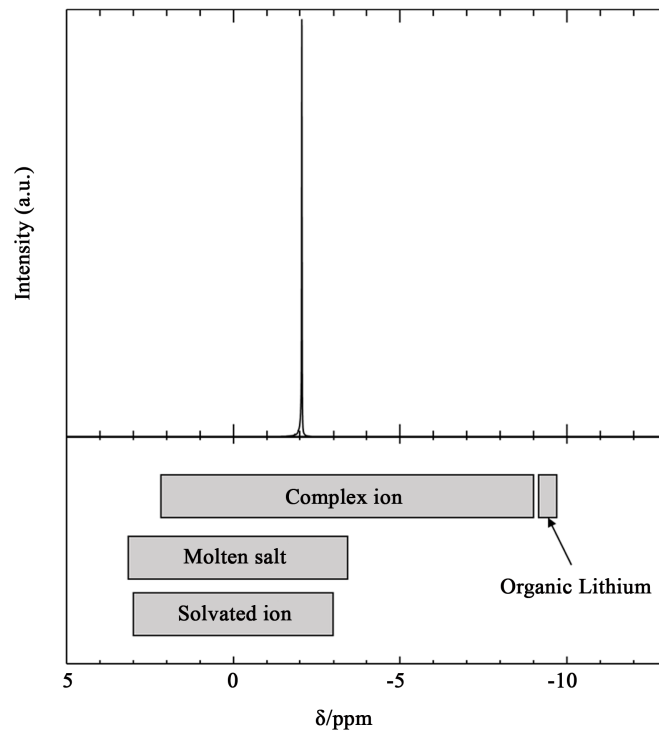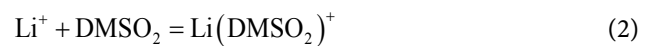

Figure 2. ^{7}Li NMR spectra of 15 mol% LiCl/DMSO₂ electrolytes.

vicinity of −2 ppm in the bath containing 15 mol% LiCl. Because this peak coincides with the chemical shift [47] of solvated ions, it is considered that Li^+ and $DMSO_2$ as well as Al^{3+} in $DMSO_2$ form complex ions with the reaction represented in Equation (2).

$$Li^+ + DMSO_2 = Li(DMSO_2)^+ \qquad (2)$$

It is considered that Li was electrodeposited from the complex ion at the cathode by the reaction in Equation (3).

$$Li(DMSO_2)^+ + e^- = Li + DMSO_2 \qquad (3)$$

To confirm Li deposition, electrolysis was conducted at potentials of −2.0 V, −2.5 V, −3.0 V, and −3.5 V for 1 h using a Cu plate as a working electrode. The appearance of the electrode surface is shown in Figure 3. No deposits were observed on the surface at −2.0 V, slightly black at −2.5 V, and silver film whitened after washing at −3.0 V and −3.5 V. The whitened deposits are thought to be Li metal reacting with moisture in the air to form hydroxide after electrolysis. Gas evolution was also observed at the Cu electrode during electrolysis at every potential, which may be H_2 caused by the moisture contained in the LiCl resource. In addition, to determine which electrochemical reaction occurred at several potentials for 1 h from the $DMSO_2$ bath with 15 mol% LiCl, XRD analysis was employed. Figure 4 shows that $LiOH \cdot H_2O$ was slightly detected on the deposits obtained at −2.5 V, and a multiplicity of peaks of Li compounds such as LiOH and $LiOH \cdot H_2O$ are identified at −3.0 V and −3.5 V.
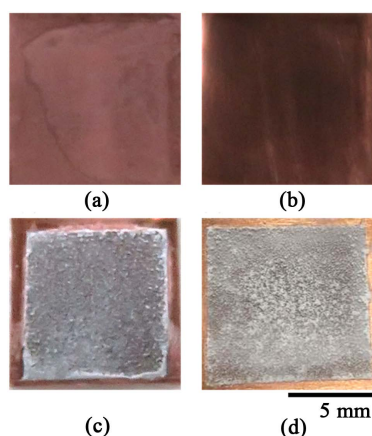

