Abs. 37, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Preparation of Binder-free Porous Electrode of $Li_4Ti_5O_{12}$ for All Solid-state Rechargeable Lithium Battery

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Introduction

Rechargeable lithium ion battery using liquid electrolytes suffers from several safety concerns. The most significant problem is its flammability. In order to solve safety problem of rechargeable lithium ion battery, solid electrolytes have been studied to construct all solid-state rechargeable lithium batteries that exhibit no flammability. However, several problems still remain to realize all solid-state battery. The ionic conductivities of most solid electrolytes are smaller than those of liquid electrolytes, and the resistance of the interface between solid electrolyte and electrode material is high due to poor contact. In this study, monodisperse spherical $Li_4Ti_5O_{12}$ particles were prepared as a candidate of anode material. Using these monodisperse particles, binder free porous electrode of $Li_4Ti_5O_{12}$ was fabricated on Pt substrate. In this study, we evaluated the possibility of this electrode for all solid-state lithium battery.

Experimental

Monodisperse $Li_4Ti_5O_{12}$ spherical particles were prepared from amorphous Li-Ti-O spherical particles as precursor. Amorphous Li-Ti-O spherical particles were synthesized with emulsion method as follows. Titanium tetraisopropoxide (TTIP) was mixed with n-octanol, solution in which hydroxypropyl cellulose was dissolved, and stirred at 40 °C for 15 min. Acetonitrile was added into the TTIP solution, and stirred for 30 min, then lithium hydroxide solution was added into the mixed solution, and stirred for 60 min, again. Obtained Li-Ti-O particles were separated from the solution with centrifugation, and the precipitate was washed with ethanol, and dried with freeze- drier. It was heated at 500 °C and then it was heated at 800 °C in a short time with infrared furnace. The spherical $Li_4Ti_5O_{12}$ particles were accumulated on Pt substrate by solvent evaporation process for $Li_4Ti_5O_{12}$ ethanol suspension, and it was heat treated at 800 °C for 1 min. Consequently, a porous $Li_4Ti_5O_{12}$ electrode was successfully fabricated of Pt substrate without organic binder and conductive agent. The $Li_4Ti_5O_{12}$ powder were observed with a scanning electron microscope (SEM), and analyzed with X-ray diffraction (XRD). The electrochemical characteristics were evaluated by charge and discharge test.

Results and Discussion

Figure 1 shows SEM image of the monodisperse spherical $Li_4Ti_5O_{12}$ particles prepared under optimized conditions. The spherical shape of the particle was maintained after heat treatment. The results of XRD analysis indicated that the samples were single phase of $Li_4Ti_5O_{12}$ spinel.

Figure 2 shows SEM image of the binder free porous electrode (BFPE) of $Li_4Ti_5O_{12}$. Thickness of the BFPE was about 5 μm, and its porosity was about 40 %. From the result of charge and discharge test in a liquid electrolyte, the BFPE of $Li_4Ti_5O_{12}$ exhibited 160 mA h g^{-1} at 0.1 C and it was very close to theoretical capacity (167.5 mA h g^{-1}). Figure 3 shows the capacity at various charge and discharge rate. The porous electrode showed 80 % of a theoretical capacity even at 2 C, and cycle stability was very good.

A gel electrolyte consisted of PMMA was injected into the pore of BFPE, and charge-discharge test of BFPE / gel / Li cell was carried out. The cell operated in reversible manner. These results suggest the high applicability of this electrode system to an all solid-state lithium battery. Further optimization and preparation of BFPE of other materials are now underway in our group.

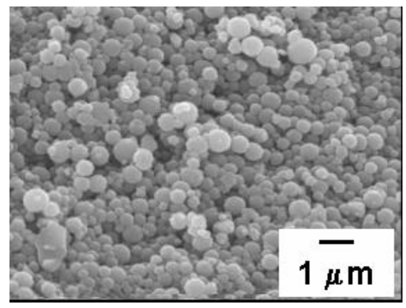

Figure 1. SEM image of $Li_4Ti_5O_{12}$ spherical particles.

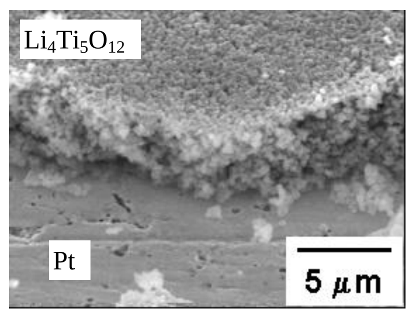

Figure 2. SEM image of $Li_4Ti_5O_{12}$ spherical particles deposited of Pt substrate.

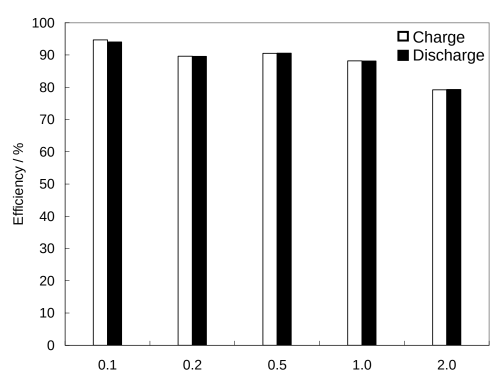

Figure 3. Coulombic efficiencies of $Li_4Ti_5O_{12}$ electrode in 1 mol dm^{-3} $LiClO_4$ / ethylene carbonate + diethyl carbonate (1 : 1 in volume) at various charge and discharge rates.