Development of Nonflammable Lithium Secondary Battery with Ambient Temperature Molten Salt Electrolyte - Performances of Positive Electrode -

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INTRODUCTION

Recently the problems with safe aspects such as ignition and explosion are pointed out because organic solvents are used for the electrolyte for a lithium secondary battery. Then, we have investigated useful the ambient temperature molten salt having useful characteristics such as nonflammability, nonvolatility, and wide potential window as a lithium secondary battery electrolyte from a view point of safety\(^{(1)(3)}\). We also reported that the binder-free carbon electrode operated well as the negative electrode in the AlCl\(_3\)-1-ethyl-3-methylimidazolium chloride (EMIC)-LiCl\(_{2}\) melt electrolyte\(^{(1)}\).

In this study, we evaluated the possibility of the nonflammable lithium secondary battery with the ambient temperature molten salt electrolyte by examining the performance of LiCoO\(_2\) positive electrode in the melt.

EXPERIMENTAL

AlCl\(_3\)-EMIC melt was prepared by mixing EMIC with anhydrous AlCl\(_3\) of the predetermined molar ratio below 60\(^{\circ}\). 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.

LiCoO\(_2\) electrode was prepared on a Mo sheet by coating the mixture of LiCoO\(_2\) AB, and PVdF with 82:10:8 in 1-methyl-2-pyrrolidine (NMP). 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.

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

RESULTS AND DISCUSSION

In the cyclic voltamogram (C. V.) of LiCoO\(_2\) electrode in the AlCl\(_3\)-EMIC-LiCl\(_{2}\)+SOCl\(_2\) melt, the oxidation and reduction waves corresponding to the electrochemical intercalation / deintercalation reactions of Li\(^{+}\) were observed at 3.5-4.2 V (vs. Li\(^+/\)Li), and it suggested that the LiCoO\(_2\) electrode operated well in above melt. In charge and discharge operation examinations, the discharge capacity was about 120-130 mAh/g and the coulombic efficiency maintained more than 93% during ten cycles. In addition, we also understood that the potential and capacity of LiCoO\(_2\) electrode put into the melt electrolyte under 5 x 10\(^{-4}\) m\(\text{m}^{-3}\)Hg were higher than under the atmosphere. Next, we examined the influence of the composition of acidic melt (50 mol% concentration of AlCl\(_3\) in AlCl\(_3\)-EMIC melt as addition \(\leq 66.7\text{mol}\%\) on the electrode characteristics. The difference was not seen in the discharge capacity and the coulombic efficiency, but the electrode potential in the electrolyte of 66.7mol%AlCl\(_3\) melt was the highest in the case of current density 1.0mA/cm\(^2\) (equivalent to 1C) as shown in Fig. 1. The concentration of Li\(^{+}\) in this melt becomes high with increasing concentration of AlCl\(_3\) in the AlCl\(_3\)-EMIC melt\(^{(5)}\). Therefore, we carried out C. V. measurement of LiCoO\(_2\) in various melt compositions. The cathodic current peaks corresponding to Li\(^{+}\) intercalation became high with increasing the concentration of AlCl\(_3\), in the melt as shown in Fig. 2. Because the viscosity of this electrolyte became high with increasing the concentration of AlCl\(_3\) in the melt, it was thought that Li\(^{+}\) intercalation reaction (discharge reaction) rate becomes slow. However, in this electrolyte, a reverse result was obtained. In the case of this melt, it was thought that the intercalation reaction of Li\(^{+}\) was strongly influenced by the concentration of Li\(^{+}\) than properties of the melt.

From these results, it was finally known that higher current density was obtained at the positive electrode, if the melt with higher concentration of Li\(^{+}\) was used.

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REFERENCES


Fig. 1 Charge and discharge curves of LiCoO\(_2\) electrode in various composition melts of AlCl\(_3\)-EMIC-LiCl\(_{2}\)+SOCl\(_2\) (25\(^{\circ}\)).

C. D. : 1.0mA/cm\(^2\)1C)

-56.0mol% AlCl\(_3\)
-60.0mol% AlCl\(_3\)
-66.7mol% AlCl\(_3\)

Potential / V vs. Li/Li\(^+\)
Capacity / mAh g\(^{-1}\)

Fig. 2 Cyclic voltammograms of LiCoO\(_2\) electrode in various composition melts of AlCl\(_3\)-EMIC-LiCl\(_{2}\)+SOCl\(_2\) (25\(^{\circ}\)).

Scan rate : 0.5mV/s.