

Preparation of Micro-Dot Electrodes of LiCoO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for Micro Rechargeable Lithium Batteries

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Introduction

Recently, many researchers have studied micro rechargeable lithium batteries. If an all solid-state micro-battery is realized, it will be utilized in various application fields related to microsystems, such as microsensors, micromechanics, microelectronics, and so on. Fabrication techniques of all solid-state lithium batteries have been explored intensively in our group. Ink jet technique can be applied to a production of micro rechargeable batteries by using precursor solutions of battery active materials as ink for ink jet printers. In this study, micro-dot electrodes for micro rechargeable batteries were prepared by using micro injection device.

Experimental

A molar ratio of each component in the Li-Co-O sol was $\text{CH}_3\text{COOLi} : \text{Co}(\text{CH}_3\text{COO})_2 : \text{poly}(\text{vinylpyrrolidone}) (\text{PVP}, \text{VP monomer unit}, M_w: 55000) : \text{CH}_3\text{COOH} : \text{H}_2\text{O} = 1.1 : 1 : 0.5 : 1 : 50$. Composition of Li-Ti-O sol was $\text{Li}(\text{OC}_3\text{H}_7) : [(\text{CH}_3)_2\text{CHO}]_4\text{Ti} : \text{PVP} : \text{CH}_3\text{COOH} : i\text{-C}_3\text{H}_7\text{OH} = 4.5 : 5 : 2 : 60 : 100$. To increase the viscosity of the Li-Ti-O sol, 10 mass % of Glycerin ($\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$) was added. By using the micro-injection device, micro-dots were drawn with sol solutions on Au substrates under an optical microscope observation. The dot population on the substrate is 2400 dots per cm^2 . The sol converted into gel in air at room temperature. Then, it was calcinated at high temperatures. The calcination of LiCoO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were carried out in air at 800 °C for 10 to 60 min, and 700 to 900 °C for 20 min, respectively. Their surface morphologies were observed with scanning electron microscope (SEM), and crystallographic structures were characterized by X-ray diffraction (XRD) and micro-Raman spectroscopy. The cyclic voltammetry (CV) was applied to examine the electrochemical activity of the samples.

Results and Discussion

Figure 1 shows the SEM images of the LiCoO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ micro-dot electrodes. The size of a dot is 100-150 μm in diameter for both samples. Any cracks were not observed on the entire surface of them, however, their surface morphologies were rough. In the XRD patterns of the LiCoO_2 sample prepared by heat treatment at 800 °C for various duration, a main peak corresponding to the (003) plane was observed for all samples. The micro-Raman spectroscopy revealed that LiCoO_2 samples were the hexagonal phase ($R\bar{3}m$ symmetry) with two Raman active modes at 592, 482 cm^{-1} arising from E_g and A_{1g} , respectively. The additional Raman peaks (686, 518 cm^{-1}) of impurity phase were observed.

XRD measurements of the prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ revealed that existence of very small amount of TiO_2 (anatase and rutile) as impurity phases.

Figure 2 shows the cyclic voltammograms of the prepared LiCoO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ micro dot electrodes. As shown in Fig. 2(a), three reversible peaks of LiCoO_2 were observed, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample also showed reversible redox behavior at 1.5 V (Fig. 2(b)). The prepared LiCoO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ micro-dot electrodes showed intrinsic electrochemical properties of the materials. The results of charge-discharge measurement of micro-dot electrodes combined with gel electrolytes will be also reported.

Acknowledgment

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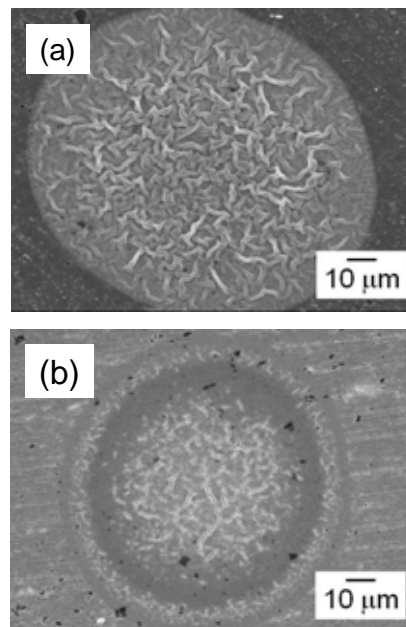


Figure 1. SEM images of (a) LiCoO_2 and (b) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ dot electrodes prepared at 800 °C for 20 min.

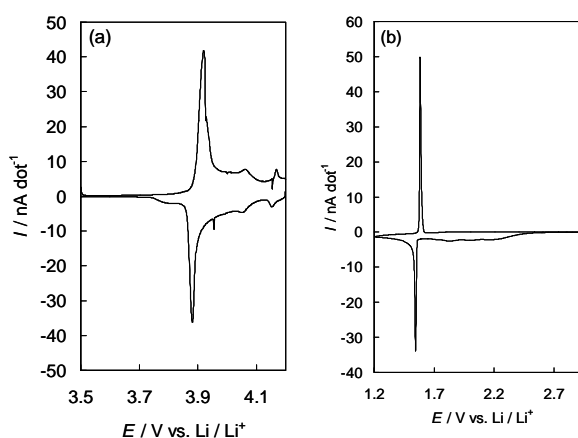


Figure 2. CVs of (a) LiCoO_2 and (b) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ dot electrode prepared at 800 °C for 20 min in electrolyte (1.0 mol dm^{-3} LiClO_4 (EC+DEC / 1:1 (volume ratio))).