Figure 3. Surface photographs of deposits on Cu substrate for 1 h in 15 mol% $LiCl/DMSO_2$ baths at 403 K under constant potential electrolysis at (a) −2.0 V; (b) −2.5 V; (c) −3.0 V; and (d) −3.5 V.
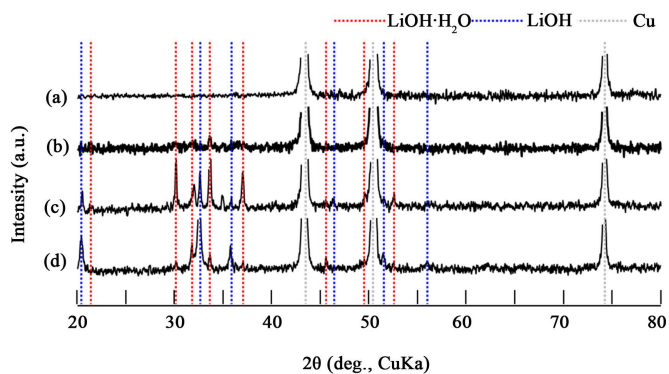

Figure 4. XRD patterns for the deposits obtained on Cu electrodes at 403 K for 1 h in $DMSO_2$ bath with 15 mol% LiCl at (a) −2.0 V; (b) −2.5 V; (c) −3.0 V; and (d) −3.5 V.

As a confirmation that the precipitate must be Li metal, the deposits were dissolved in 1 M HCl and diluted 100-fold, then qualitative and quantitative analyses were carried out using ICP-AES analysis. The results by ICP-AES analysis of the amount of Li contained in the film electrodeposited on the Cu substrate are summarized in Table 1. The lithium component is obtained at potentials less than −2.5 V. The cathodic current in electrolysis at −2.0 V corresponds to the H_2 evolution without Li deposition.

3.2. Electrochemical Behavior in $DMSO_2$ Bath Containing $AlCl_3$ and LiCl

It is known that Al is electrodeposited from a bath of $AlCl_3$-$DMSO_2$ [33] [43] [45] [46]. Therefore, it was verified whether it could be precipitated as an Al alloy by adding another metal chloride to this system. An attempt was made to determine by CV the oxidation-reduction peak of Al and the oxidation-reduction peak of the mixed metal species. The deposition/dissolution reaction of Al ion/metal takes place at around 0 V based on the redox potential of Al as a reference electrode. Cyclic voltammograms were measured on Pt electrodes in the potential range from −2 V to +2 V at 403 K in $DMSO_2$ baths containing 10 mol% $AlCl_3$ and 20 mol% $AlCl_3$, accompanied with 0 to 20 mol% LiCl. The electrode potential was scanned from the open-circuit potential near 0 V to the negative direction, followed by scanning to the positive direction and then cycled. As shown in Figure 5, deposition and dissolution currents for Al were observed around 0 V in 10 mol% and 20 mol% $AlCl_3$ baths without LiCl. The first voltammogram (Figure 5(a)) exhibited one reduction peak and a broad oxidation peak. In 10 mol% $AlCl_3$ bath, the currents corresponding to Al redox reaction were obviously suppressed in peak magnitude by Li coexistence of 5 mol% or more of LiCl (Figures 5(b)-(e)). In contrast, several redox peaks newly appeared in the potential range between −1.5 V and −0.5 V. In 20 mol% $AlCl_3$ bath, redox currents for Al were also clearly observed from around 0 V in the bath with LiCl below 10 mol% and few changes (Figure 5(f) and Figure 5(g)). LiCl addition above 10 mol% (Figures 5(h)-(j)) led to the decrease in the Al current. This phenomenon means that Li coexistence inhibits the formation of $Al\left(DMSO_2\right)_3^{3+}$ complex ions, which is said to be necessary for Al electrodeposition.

Constant potential electrolysis was carried out for 1 h at −2 V in all baths to clarify the Al and Li deposition. The surface state of Cu electrodes after constant potential electrolysis in each bath is shown in Figure 6. In baths (a) and (f)

Table 1. Results of ICP analysis.

