Size Dependent Fast Li Ion Storage Based on Size Regulated TiO$_2$(B) Nanosheet Electrodes with Vertical, Horizontal and Random Alignment

Tomohiro YOSHIDA,$^4$ Daisuke TAKIMOTO,$^5$ Dai MOCHIZUKI,$^{6,7}$ and Wataru SUGIMOTO$^{b,8,9}$

$^a$ Materials and Chemical Engineering, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

$^b$ Interdisciplinary Cluster for Cutting Edge Research, Center for Energy and Environmental Science (X-Breed), Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

$^c$ Interdisciplinary Cluster for Cutting Edge Research, Research Initiative for Supra-Materials (RISM), Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

$^*Corresponding author: wsugi@shinshu-u.ac.jp

ABSTRACT

TiO$_2$(B) has a high theoretical capacity of 335 mAh g$^{-1}$ for Li$^+$ intercalation and thus has been considered as a candidate for lithium-ion capacitor and Li-ion battery negative electrodes. For high rate lithium storage, i.e. high power density, it is important to shorten the Li$^+$ diffusion path by using nanostructured TiO$_2$(B). In this work, TiO$_2$(B) nanosheet with different equivalent diameter of 300 nm and 30 nm were prepared. In addition, the orientation of the TiO$_2$(B) nanosheets was manipulated by altering the deposition method and drying process. Smaller size TiO$_2$(B) nanosheets had better Li$^+$ intercalation ability compared to larger sized TiO$_2$(B) nanosheets. The effect of alignment of the TiO$_2$(B) nanosheets was evident for small-sized TiO$_2$(B) nanosheets; vertical or random alignment of small-sized TiO$_2$(B) afforded higher capacity compared to horizontally oriented nanosheets.

1. Introduction

The fast and safe electrochemical Li storage properties associated with the high intercalation/de-intercalation potential of ~1.5 V vs. Li/Li$^+$ makes titanium-based oxides attractive as negative electrode materials for lithium-ion batteries as well as lithium-ion capacitors.1,2 The suppression of thick SEI (solid electrolyte interface) layer and small volume expansion allows faster charging and discharging than graphite negative electrodes. Of the many polymorphs of titania, TiO$_2$(B) has attracted interest owing to the characteristic platelet-like morphology where the Li$^+$ diffusion path is much longer than the actual thickness of the electrode.3,4 Hydrothermal synthesis of nanostructured TiO$_2$(B) such as nanowires, nanotubes, and nanoparticles have been reported to show high capacity and improved rate performance compared to micro-sized bulk TiO$_2$(B).5,6 The size and shape of such TiO$_2$(B) nanomaterials seems to have a strong effect on the lithiation behavior. Nonetheless, it is difficult to control the size of nanosized TiO$_2$(B) through hydrothermal synthesis. In addition, due to the poor electronic conductivity of TiO$_2$(B), conducting additives are usually added or coated onto the surface in fairly large amounts for high power studies, which further complicates the fundamental electrochemistry of the material.

In this study, we attempt to elucidate the governing factors of Li$^+$ intercalation in TiO$_2$(B) using a series of electrodes with well-characterized lateral size and orientation without the use of polymeric binders or conductive additives. Since the Li$^+$ diffusion in TiO$_2$(B) is along the b axis, size-regulated TiO$_2$(B) nanosheets with long and short b axis should act as a model material to understand the kinetics of Li$^+$ intercalation into TiO$_2$(B). The Li$^+$ diffusion length along the b axis is controlled by size regulation of TiO$_2$(B) nanosheets, which is varied by using TiO$_2$ nanosheet precursors with different lateral size. Furthermore, the orientation (horizontal, vertical, random alignment) of TiO$_2$(B) nanosheets was manipulated by utilizing advanced nanosheet film processing techniques. Based on the controlled morphologies, the kinetics of Li$^+$ storage in TiO$_2$(B) is discussed.
2. Experimental

2.1 Synthesis of large and small size TiO_2 nanosheets

Ultrapure water (Milli-Q, >18 MΩ cm) was used for all synthesis and characterization. TiO_2 nanosheets were derived from layered K_2Ti_4O_9·H_2O (see Supporting Information S1 for details of synthesis). Bi-layered TiO_2 nanosheets were obtained by centrifugal separation. TiO_2 nanosheets with reduced lateral size were obtained by ultrasonating the TiO_2 nanosheet colloid with a homogenizer (225 W power at 20 kHz, 5 s pulse and 10 s interval of off-power for 30 min).

