

Application of Electroplated Al film to Negative Electrode for Nonflammable Lithium Secondary Battery with Ambient Temperature Molten Salt Electrolyte

K. Ishikawa, T. Minami, K. Ui, Y. Idemoto, N. Koura

Department of Pure and Applied Chemistry,
Faculty of Science and Technology,
Tokyo University of Science
2641 Yamazaki, Noda, Chiba 278-8510, Japan

INTRODUCTION

Some problems with safe aspects such as ignition and explosion are pointed out in order to use the organic solvent which is flammable as the electrolyte for lithium secondary batteries. Because of above problems, we have investigated the ambient temperature molten salt having useful characteristics such as nonflammability, nonvolatile, and wide potential window as a lithium secondary battery electrolyte from a view point of safety¹⁻³. We also reported that the binder-free carbon electrode⁴ operated well as the negative electrode in the AlCl_3 - 1-ethyl-3-methylimidazolium chloride(EMIC) - LiCl_{sat} + SOCl_2 melt electrolyte.

In this study, to get a nonflammable lithium secondary battery with high energy density, we evaluated the possibility of an electroplated Al film as a negative electrode, because the capacity of Al film could expect higher than carbon materials.

EXPERIMENTAL

AlCl_3 -EMIC melt was prepared by mixing EMIC with anhydrous AlCl_3 of the predetermined molar ratio below 60°C. The melt was purified by immersing Al wire into the melt for one week at room temperature. Excessive anhydrous LiCl was added to the melt. The LiCl saturated melt was stirred at room temperature for 24 hours, and a small quantity of SOCl_2 was added to the melt and stirred for six hours. Al was electroplated on Mo sheet from the AlCl_3 -EMIC(AlCl_3 :EMIC=2:1 molar ratio) melt at 10mA/cm² and 20C/cm². We obtained the Al plating film of about 7 μm thickness. Electrochemical experiments were carried out by using a three-electrode cell. The pressed Li foil on Ni mesh current collector was used as a counter electrode and a reference electrode. We analyzed the structure of the Al plating film before and after charging (cathodic polarization) by the X-ray diffraction (XRD) method.

All experiments were carried out in dry Ar atmosphere glove box at room temperature.

RESULTS AND DISCUSSION

To examine the oxidation and reduction behaviors of the electroplated Al electrode in the AlCl_3 -EMIC- LiCl_{sat} + SOCl_2 melt electrolyte, cyclic voltammetry was carried out, and we observed the reduction wave at 0.35~0V(vs. Li^+/Li) and the oxidation wave at 0.35~0.80V. It was thought that electrochemical deposition and dissolution of Li on the Al electrode occurred. In addition, the reversibility can be said to be good from the fact that the reduction wave and oxidation wave at the second cycle increased than that at the first cycle. From these results, it was suggested that the electroplated Al electrode operated well in above melt.

Fig. 1 shows the charge and discharge curves for the electroplated Al electrode in the melt. Discharge potential of the electroplated Al electrode was about 0.45V, the discharge capacity and coulombic efficiency of the first cycle were 282mAh/g and 80.9%. The coulombic efficiencies were stable after second cycle, and the discharge capacity and coulombic efficiency at fifth cycle showed 314mAh/g and 89.7%.

From these results, it became clear that the electroplated Al electrode functioned as a negative electrode in this melt.

Fig. 2 shows the XRD patterns of before charging and after charging of the electroplated Al electrode in the melt. As shown at Fig. 2(b), XRD peaks of the electroplated Al electrode after charged up to $\text{Li}_{0.35}\text{Al}$ were observed at 24.1, 40.1, 47.3 and 63.7°, and these were belonged to β -Li-Al. In a reason, it became clear to form intermetallic compound β -Li-Al in the melt.

In these results we understood that Al film made by the electroplating method showed a good characteristic as a negative electrode.

ACKNOWLEDGEMENTS

This work was partially supported by Grant-in-Aid for Young Scientist (B), Ministry of Education, Culture, Sports, Science and Technology, Japan.

REFERENCES

- 1) K. Ui, *et al.*, *Denki Kagaku*, **65**, 161 (1997).
- 2) N. Koura, *et al.*, *Electrochemistry*, **67**, 706 (1999).
- 3) N. Koura, *et al.*, *Chem.Lett.*, p.1320 (2001).
- 4) N. Koura, *et al.*, *Hyomen Gijyutsu*, **52**, 143(2001).
- 5) S. Takahashi, *et al.*, *Hyomen Gijyutsu*, **40**, 548(1989).

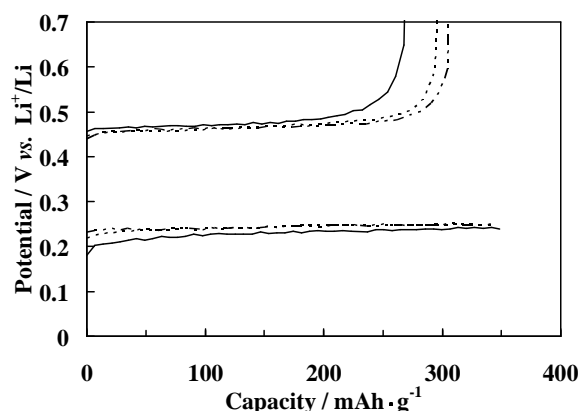


Fig. 1 Charge and discharge curves of the electroplated Al electrodes charged up to $\text{Li}_{0.35}\text{Al}$ in the 60mol% AlCl_3 -40mol%EMIC- LiCl_{sat} + SOCl_2 melt. C.D. : 0.5 mA/cm²

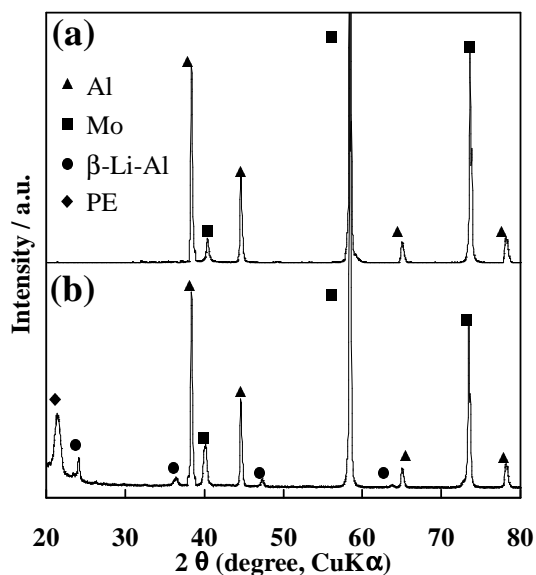


Fig. 2 X-ray diffraction patterns of the electroplated Al electrode before (a), and after (b) charged up to $\text{Li}_{0.35}\text{Al}$ in the melt. In measuring XRD, the charged Al electrode was covered with polyethylene film. The substrate for Al plating was Mo.