



## Short communication

## Development of non-flammable lithium secondary battery with room-temperature ionic liquid electrolyte: Performance of electroplated Al film negative electrode

Koichi Ui\*, Keigo Yamamoto, Kohei Ishikawa, Takuto Minami, Ken Takeuchi, Masayuki Itagaki, Kunihiro Watanabe, Nobuyuki Koura

Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

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## ABSTRACT

The negative electrode performance of the electroplated Al film electrode in the LiCl saturated  $\text{AlCl}_3$ -1-ethyl-3-methylimidazolium chloride (EMIC)+ $\text{SOCl}_2$  melt as the electrolyte for use in non-flammable lithium secondary batteries was evaluated. In the cyclic voltammogram of the electroplated Al film electrode in the melt, the oxidation and reduction waves corresponding to the electrochemical insertion/extraction reactions of the  $\text{Li}^+$  ion were observed at 0–0.80 V vs.  $\text{Li}^+/\text{Li}$ , which suggested that the electroplated Al film electrode operated well in the electrolyte. The almost flat potential profiles at about 0.40 V vs.  $\text{Li}^+/\text{Li}$  on discharging were shown. The discharge capacity and charge–discharge efficiency was  $236 \text{ mAh g}^{-1}$  and 79.2% for the 1st cycle and it maintained  $232 \text{ mAh g}^{-1}$  and 77.9% after the 10th cycle. In addition, the initial charge–discharge efficiencies of the electroplated Al film electrode were higher than that of carbon electrodes. The main cathodic polarization reaction was the insertion of  $\text{Li}^+$  ions, and side reactions hardly occurred due to the decomposition reaction of the melt because the Li content corresponding to the electricity was almost totally inserted into the film after charging.

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### 1. Introduction

In recent years, lithium secondary batteries have attracted attention as a power supply for portable electronic devices such as cellular phones. However, a battery having a further high energy density is demanded. At the same time, the development of a novel electrolyte and electrode material which insures good battery safety is very important. From this view point, an ambient-temperature molten salt (room-temperature ionic liquid), which has features, such as a low volatility and non-flammability, has been investigated as an electrolyte with an excellent safety [1–10]. We have developed lithium secondary batteries using the  $\text{AlCl}_3$ -1-ethyl-3-methylimidazolium chloride (EMIC) melt as a non-flammable electrolyte [11–14] because the 60.0 mol% $\text{AlCl}_3$ -40.0 mol%EMIC- $\text{LiCl}_{\text{sat}}$ . + 0.1 mol  $\text{l}^{-1}$   $\text{SOCl}_2$  melt exhibited relatively high ionic conductivity ( $11.5 \text{ mS cm}^{-1}$ ), low viscosity (23.4 mPa s), and low melting point (grass transition point  $-86.2^\circ\text{C}$ ) [14]. The amount of LiCl dissolution in the  $\text{AlCl}_3$ -EMIC

melt is dependent on the existing  $\text{Al}_2\text{Cl}_7^-$  concentration [15] in a Lewis acidic melt ( $\text{AlCl}_3 > 50 \text{ mol}\%$ ). The  $\text{Li}^+$  ion can exist in the melt according to the following equation [16]:



We reported that the addition of Li metal to a LiCl-saturated  $\text{AlCl}_3$ -EMIC melt, which was prepared using excess LiCl at saturation in the  $\text{AlCl}_3$ -EMIC melt,  $\text{Al}_2\text{Cl}_7^-$ , which was the ionic species for the deposited Al, was completely removed from the melt [11]. Fuller et al. then found that the deposition reaction of Al did not occur and the nearly reversible deposition/dissolution behavior of Li was enabled by adding  $\text{SOCl}_2$  [17]. We found that the various binder-free carbon electrodes made by an electrophoretic deposition method enabled the reversible charge ( $\text{Li}^+$  ion intercalation) and discharge (deintercalation) reaction in the melt [14,18,19]. The initial charge–discharge efficiencies of all the carbon electrodes showed the low value of ca. 40–50% though they exhibited an excellent cycle performance.