2.2 Fabrication of TiO_2(B) nanosheets with different orientation

TiO_2 nanosheets were fabricated by electrophoretic deposition based on a process similar to a previous study. A pair of Pt plates were placed in the TiO_2 nanosheet colloid (0.5 g L^{-1}) with a distance of 1 cm. A voltage of 4 V was applied for 30 minutes, and then vacuum-dried. TiO_2 nanosheets deposit on the electrode due to the negative charge (negative Zeta potential) of the TiO_2 nanosheets. Vertically-aligned TiO_2 nanosheets were fabricated by a process developed for fabricating vertically-aligned graphene oxide electrodes. Following electrophoretic deposition (EPD) of TiO_2 nanosheets, the as-deposited film was freeze dried by transferring the EPD cell quickly to a liquid N_2 bath and then vacuum-dried.

3. Results and Discussion

3.1 Synthesis of TiO_2(B) nanosheet electrodes with different size and orientation

When exfoliated [TiO_2]_{2-} nanosheets composed of mono-layered [TiO_2]_{2-} slabs were used as the starting material, topochemical transformation to TiO_2(B) did not occur and anatase TiO_2 was formed. The topochemical transformation process of TiO_2(B) from H_2Ti_4O_9 involves the dehydration and condensation of adjacent layers in H_2Ti_4O_9 and the presence of TBA^+ in the interlayer inhibits interlayer dehydration. Therefore, it was necessary to use a precursor which is free from organic intercalants and a TBA-Ti_4O_9 intercalation compound with bi-layered [TiO_2]_{2-} nanosheets. Nanosheet electrode fabrication through EPD or flocculation processes leads to TBA-free thin films, and was applied in this study for TiO_2(B) film fabrication. Bi-layered TiO_2 nanosheets were obtained by separating mono-layered TiO_2 nanosheets by centrifugal separation. [TiO_2]_{2-} nanosheet colloid was ultracentrifugally collected at 15000 rpm for 15 min to remove mono-layered [TiO_2]_{2-} nanosheets which are present in the supernatant. The sediment was re-dispersed in water and centrifuged at 2000 rpm for 30 min to produce a colloidal suspension predominantly bi-layered [TiO_2]_{2-} nanosheets.

X-ray diffraction (XRD) data of films fabricated by casting the bi-layered [TiO_2]_{2-} nanosheet colloid on a glass slide (Fig. S3) reveal a lamellar structure with a d-spacing of ~2.0 nm, which is 0.2 nm larger than that of a TBA-Ti_4O_9 intercalation compound prepared from mono-layered [TiO_2]_{2-} nanosheets. Atomic force microscopy (AFM) images of bi-layered [TiO_2]_{2-} nanosheets with and without ultrasonication are shown in Fig. 1. Small sized nanosheets were prepared by ultrasonication of the bi-layered [TiO_2]_{2-} nanosheet colloid with a homogenizer. The thickness of the obtained individual bi-layered [TiO_2]_{2-} nanosheets are uniform at ~2.0 nm. The thickness of mono-layered [TiO_2]_{2-} nanosheets characterized by AFM are about 1.2 nm. The results from XRD and AFM clearly reveals that the obtained nanosheets are composed of two layers of [TiO_2]_{2-} slabs.

The lateral size of individual bi-layered [TiO_2]_{2-} nanosheets were analyzed from AFM images (Fig. 1) using the equivalent diameter (D_e) as an index. D_e was calculated according to the following equation,

\[ D_e = \frac{4 \times A}{P} \]

where A is the area and P is the perimeter of individual nanosheets. The D_e of bi-layered [TiO_2]_{2-} nanosheets without ultrasonication had a wide distribution from 100–500 nm with an average D_e of 300 nm. The TiO_2 nanosheets obtained with ultrasonication had a
much narrower size distribution of $D_e$ = 10–60 nm with an average $D_e$ of 30 nm (Fig. S4).

