Li^+ Insertion/Extraction Properties for $TiNb_2O_7$ Single Particle Characterized by a Particle-Current Collector Integrated Microelectrode

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A single particle measurement is known as a characterization method of battery electrode material [1]. In a conventional single particle measurement, electrical contact between a microelectrode and an electrode particle is made while observing with an optical microscope. However, the applicability of this technique is limited with respect to the size and shape of particles. Recently, our group successfully evaluated electrochemical property of $Li_4Ti_5O_{12}$ (LTO) single particle by using "a particle - current collector integrated microelectrode", in which the single active material particle was directly-bonded on the tip of the microelectrode [2, 3]. In this study, we evaluate the electrochemical properties of $TiNb_2O_7$ (TNO) single particle using a particle - current collector integrated microelectrode.

TNO was synthesized via a conventional solid-state reaction method. In order to obtain TNO particle with suitable particle size for contacting with a microelectrode, the mixture of TiO_2 and Nb_2O_5 was annealed at 1300°C for 24h in air. TNO particle - current collector integrated microelectrodes were prepared as follows using a focused ion beam process unit (FIB): After attaching a tungsten probe coated with fluorinated resin to a manipulator in the FIB, the tip of the probe was cut off to expose the inner conductive probe. An ionic beam of platinum was positioned and deposited on contact between the top of the cut probe and a single TNO particle with the size around 10 μm. The particle - current collector integrated microelectrode as the working electrode was assembled in a three-electrode flange cell with Li metals as the counter and reference electrodes. The electrolyte employed was 1mol/L Li(TFSI)/EC+PC(1:1 v/v%). Electrochemical measurements of the TNO single particle were carried out at 20°C.

Cyclic voltammogram of TNO single particle showed the reversible redox peaks at around 1.6−1.7 V vs. Li/Li^+. Anodic peak current is higher than cathodic one at a fixed scan rate, indicating faster reaction during Li^+ extraction (i.e. discharge) than Li^+ insertion (i.e. charge) of TNO particle. This tendency was also confirmed in C-rate dependence of charge or discharge capacities. From the results for galvanostatic intermittent titration testing (GITT), we confirmed that at the potential vs. Li/Li^+ below 1.6 V, apparent chemical diffusion coefficient of Li^+ in TNO at Li^+ extraction process is much larger than at Li^+ insertion process. Furthermore, the capacity retention of TNO single particle tested at current of 10C after 2000 cycles was ~100%, indicating excellent reversibility of TNO single particle during Li^+ insertion and extraction reaction.

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