In this study, we evaluated the possibility of using an electroplated Al film electrode in order to improve the negative electrode characteristic of non-flammable lithium secondary batteries because the capacity of aluminum thin films could be expected to be higher than that of carbon materials [20]. To the best

\* Corresponding author. Present address: Department of Frontier Materials and Functional Engineering, Graduate School of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan. Tel.: +81 19 621 6340; fax: +81 19 621 6314.  
E-mail address: [kui@iwate-u.ac.jp](mailto:kui@iwate-u.ac.jp) (K. Ui).

of our knowledge, there has been little report on the Al negative electrode for lithium secondary batteries using room-temperature ionic liquid electrolytes [1]. The Al film electrode made by an electroplating method requires no binders and conductive materials. In addition, an electrode with an excellent adhesion can be made on a current collector [21]. We reported that the electroplated Al film electrode as the negative electrode for lithium secondary batteries operated quite effectively in an organic solvent electrolyte containing a lithium salt [22].

## 2. Experimental

EMIC was synthesized as previously reported [23]. The  $\text{AlCl}_3$ -EMIC melt was prepared by mixing EMIC with anhydrous  $\text{AlCl}_3$  (Wako Pure Chemical Industries, Ltd.) at the predetermined molar ratio below  $60^\circ\text{C}$ . The melt was purified by immersing Al wire into the melt for 1 week at room temperature [24]. Excessive anhydrous LiCl (Aldrich, 99.99%) was then added to the melt. The LiCl-saturated melt was stirred at room temperature for 24 h, and a small quantity of  $\text{SOCl}_2$  (Wako Pure Chemical Industries, Ltd.) was added to the melt and stirred for 6 h. The  $\text{AlCl}_3$ -EMIC-LiCl<sub>sat.</sub> +  $0.1 \text{ mol l}^{-1}$   $\text{SOCl}_2$  melt was then obtained.

The electroplating was carried out by using a three-electrode cell, which consisted of the Al(III)/Al reference electrode, a Ni foil (99.9%,  $100 \text{ mm} \times 300 \text{ mm}$ ,  $0.20 \text{ mm}$ , Nilaco) cathode, a soluble Al foil (99.999%,  $100 \text{ mm} \times 300 \text{ mm}$ ,  $1.0 \text{ mm}$ , Nilaco) anode, and the  $66.7 \text{ mol}\% \text{AlCl}_3$ - $33.3 \text{ mol}\% \text{EMIC}$  melt as the electroplating bath [22]. The Al film was electroplated on one side of the Ni foil from the bath at a current density of  $10 \text{ mA cm}^{-2}$  and an electricity of  $100 \text{ C cm}^{-2}$  at room temperature. The Ni cathode was polished with sandpapers (nos. 600, 1200, and 2000), electrolytically degreased with 20 wt% sodium silicate solution for 5 min, and treated with 10 wt% HCl for 10 min. It was then washed successively with distilled water, methanol, and acetone.

The three-electrode cell, which consisted of the electroplated Al film electrode (W.E.) and a pressed Li foil on a Ni mesh current collector (R.E. and C.E.), was used for the electrochemical measurements. The electrochemical experiments were performed using a computer-controlled electrochemical measuring system (Hokuto Denko, HZ-3000) and an automatic battery charging-discharging instrument (Hokuto Denko, HJR-110mSM6). The scan rate of the cyclic voltammetry (CV) was  $5.0 \text{ mV s}^{-1}$ . The electrodes were galvanostatically charged by controlling the electricity and fully discharged up to  $1.5 \text{ V vs. Li}^+/\text{Li}$  at room temperature.

