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Short communication

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

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ABSTRACT

The negative electrode performance of the electroplated Al film electrode in the LiCl saturated $AlCl_3$–1-ethyl-3-methylimizadolium chloride (EMIC) + $SOCl_2$ 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 Li^+ ion were observed at 0–0.80 V vs. Li^+/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. Li^+/Li on discharging were shown. The discharge capacity and charge–discharge efficiency was 236 mAh g^{-1} and 79.2% for the 1st cycle and it maintained 232 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 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.

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 $AlCl_3$–1-ethyl-3-methylimizadolium chloride (EMIC) melt as a non-flammable electrolyte [11–14] because the 60.0 mol%$AlCl_3$–40.0 mol%EMIC–$LiCl_{sat.}$ + 0.1 mol l^{-1} $SOCl_2$ melt exhibited relatively high ionic conductivity (11.5 mS cm^{-1}), low viscosity (23.4 mPa s), and low melting point (grass transition point −86.2 °C) [14]. The amount of LiCl dissolution in the $AlCl_3$–EMIC melt is dependent on the existing $Al_2Cl_7^-$ concentration [15] in a Lewis acidic melt ($AlCl_3$ > 50 mol%). The Li^+ ion can exist in the melt according to the following equation [16]:

$$Al_2Cl_7^- + LiCl \rightleftarrows Li^+ + 2AlCl_4^- \qquad (1)$$

We reported that the addition of Li metal to a LiCl-saturated $AlCl_3$–EMIC melt, which was prepared using excess LiCl at saturation in the $AlCl_3$–EMIC melt, $Al_2Cl_7^-$, 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 $SOCl_2$ [17]. We found that the various binder-free carbon electrodes made by an electrophoretic deposition method enabled the reversible charge (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

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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 $AlCl_3$–EMIC melt was prepared by mixing EMIC with anhydrous $AlCl_3$ (Wako Pure Chemical Industries, Ltd.) at the predetermined molar ratio below 60 °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 $SOCl_2$ (Wako Pure Chemical Industries, Ltd.) was added to the melt and stirred for 6 h. The $AlCl_3$–EMIC–$LiCl_{sat.}$ + 0.1 mol l^{-1} $SOCl_2$ 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 mm × 300 mm, 0.20 mm, Nilaco) cathode, a soluble Al foil (99.999%, 100 mm × 300 mm, 1.0 mm, Nilaco) anode, and the 66.7 mol%$AlCl_3$–33.3 mol%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 mA cm^{-2} and an electricity of 100 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 mV s^{-1}. The electrodes were galvanostatically charged by controlling the electricity and fully discharged up to 1.5 V vs. Li^+/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 Kα radiation ($\lambda = 0.15418$ 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 mA cm^{-2} up to $Li_{0.35}Al$, 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.

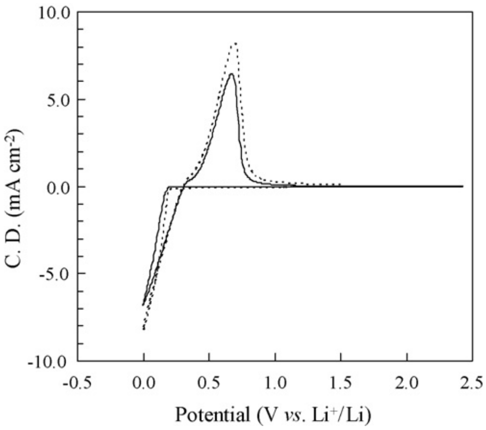

Fig. 1. Cyclic voltammograms for the electroplated Al film electrode in the 60.0 mol%$AlCl_3$–40.0 mol%EMIC–$LiCl_{sat.}$ + 0.1 mol l^{-1} $SOCl_2$ electrolyte; scan rate: 5.0 mv s^{-1}; (—) 1st cycle; (. . .) 10th cycle.

All procedures were carried out in a grove-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 μm. The CV was measured in the 60.0 mol%$AlCl_3$–40.0 mol%EMIC–$LiCl_{sat.}$ + 0.1 mol l^{-1} $SOCl_2$ 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 V (vs. Li^+/Li). The reduction and oxidation currents corresponding to the insertion and extraction reaction of the Li^+ ion into and from the electroplated Al film electrode were observed in the potential range from 0 to 0.35 V and from 0.35 to 0.80 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 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 mA cm^{-2}, respectively. In this paper, the cathodic polarization due to the Li^+ ion insertion into the electroplated Al film is defined as the charge and the anodic polarization due to the Li^+ ion extraction from it is defined as the discharge. The Li_xAl indicates that the molar ratio, *i.e.*, the amount of 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 $Li_{0.30}Al$ because cracking was generated in the film when the charge depth was around $Li_{0.50}Al$ [22]. The discharge potential of the film electrode almost showed a flat potential plateau at about 0.40 V, and the discharge capacity and the charge–discharge efficiency of the 1st cycle were 236 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 mAh g^{-1} and 77.9%, respectively. Based on these results, it was found that the