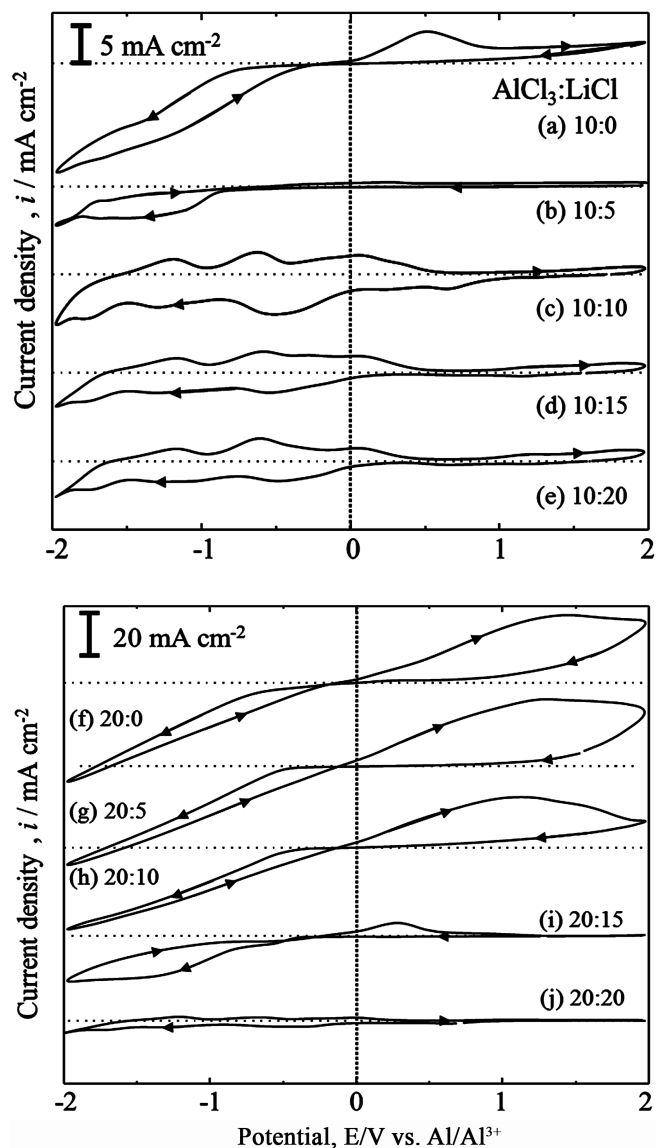| Potential	Li (μmol)
−2.0 V	0
−2.5 V	11
−3.0 V	44
−3.5 V	43

Figure 5. Cyclic voltammograms of Pt electrode at 403 K in baths containing various concentrations of $AlCl_3$ and LiCl in mol%.

without LiCl, a black deposit and a glossy deposit were obtained, respectively. These deposits must be Al containing many impurities. With the increase in the amount of LiCl in the bath, the surface of the deposits after washing became whitened (**Figures 5(b)-(e)**). These white precipitates seem to be lithium hydroxide reacted with moisture in the air after electrolysis. Glossy deposits (**Figure 5(f)** and **Figure 5(g)**) also changed to whitened ones with the addition of LiCl. A smooth black precipitate was obtained in the baths containing 15 mol% LiCl and more (**Figure 5(i)** and **Figure 5(j)**).

To identify the electrodeposits, XRD analysis was carried out as qualitative analysis of precipitates, and analysis by ICP-AES was decided as quantitative analysis. In **Figure 7**, Al peaks decreased and multiple peaks of LiOH and $LiOH \cdot H_2O$ increased with the increase in LiCl in the bath. In particular,
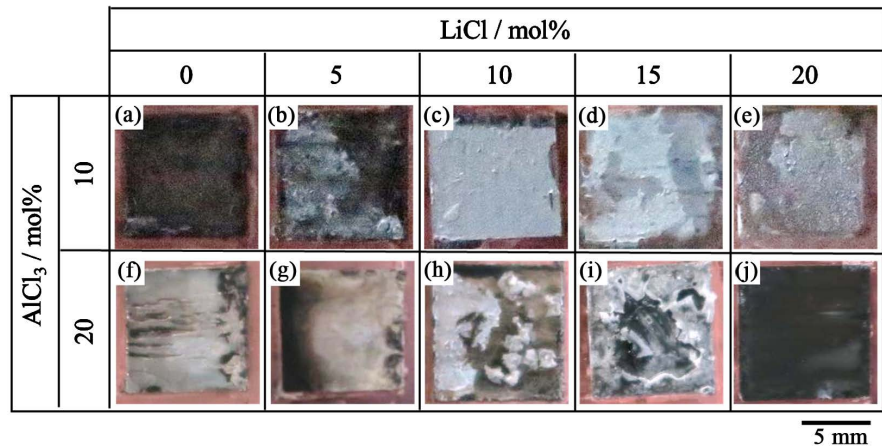
Figure 6. Surface photographs of deposits on Cu electrode formed at −2 V, 403 K in DMSO$_2$ bath with various concentrations of AlCl$_3$ and LiCl.
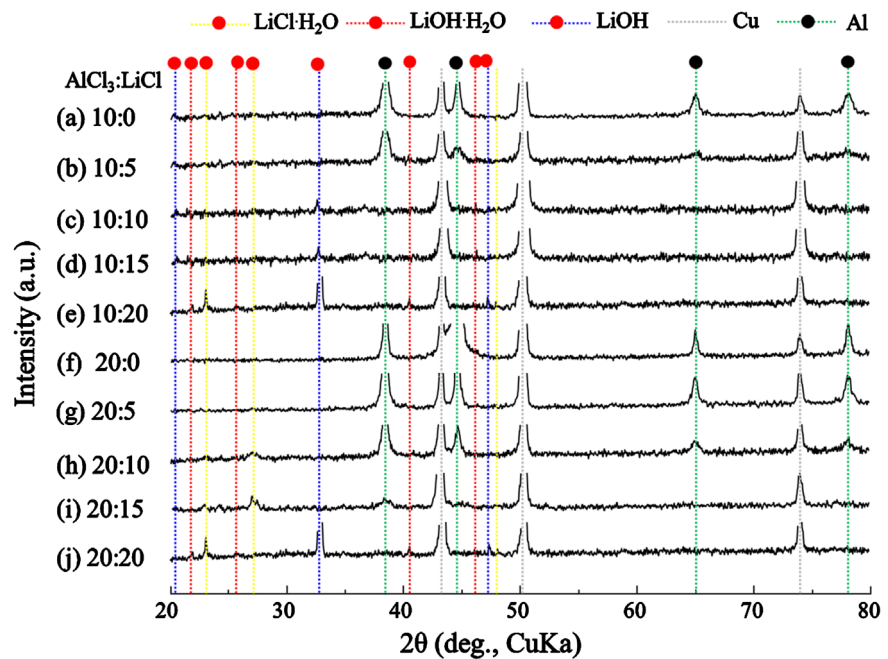