The crystal structure of the film electrodes before and after the charge-discharge tests was examined using an X-ray diffractometer (Rigaku Denki, RAD-X SYSTEM) with Cu  $K\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ). For the *ex situ* X-ray diffraction (XRD) measurements of the electroplated Al film electrode, the electrode was charged at a constant current of  $0.1 \text{ mA cm}^{-2}$  up to  $\text{Li}_{0.35}\text{Al}$ , and the cell was then disassembled in the glove box to obtain the sample electrode. The obtained electrode was then washed with ethanol and acetone, and packaged in polyethylene film to prevent the sample from contacting with air. The Li content in the electroplated Al film containing Li was determined by dissolving the electrode in 10 wt% HCl and measuring the concentration of its dilute solution by inductively coupled plasma atomic-emission spectroscopy (ICP, SHIMADZU ICPS-7500). The depth profile of the elements in the electroplated Al film containing Li after being charged and discharged was determined by glow discharge plasmas-optical emission spectroscopy (GD-OES, HORIBA, JY-5000RF) after the test specimens were successively washed with distilled water, ethanol, and acetone.

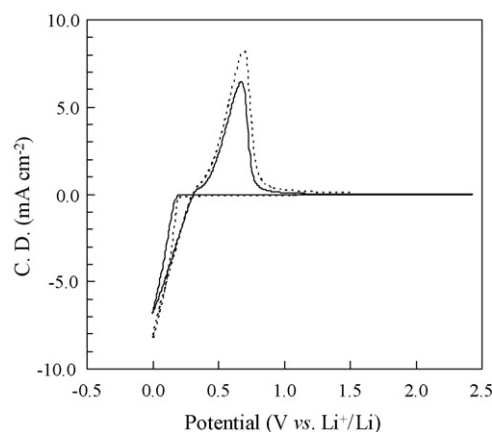


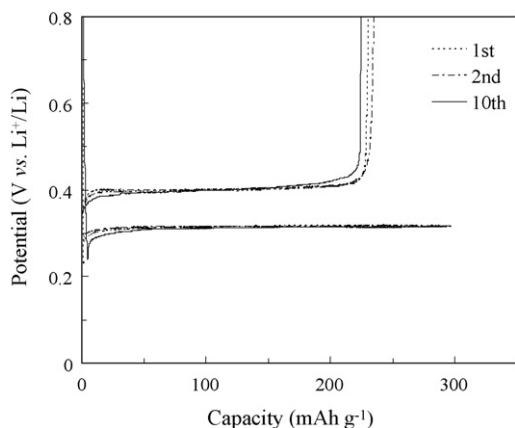
Fig. 1. Cyclic voltammograms for the electroplated Al film electrode in the  $60.0 \text{ mol}\% \text{AlCl}_3$ - $40.0 \text{ mol}\% \text{EMIC}$ - $\text{LiCl}_{\text{sat.}}$  +  $0.1 \text{ mol l}^{-1}$   $\text{SOCl}_2$  electrolyte; scan rate:  $5.0 \text{ mV s}^{-1}$ ; (—) 1st cycle; (···) 10th cycle.

All procedures were carried out in a glove-box with an Ar atmosphere (MIWA MFG Co., Ltd., 1ADB-3LL).

## 3. Results and discussion

The thickness of the electroplated Al film was about  $20 \mu\text{m}$ . The CV was measured in the  $60.0 \text{ mol}\% \text{AlCl}_3$ - $40.0 \text{ mol}\% \text{EMIC}$ - $\text{LiCl}_{\text{sat.}}$  +  $0.1 \text{ mol l}^{-1}$   $\text{SOCl}_2$  melt in order to investigate the electrochemical redox behavior of the electroplated Al film electrode (Fig. 1). The coupled redox peak was clearly observed in the potential range from 0 to  $0.80 \text{ V vs. Li}^+/\text{Li}$ . The reduction and oxidation currents corresponding to the insertion and extraction reaction of the  $\text{Li}^+$  ion into and from the electroplated Al film electrode were observed in the potential range from 0 to  $0.35 \text{ V}$  and from  $0.35$  to  $0.80 \text{ V}$ , respectively, and the coulomb efficiency was ca. 93%. The CV profile of the 10th cycle was very similar to that of the 1st cycle, indicating that the electrochemical behavior was reversible. Moreover, it is noteworthy that irreversible reduction current was not observed in the potential range from  $2.0$  to  $0.35 \text{ V}$  compared to the voltammetric behavior of a carbon electrode [18]. Judging from the similar phenomenon observed in an ethylene carbonate-based solution containing a lithium salt [18,25], it may be considered that the electroplated Al film electrode did not show the side reaction in the melt due to the difference of the reaction sites of carbon and Al electrodes. Based on this result, it was suggested that the electroplated Al film electrode operated well in the melt.

