Fabrication of All Solid State Rechargeable Lithium Batteries with a Sol-Gel Method

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$Li_4Ti_5O_{12}$ film electrode for all solid-state rechargeable lithium battery was successfully prepared on ceramic electrolytes with a sol-gel method. The cell was constructed with lithium metal and solid electrolyte, and electrochemically evaluated by impedance measurement and cyclic voltammetry. Sharp redox peaks were observed at around 1.55 V. The impedance of this cell was about 700 Ω. From these results, it can be said that the sol-gel method was very useful for the preparation of $Li_4Ti_5O_{12}$ electrode on ceramic solid electrolytes.

Much interest has been paid to a possibility of solving a safety problem on rechargeable lithium batteries. Several researches on non-liquid electrolyte system, such as a gel-polymer electrolyte and a polymer electrolyte, have been performed, and some of non-liquid electrolyte systems have been commercialized. However, they still involved a small amount of liquid electrolyte to keep their high ionic conductivity. Another research direction on solid-state rechargeable lithium batteries is an application of solid electrolyte based on Li^+ ion conductive ceramics. In this case, most of all, lithium ion conductivity of over 10^{-3} ~ 10^{-4} S cm^{-1} is required for practical rechargeable lithium batteries. Many researchers have developed some electrolytes with a high conductivity of Li^+ ion, such as $Li_{0.33}La_{0.55}TiO_3$ with a perovskite structure and $LiTi_2(PO_4)_3$-$AlPO_4$ (LTP) with a NASICON type structure [1-3].

In this study, $Li_4Ti_5O_{12}$ was used as an anode material for ceramic rechargeable lithium batteries. $Li_4Ti_5O_{12}$ with a spinel structure has been studied as a promising candidate of negative active material for rechargeable lithium batteries, due to a flat discharge and charge curve and an infinitesimal structural change during discharge and charge cycle. When using the ceramic electrolytes, a high resistance is produced owing to an insufficient contact at an interface between the ceramic electrolyte and both electrode sheets which are prepared by pressing a mixture of active material, solid electrolyte powder, and binding material (for example, Teflon®). In order to improve the contact between electrodes and ceramic electrolytes, a thin film of active material is useful. So far, many kinds of thin film preparation techniques have been utilized. In this study, the sol-gel method was used for a thin film formation of active material.

Li-Ti-O sol was synthesized with poly(vinylpyrrolidone) (PVP) powders as previously reported [4-5]. Molar compositions of starting solutions were $Li(OC_3H_7^i)$: $((CH_3)_2CHO)_4Ti$: PVP : CH_3COOH : i-C_3H_7OH = 4 : 5 : 5 : 100 : 100. Spin coating was conducted under a rotation speed of 3000 rpm in order to prepare Li-Ti-O gel film on ceramic electrolytes as a substrate. The gel film was converted to ceramic thin film by heating at temperature of 600 °C for 20 min. Here, LTP sheet with 0.5 mm thickness was used as the substrate. This LTP sheet had a high Li^+ ion conductivity (10^{-4} S cm^{-1}).

Impedance measurement was carried out in a range of 5 Hz to 13 MHz. A cyclic voltammetry was also performed at a scan rate of 1 mV min^{-1}. Both measurements were performed using two-electrodes configuration. Counter electrode was pure lithium metal. In order to avoid undesirable reaction between ceramic electrolytes and lithium metal, PMMA gel-polymer electrolyte was used. All electrochemical experiments were conducted in an argon-filled glove box at room temperature.

Fig. 1 shows the cole-cole plot of Li/Gel-polymer/LTP/ $Li_4Ti_5O_{12}$ cell. The plot shows two semi-circles. The total resistance of the cell was under 700 Ω. Fig. 2 shows the cyclic voltammogram of the cell. As shown in the figure, two sharp peaks were observed at around 1.55 V vs. Li/Li^+. This result is comparable with that of $Li_4Ti_5O_{12}$ using liquid electrolyte.

From the above results, it can be said that the PVP sol-gel method was useful for fabricating electrodes on ceramic electrolytes.

This Work was partly supported by a Grant-in-Aid for Scientific Research (A) (Grant No. 14205097) from The Ministry of Education, Science, Sports and Culture, Japan. And, we would like to thank Mr. Y. Inda in Ohara inc. for providing the LTP glass ceramic electrolyte used in this study.

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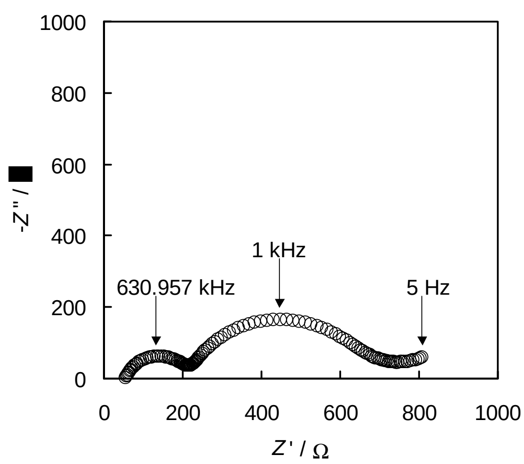

Fig. 1 Cole-cole plot of Li metal / Gel electrolyte / LTP / $Li_4Ti_5O_{12}$ cell.

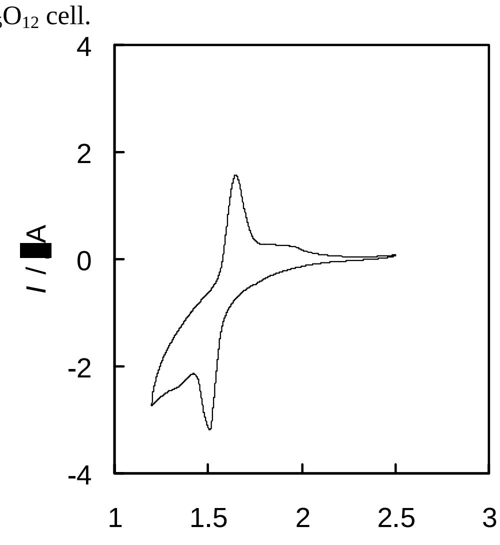

Fig. 2 Cyclic voltammogram of Li metal / Gel electrolyte / LTP / $Li_4Ti_5O_{12}$ cell at a scan rate of 1 mV min^{-1}.