Figure 7. XRD patterns for deposits obtained on Cu electrodes at −2 V, 403 K for 1 h in baths with various concentrations of AlCl$_3$ and LiCl in mol%.

LiOH·H$_2$O peaks were detected in the results of 20 mol% LiCl. It is considered that Li metal electrodeposited on the Cu electrode reacts with moisture and appears on the surface as hydroxide.

To calculate the amounts of Al and Li contained in the deposits on the Cu substrate, ICP-AES quantitative analysis was performed as shown in **Figure 8**. In both 10 mol% AlCl$_3$ and 20 mol% AlCl$_3$ baths, the Al amount decreased with increase in LiCl in the bath. In addition, Li increased accompanied with LiCl concentration in the bath. Although Al and Li were contained in deposits from **Figure 8**, it was not possible to identify the XRD peaks corresponding to Al-Li alloys such as Al$_2$Li$_3$ or Al$_3$Li in the electrodeposit from **Figure 7**.

In addition, to estimate the effect of ions present in the bath on the deposit component, the NMR analysis on all electrolytic baths was carried out for 10 mol% $AlCl_3$ bath (**Figure 9**) and for 20 mol% $AlCl_3$ bath (**Figure 10**), where it is clarified that $AlCl_4^-$, $Li(DMSO_2)^+$, and $Al(DMSO_2)_3^{3+}$ exist in the baths.
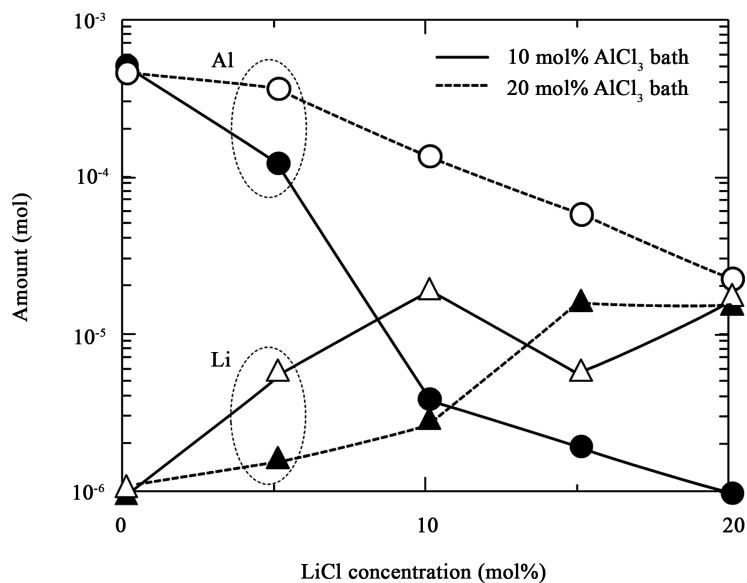