The charge-discharge tests of the electroplated Al film electrode were next carried out. Figs. 2 and 3 indicate the charge-discharge curves and the cycle performance at a current density of  $0.1 \text{ mA cm}^{-2}$ , respectively. In this paper, the cathodic polarization due to the  $\text{Li}^+$  ion insertion into the electroplated Al film is defined as the charge and the anodic polarization due to the  $\text{Li}^+$  ion extraction from it is defined as the discharge. The  $\text{Li}_x\text{Al}$  indicates that the molar ratio, *i.e.*, the amount of  $\text{Li}^+$  ion insertion calculated from the electricity, was defined as  $x$  when the electroplated Al film was defined as 1 mol. The charge depth was set to  $\text{Li}_{0.30}\text{Al}$  because cracking was generated in the film when the charge depth was around  $\text{Li}_{0.50}\text{Al}$  [22]. The discharge potential of the film electrode almost showed a flat potential plateau at about  $0.40 \text{ V}$ , and the discharge capacity and the charge-discharge efficiency of the 1st cycle were  $236 \text{ mAh g}^{-1}$  and 79.2%, respectively. The cycle performance was stable after the 2nd cycle because the discharge capacity and charge-discharge efficiency at the 10th cycle were  $232 \text{ mAh g}^{-1}$  and 77.9%, respectively. Based on these results, it was found that the

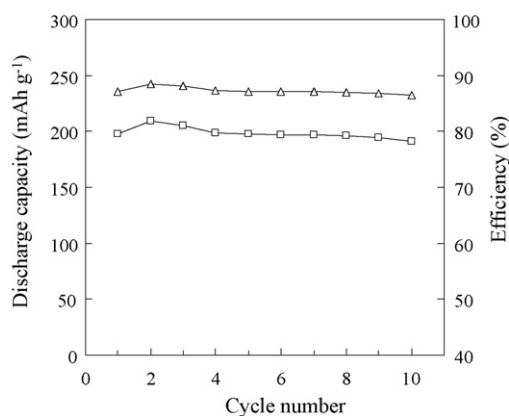


**Fig. 2.** Charge–discharge curves of the electroplated Al film electrode charged to  $\text{Li}_{0.30}\text{Al}$  in the 60.0 mol% $\text{AlCl}_3$ –40.0 mol%EMIC– $\text{LiCl}_{\text{sat}}$  + 0.1 mol  $\text{l}^{-1}$   $\text{SOCl}_2$  electrolyte; C.D., 0.1  $\text{mA cm}^{-2}$ .

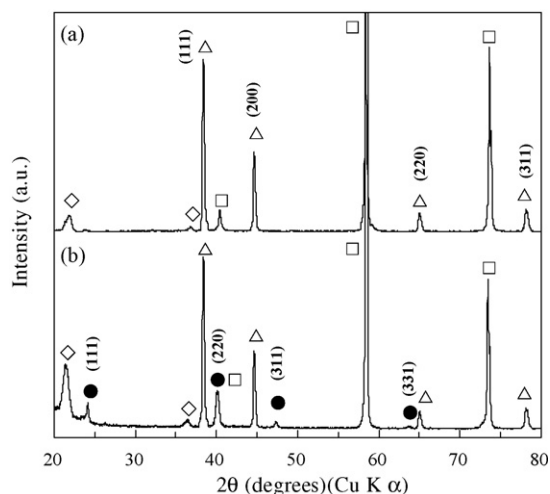
electroplated Al film electrode functioned as a negative electrode in the melt. In addition, because the efficiencies of  $\text{Li}_{0.25}\text{Al}$  and  $\text{Li}_{0.35}\text{Al}$  during the 1st cycle were 84.7% and 84.4% in the organic solvent electrolyte, respectively [22], the efficiency of the 1st cycle in the melt was almost similar to them. Thus we see that the initial efficiency of the electroplated Al film electrode in the melt was much higher than that of carbon electrodes [14,18,19].

