—Communication—

Positive Electrode Active Material for a Nonflammable Rocking Chair Type Lithium Secondary Battery with an Ambient Temperature Molten Salt Electrolyte

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1 INTRODUCTION

Ambient temperature molten salts, *e.g.*, an AlCl_3 -1-ethyl-3-methylimidazolium chloride (EMIC) system and an AlCl_3 -1-butylpyridinium chloride (BPC) system have been investigated for more than ten years as electrolytes for high energy density batteries¹⁻³⁾. Particularly, since an AlCl_3 -EMIC melt has a wide electrochemical window and is nonflammable, it is being considered as a non-flammable electrolyte for the Li secondary battery.

In a previous paper⁴⁾, Li metal was added to the LiCl saturated AlCl_3 -EMIC melt (50mol% < AlCl_3) in order to completely remove Al_2Cl_7^- that remained in the melt. As a result, Al was not deposited during cathodic polarization, and the electrochemical window of the melt was *ca.* 4.4V. When an Al foil was used as the negative substrate, Li was deposited on the substrate within the electrochemical window. Furthermore, since *ca.* 280Ah/kg of discharge capacity was obtained in the potential plateau range of about -1.5V vs. Al at 0.4mA/cm², it was found that an Li-Al alloy could perform as the negative electrode active material.

The positive active material should then be investigated to evaluate this molten salt as the electrolyte for the rocking chair type Li secondary battery. In this study, several intercalation compounds, LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and crystalline V_2O_5 (*c-V}_2\text{O}_5*) were investigated for the positive electrode active material.

2 EXPERIMENTAL

Melts were made by slowly adding anhydrous AlCl_3 to EMIC (Tokyo Kasei Kogyo Co., Ltd.) with stirring until the desired molar ratio was obtained. The melts were purified by the Al substitution method⁵⁾. Anhydrous LiCl was dried under vacuum at 200°C for one week. On the basis of the calculated concentration of Al_2Cl_7^- , a 10~20% molar excess of LiCl was added to the AlCl_3 -EMIC melt. The melt was stirred overnight at 50°C. Further-

more, Li metal was added to the melt in order to reduce Al_2Cl_7^- that remained in the melt to Al and AlCl_4^- . The melt was used as the electrolyte after standing for 24h. Commercial *c-V}_2\text{O}_5* and LiCoO_2 were used, and LiMn_2O_4 and LiNiO_2 were prepared by conventional methods as the positive electrode active material. The working electrode was prepared by pressing 20.0mg of the mixtures of the active materials, 10.0mg acetylene black (AB), 10.0mg artificial graphite (AG), and 13.0mg polytetrafluoroethylene (PTFE) onto a current collector (Mo mesh: 1.0 cm²). A 99.99% Al wire (ϕ 2mm) immersed in the 66.7mol% AlCl_3 -33.3mol% EMIC melt in a pyrex tube (ϕ 10mm) separated by a G4 glass frit was used as the reference electrode. Li-Al alloy was used as the negative electrode. The alloy was made by an electrolytic reduction method in the same melt by using an Al foil substrate (thickness 90 μm , 8.0cm²).

Fifty mg sample powders crushed into a particle size of several μm were immersed in an LiCl saturated 64.0mol% AlCl_3 -36.0mol% EMIC (50.0mol% AlCl_3 -28.1mol% EMIC-21.9mol% LiCl) melt of 15 ml for 20 days to determine the solubility⁶⁾. The dissolved metal ion was measured by ICP (Seiko electron SPS-7000).

The experiments were carried out in a glove box with a dry N_2 atmosphere.

3 RESULTS and DISCUSSION

The LiCl saturated melt must have a carrier ion to function as a battery electrolyte. The constant resistance discharge test was examined using *c-V}_2\text{O}_5* as the positive electrode and an Li-Al alloy as the negative electrode (Fig. 1). The open-circuit voltage indicated 3.2V. It was confirmed that the LiCl saturated melt functions as the battery electrolyte and that the Li-Al/LiCl saturated AlCl_3 -EMIC melt/*c-V}_2\text{O}_5* cell operates.

Next, a charge-discharge test was carried out at a constant current using several intercalation compounds, *i.e.*, LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and *c-V}_2\text{O}_5* as the positive electrode active material (Fig. 2). The rest potential of Li-Al alloy is -1.7V vs. Al⁴⁾. The LiCoO_2 (Fig. 2a) showed a charge capacity of 135Ah/kg and the discharge capacity of 124Ah/kg at a discharge potential of 1.9~0.9 V

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vs. Al. The charge-discharge efficiency was 91.9%. The LiNiO_2 (Fig. 2b) showed a 135Ah/kg charge capacity, a 100Ah/kg discharge capacity at 1.8~0.8V vs. Al, and 74.0% efficiency. The LiMn_2O_4 (Fig. 2c) showed a 140Ah/kg charge capacity, a 92Ah/kg discharge capacity at 2.0~1.0V vs. Al, and 65.7% efficiency. The $\text{c-V}_2\text{O}_5$ (Fig. 2d) showed a 146Ah/kg charge capacity, a 146Ah/kg discharge capacity at 1.4~0.4V vs. Al, and 100% efficiency. From these results, it was suggested that the charge-discharge is possible within the electrochemical window (2.3~-2.1V vs. Al)⁴⁾.

The graphite compound used as a conductive additive is a typical intercalation compound and it can be intercalated by cations and anions⁷⁾. So, charge-discharge tests for AG (e) and AB (f) were also performed. The capacities for AG and AB were ca. 2 and 4 Ah/kg, respectively. It was confirmed that these (e and f) capacities correspond to only 1~3 % of a, b, c, and d.

On the other hand, the active material should be stable in the melt in order to lengthen the cycle life. The solubility of the positive electrode active materials for Li secondary battery in the melt was investigated (Table 1). The solubility of the compounds was less than 0.1wt%. It was confirmed that the compounds are chemically stable in the melt.

The possibility of the rocking chair type Li secondary battery operating at room temperature with the LiCl saturated melt electrolyte was suggested using the above compounds as the positive electrode active material.

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Fig. 1 Discharge curves for a Li-Al/LiCl saturated 64.0mol% AlCl_3 -36.0mol%EMIC/ $\text{c-V}_2\text{O}_5$ cell at 25°C. Constant resistance : 9.9k Ω .

Fig. 2 First charge and discharge curves for a Li-Al/LiCl saturated 64.0mol% AlCl_3 -36.0mol%EMIC/metal intercalation compounds cell at 25°C. — : LiCoO_2 (a), --- : LiNiO_2 (b), : LiMn_2O_4 (c), - - - - : $\text{c-V}_2\text{O}_5$ (d), : AG (e), and - - - - : AB (f). Current density: 0.2 $\text{mA} \cdot \text{cm}^{-2}$.

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Table 1 Solubility of metal intercalation compounds at 25°C in an LiCl saturated 64.0mol% AlCl_3 -36.0mol%EMIC melt electrolyte.

	LiCoO_2	LiNiO_2	LiMn_2O_4	a- V_2O_5	c- V_2O_5
Solubility / $\text{mg} \cdot \ell^{-1}$	0.336	0.185	0.3921	2.972	4.372
c- V_2O_5 : crystalline V_2O_5 , a- V_2O_5 : amorphous V_2O_5					