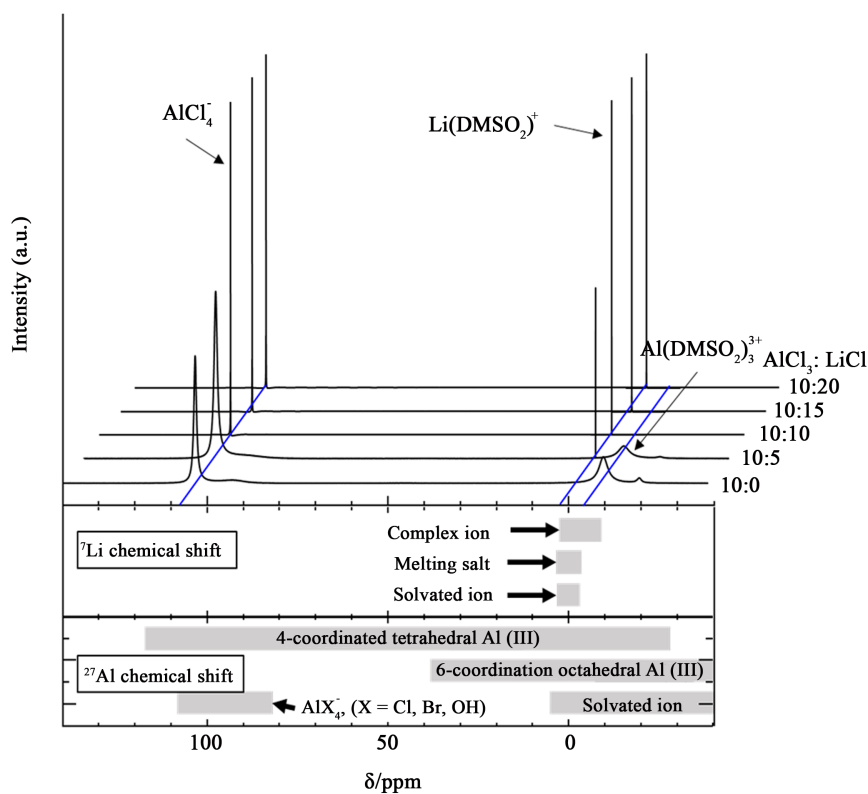**Figure 8.** Amount of Al and Li in deposits by ICP analysis.

Figure 9. ^7Li and ^{27}Al NMR spectra of 10 mol% $AlCl_3/DMSO_2$ containing from 0 to 20 mol% LiCl.

$Al_2Cl_7^-$ was never observed. $DMSO_2$ is therefore found to act as a Lewis base weaker than Cl^- but stronger than $AlCl_4^-$ leading to the following equilibria in $DMSO_2$-based electrolytes [38].

$$4AlCl_3 + 3DMSO_2 = Al(DMSO_2)_3^{3+} + 3AlCl_4^- \tag{1}$$

$$AlCl_3 + Cl^- = AlCl_4^- \tag{4}$$
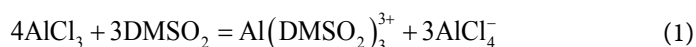
A peak corresponding to $AlCl_4^-$ was detected in the vicinity of 104 ppm in all baths [33]. In the bath containing LiCl, a peak corresponding to $Li(DMSO_2)^+$ was detected around −2 ppm [47]. The peak of $Al(DMSO_2)_3^{3+}$ appearing between −22 ppm and −2 ppm decreased with increase in LiCl. The peak of $Al(DMSO_2)_3^{3+}$ was not detected in 10 mol% $AlCl_3$ baths with 10 mol% or more LiCl and in 20 mol% $AlCl_3$ baths with 20 mol% LiCl. **Table 2** lists data for relative species abundances corresponding to the spectra of **Figure 9** and **Figure 10**, where the contributions from underlying peaks were estimated by deconvolution of shoulders in some cases if sufficiently distinct. These ratios were calculated from the compositional ratio ($AlCl_3/LiCl$) of the baths determined by titration and alternately from the integrated areas under the assigned NMR peaks, and are compared here. The values determined from titration and the NMR signals for a given bath should agree; thus, comparing them, should serve as a cross-check of the composition. Since $Al(DMSO_2)_3^{3+}$ decreased and $Li(DMSO_2)^+$ increased with the addition of LiCl, Li^+ tended to form a complex with $DMSO_2$, and it is considered that LiCl inhibits the formation of $Al(DMSO_2)_3^{3+}$.