As shown in Fig. 2, the flat potential plateau suggested the formation of two-phase coexistence. We analyzed the structure of the electroplated Al film (a) before and (b) after charged by using the X-ray diffraction (Fig. 4). As shown in Fig. 4(b), the peaks of the electroplated Al film electrode after charged up to  $\text{Li}_{0.35}\text{Al}$  were observed at  $2\theta = 24.1, 40.1, 47.3,$  and  $63.7^\circ$ , and these indexed to  $\beta$ -Li–Al. It became clear to remain metallic Al and form intermetallic compound  $\beta$ -Li–Al in the melt during the 1st charge. Based on these results, it was found that the flat potential plateau appeared due to the formation of two-phase coexistence.

So far, we have seen that the initial efficiency of the carbon electrodes was low due to the formation of a protective film, the so-called solid electrolyte interface (SEI) [14,18,19], whereas the initial efficiency of the electroplated Al film electrode was high. In other words, it is postulated that any side reaction hardly occurred. Therefore, the Li contents in the  $\text{Li}_{0.05}\text{Al}$ ,  $\text{Li}_{0.30}\text{Al}$ , and  $\text{Li}_{0.50}\text{Al}$  were measured by ICP (Fig. 5). The ICP analysis showed that the amounts of Li were 0.047 mol, 0.29 mol, and 0.49 mol for the  $\text{Li}_{0.05}\text{Al}$ ,  $\text{Li}_{0.30}\text{Al}$ , and  $\text{Li}_{0.50}\text{Al}$ , respectively. Based on these results, it became very



**Fig. 3.** Cycle performance of the electroplated Al film electrode charged to  $\text{Li}_{0.30}\text{Al}$  in the 60.0 mol% $\text{AlCl}_3$ –40.0 mol%EMIC– $\text{LiCl}_{\text{sat}}$  + 0.1 mol  $\text{l}^{-1}$   $\text{SOCl}_2$  electrolyte; ( $\Delta$ ) discharge capacity; ( $\square$ ) charge–discharge efficiency; C.D., 0.1  $\text{mA cm}^{-2}$ .

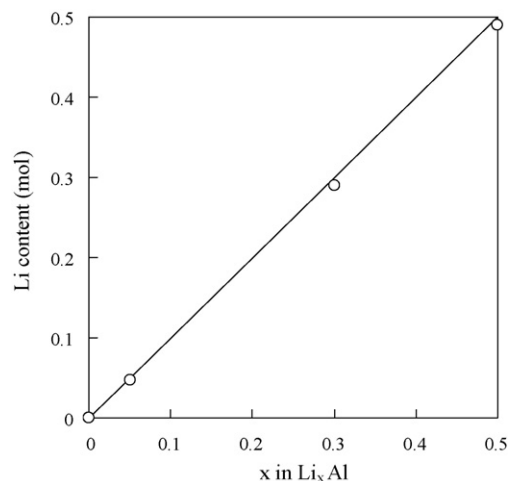


**Fig. 4.** X-ray diffraction patterns of the electroplated Al film electrode before (a) and after (b) charged up to  $\text{Li}_{0.35}\text{Al}$  in the 60.0 mol% $\text{AlCl}_3$ –40.0 mol%EMIC– $\text{LiCl}_{\text{sat}}$  + 0.1 mol  $\text{l}^{-1}$   $\text{SOCl}_2$  electrolyte. On measuring XRD, the charged Al film electrode was covered with polyethylene film. Mo is the substrate for the Al film; ( $\Delta$ ) Al; ( $\square$ ) Mo; ( $\diamond$ ) polyethylene film; ( $\bullet$ )  $\beta$ -Li–Al.

clear that the main cathodic polarization reaction was the insertion of  $\text{Li}^+$  ions into the film, and side reactions hardly occurred due to the decomposition reaction of the melt and the SEI formation.

