

Influence of TiO₂(B) Preparation from Na₂Ti₃O₇ and K₂Ti₄O₉ on Lithium Insertion and Extraction

Yasuhiro Harada, Keigo Hoshina, Hiroki Inagaki and Norio Takami

Toshiba Corporation,
Corporate Research & Development Center,
Functional Materials Laboratory
1, Komukai-Toshiba-Cho, Saiwai-Ku, Kawasaki
212-8582, Japan

Introduction

For improving power, life and safety of lithium-ion batteries, materials with a high potential of 1.5 V vs. Li/Li⁺ such as Li₄Ti₅O₁₂ (LTO) have been suggested as the anode material [1]. Recently, a monoclinic TiO₂(B) has been investigated as an alternative material to LTO. Nanostructured forms of TiO₂(B) exhibited a high reversible capacity of around 300 mAh/g [2]. Although there are many reports concerning micro-sized TiO₂(B) particles prepared from layered alkali titanates, the reversible capacities have a range of 160~240 mAh/g among the samples. TiO₂(B) is known as a metastable phase and is difficult to synthesize stably, this would be one of the reasons why the capacities are different.

In this study, we prepared TiO₂(B) particles from layered alkali titanates, and effects of synthesis conditions on the electrochemical properties were investigated to obtain TiO₂(B) with a large reversible capacity stably.

Experimental

The precursors Na₂Ti₃O₇ and K₂Ti₄O₉ were prepared by a conventional solid-state reaction method. A mixture of raw materials such as Na₂CO₃, K₂CO₃, and TiO₂ was sintered at 1000°C for 12 hours. The reground products were subjected to wet grinding to obtain uniform particle sizes. These precursors were proton-exchanged under 1M HCl from 10 min to 2 weeks at 25°C. These intermediates were dehydrated by heating at 350 to 500°C to form TiO₂(B). All the samples were analyzed by XRD and ICP analysis to check the residual alkali cations in the samples. Particle sizes, surface morphology, and domain structure of the samples were observed by SEM and TEM.

Electrodes of the TiO₂(B) samples were prepared as follows; a mixed slurry of the product powder, conductive agent, binder and solvent, was coated on a sheet of Cu foil using a doctor blade and then dried at 80°C under vacuum condition for 12 hours. These electrodes were used for electrochemical performance measurements such as charge-discharge test using a half-cell with a Li counter electrode (between 1.0 V-3.0 V vs. Li/Li⁺).

Results and Discussion

Figure 1 shows the relationship between the proton-exchange treatment time and proton exchange rate calculated from the results of ICP (where a completely proton-exchanged sample is indicated by 100 %) for the precursors Na₂Ti₃O₇ and K₂Ti₄O₉. Na₂Ti₃O₇ in particular exhibited poor exchangeability of H⁺ for Na⁺, and reached only a 89.2 % while the precursors K₂Ti₄O₉ exhibited relatively high proton-exchange speed, and reached 98.5 % after 2 weeks. To check the influence of residual alkali cations on lithium reversible capacity, the prepared intermediates were formed to TiO₂(B). The powder XRD patterns of these samples implied that the residual alkali cations inhibit crystallization of TiO₂(B) during the dehydration. Figure 2 shows the variation in reversible

capacity of TiO₂(B) synthesized from K₂Ti₄O₉ as a function of proton exchange rate. Interestingly, the reversible capacity increases rapidly at proton exchange rates of over 95 %, indicating that even a little bit of alkali residue results in a decrease of the reversible capacity.

We then optimized heat-treatment conditions for synthesizing TiO₂(B) from the well proton-exchanged intermediates. The d-spacing of (001) (*d*₀₀₁) in TiO₂(B) increased with decreasing heat-treatment temperature of the intermediates. As shown in Figure 3, the *d*₀₀₁ of over 0.620 nm led to a large reversible capacity of more than 240 mAh/g. A large *d*₀₀₁ of 0.624 nm in TiO₂(B) structure, which was successfully obtained by heating the intermediate at 350°C for 2 h, causes an expanding of the lithium storage sites along the [001] c-axis and had a large capacity of 253.1 mAh/g close to that of TiO₂(B) nanoparticles [2]. We thus suggest the *d*₀₀₁ is one of the indicators to synthesize TiO₂(B) with the large capacity.

Consequently, these synthesis conditions should be carefully optimized to obtain a large reversible capacity of TiO₂(B) prepared from the layered alkali titanates.

References

1. N. Takami et al, *Journal of the Electrochemical Society*, **156**, A128 (2009).
2. Y. Ren et al, *Angewandte Chemie International Edition*, **51**, 2164 (2012).

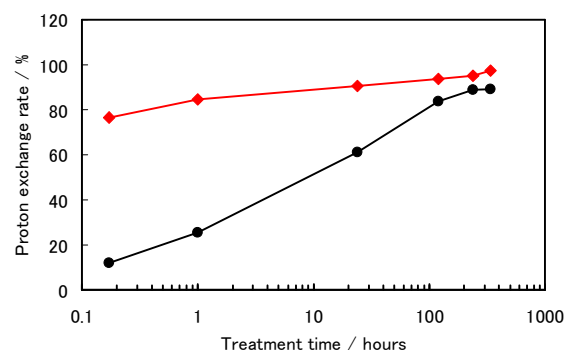


Fig. 1. Variations of proton exchange rate as a function of acid-treatment time: ●: Na₂Ti₃O₇ (a) and ◆: K₂Ti₄O₉ (b).

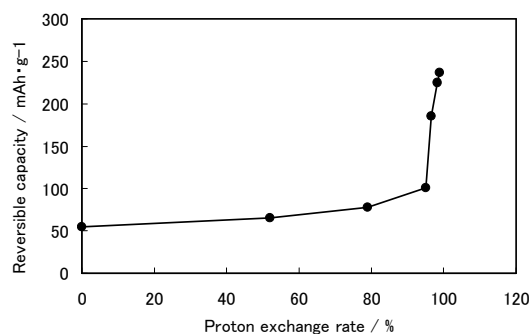


Fig. 2. Relationship between proton exchange rate and the reversible capacity of TiO₂(B).

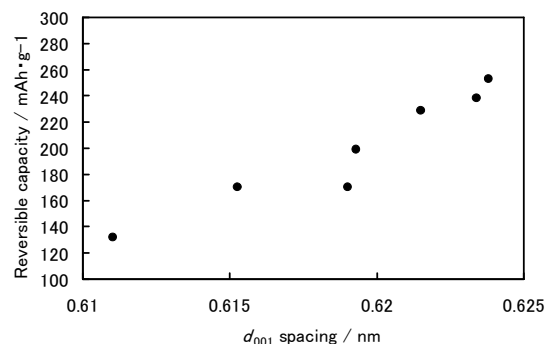


Fig. 3. Reversible capacity vs. *d*₀₀₁-spacing of TiO₂(B) samples synthesized in this work.