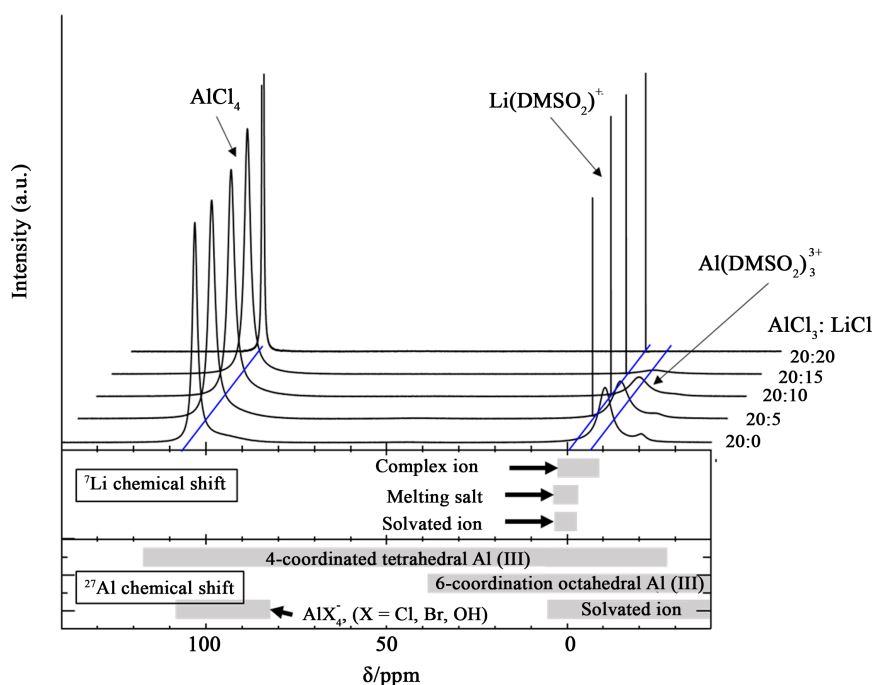**Figure 10.** ^7Li and ^{27}Al NMR spectra of 20 mol% $AlCl_3/DMSO_2$ containing from 0 to 20 mol% LiCl.

Table 2. Analysis of relative abundance of ions in baths by ^{7}Li and ^{27}Al NMR data.

Electrolytic bath		Relative abundance/%		
$AlCl_3$ (mol%)	LiCl (mol%)	$Al(DMSO_2)_3^{3+}$	$AlCl_4^-$	$Li(DMSO_2)^+$
	0	37.77	62.23	-
	5	14.42	64.66	20.92
10	10	0	52.02	47.98
	15	0	51.54	48.46
	20	0	44.44	55.56
	0	37.58	62.42	-
	5	20.25	70.10	9.65
20	10	13.39	60.61	26.00
	15	7.81	54.95	37.24
	20	0	51.56	48.44

4. Conclusions

In this study, in addition to how Li ion behaves in a LiCl-containing $DMSO_2$ bath, we also investigated how to change the behavior of Al ions and Li ions by adding LiCl in an $AlCl_3$-$DMSO_2$ bath capable of Al electrodeposition. Furthermore, after conducting constant potential electrolysis in each bath, surface analysis of the working electrode and analysis of ions in the electrolytic bath were carried out to obtain the following findings.

1) In the CV measurement in a LiCl-containing $DMSO_2$ bath, the rise of current from around −1.4 V, which is considered to be the redox of Li ions, was observed. Li can also be precipitated from $DMSO_2$ as in Al from the analysis result of electrodeposition obtained by constant potential electrolysis in $DMSO_2$-15 mol% LiCl bath. From the NMR analysis in a $DMSO_2$-15 mol% LiCl bath, both Li form a complex ion with $DMSO_2$.

2) In CV measurement in a bath containing LiCl added to an $AlCl_3$-$DMSO_2$ bath, current responses considered as oxidation and reduction of Al ions and Li ions are observed simultaneously. In the constant potential electrolysis in a bath in which LiCl was added to an $AlCl_3$-$DMSO_2$ bath, the state of the electrodeposition changed as the amount of LiCl added increased. Because LiCl inhibits the formation of $Al(DMSO_2)_3^{3+}$, which is necessary for Al electrodeposition from $DMSO_2$, it inhibits the electrodeposition of Al.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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