Added to the results, in order to investigate the reason for the initial efficiency loss, the depth profiles of Li in the  $\text{Li}_{0.30}\text{Al}$  film after the charge–discharge tests were measured by GD-OES. Fig. 6 shows the GD-OES analysis of the charged Al film electrode up to  $\text{Li}_{0.30}\text{Al}$  after the 1st charge. A significant amount of Li existed near the surface of the Al film, while the amount of Li gradually decreased with increasing the sputtering time. Fig. 7 shows the GD-OES analysis of the discharged Al film electrode after the 1st charge. Li was extracted from the film because the intensity of Li decreased after discharging. However, all the Li was not extracted from the film and some of the Li remained in the Al film and especially near surface of the film after the 1st discharge. Based on these results, it was suggested that the Li remaining in the film was the main reason for the initial efficiency loss.

In the future, in order to improve the charge–discharge efficiency, it would be necessary to design an electroplated Al film electrode from which the  $\text{Li}^+$  ion is easily extracted.



**Fig. 5.** Li content in  $\text{Li}_x\text{Al}$  during the 1st charge stage; (–) calculated; ( $\circ$ ) measured.

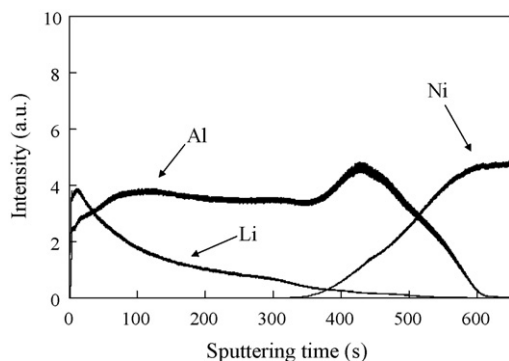


Fig. 6. GD-OES analysis of the charged Al film electrode up to  $\text{Li}_{0.30}\text{Al}$  after the 1st charge.

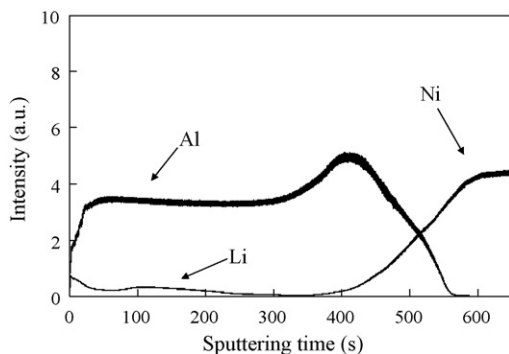


Fig. 7. GD-OES analysis of the discharged Al film electrode after the 1st charge.

#### 4. Conclusions

We evaluated an electroplated Al film electrode as the negative electrode for use in non-flammable lithium secondary batteries utilizing room-temperature ionic liquid electrolytes. When the charge depth was set to  $\text{Li}_{0.30}\text{Al}$ , the discharge capacity and the charge–discharge efficiency of the 1st cycle were  $236 \text{ mAh g}^{-1}$  and 79.2%, respectively. The cycle performance was stable after the 2nd cycle because the discharge capacity and charge–discharge efficiency at the 10th cycle showed  $232 \text{ mAh g}^{-1}$  and 77.9%, respectively. The charge–discharge tests and *ex situ* XRD analysis indicated that the flat potential plateau appeared due to the formation of two-phase coexistence. The initial efficiency of the electroplated Al film electrode in the melt was higher than that of carbon electrodes. Side reactions hardly occurred due to the decomposition

reaction of the melt and the SEI formation because the Li content corresponding to the electricity was almost totally inserted into the film after charging. Judging from the GD-OES analysis, it was suggested that the Li remaining in the film was the main reason for the initial efficiency loss. Based on these results, we may reasonably conclude that the electroplated Al film electrode is possible to use as a negative electrode in non-flammable lithium secondary batteries containing room-temperature ionic liquid electrolytes.

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