Bi-layered $[\text{Ti}_4\text{O}_9]^{2-}$ nanosheets with different lateral size were converted to TiO$_2$(B) nanosheets by thermal treatment. The samples will be denoted as TiO$_2$(B)($D_e$) nanosheets, where $D_e$ represents the equivalent diameter of the nanosheets. Cross-sectional SEM images of horizontally, randomly, and vertically aligned TiO$_2$(B)($D_e$) nanosheets are shown in Fig. 2. During the drying process, bi-layered $[\text{Ti}_4\text{O}_9]^{2-}$ nanosheets re-stack. In the case of vacuum-dried EPD film, bi-layered $[\text{Ti}_4\text{O}_9]^{2-}$ nanosheets collapse to form a relatively smooth film with a thickness of ~10 µm. Based on the theoretical density of 3.64 g cm$^{-3}$ for TiO$_2$(B) and thickness of individual $[\text{Ti}_4\text{O}_9]^{2-}$ nanosheets, the film should be composed of $1 \times 10^7$ TiO$_6$ octahedra in terms of thickness. The horizontally aligned TiO$_2$(B)($D_e$) films appear fairly dense in the SEM images, but is actually quite porous; the electrode density estimated from the cross-sectional SEM analysis and mass loading was ~0.35 g cm$^{-3}$, or 90% porosity based on the theoretical density for TiO$_2$(B). By conducting freeze-drying instead of vacuum-drying after EPD, the bi-layered $[\text{Ti}_4\text{O}_9]^{2-}$ nanosheets align vertically and thus can be converted to vertically-aligned TiO$_2$(B)($D_e$) without collapse of the macroscopic orientation. The mechanism of vertical alignment of nanosheets via EPD-freeze drying has been discussed earlier.\(^9\)

The experimental conditions in this study were controlled so that the mass loading of all electrodes are constant at 0.350 mg cm$^{-2}$. The thickness of TiO$_2$(B)($D_e$) nanosheet electrodes with horizontal, random, and vertical alignment are 10, 20, to 100 µm, respectively. Note that as long as the film fabrication process is the same, the difference in the nanosheet size $D_e$ of the precursor does not affect the film thickness and tap density. Thus, by decreasing the $D_e$ of TiO$_2$(B) nanosheets from 300 nm to 30 nm, the $b$ axis, which is the direction of Li$^+$ diffusion, should be decreased to 1/10 and the relative number of Li$^+$ insertion sites should increase by 10 times.

3.2 Electrochemical properties of TiO$_2$(B) nanosheets with different size and orientation

Galvanostatic charge/discharge curves and the corresponding $dQ/dE$ plots calculated from the potentiograms are shown in Fig. 3. The $dQ/dE$ plots show typical characteristics of TiO$_2$(B) with a broad redox peak at $E_{1/2} \sim 1.55$ V vs. Li/Li$^+$. A small shoulder peak is observed at $E_{1/2} \sim 2.0$ V vs. Li/Li$^+$, which may be ascribed to minor anatase TiO$_2$ impurities. The discharge capacity is plotted as a function of the C rate for TiO$_2$(B)(300 nm) and TiO$_2$(B)(30 nm) in Fig. 4. For the case of TiO$_2$(B)(300 nm), the orientation of TiO$_2$(B) does not strongly affect the Li$^+$ intercalation kinetics and the amount of Li$^+$ intercalated at 0.2 C is 1/5 of the theoretical capacity (Li$_{0.2}$TiO$_2$). The effect of orientation becomes clear by downsizing the lateral dimension of TiO$_2$(B). When electrodes with the same orientation but different nanosheet size are compared, the reduction in Li$^+$ diffusion path results in a higher capacity at the same C rate. The capacity at 0.2 C for TiO$_2$(B)(30 nm) is increased to Li$_{0.2}$TiO$_2$ ($x = 0.28$–0.42). The lack of full charging of TiO$_2$(B)($D_e$) indicates that the penetration depth of Li$^+$ into the TiO$_2$(B) structure is very shallow, even for TiO$_2$(B)(30 nm). This result suggests that the poor electronic conductivity does not allow electrons to conduct through the entire film, and only 30 to 40 percent of the film is active for electrochemical lithiation. The lack of full charging may also be due to the presence of anatase TiO$_2$ as impurity.

Another important trend that can be pointed out for the TiO$_2$(B)(30 nm) electrodes is that vertical and random alignment is superior to horizontal alignment. Vertical alignment shows the highest capacity at low C rate (<1 C), but at C rates above 1 C, the randomly aligned electrodes outperforms vertical alignment. Since the Li$^+$ diffusion length of these three electrodes should be the same, the results again implies that the electronic conductivity of the electrodes is the dominating factor at high C; 100 µm thick vertical electrode performs well at low C rate but is a poor material at high C rate.

4. Conclusions

The effect of the size and orientation of TiO$_2$(B) nanosheets towards electrochemical lithiation was studied. Large-sized TiO$_2$(B)
nanosheets and small-sized TiO$_2$(B) nanosheets with an equivalent diameter of 300 nm and 30 nm were prepared by downsizing the dimension of the precursor, bi-layered [Ti$_4$O$_9$]$^{2-}$ nanosheets, by ultrasonication of the nanosheet colloid. TiO$_2$(B) nanosheet electrodes with three different orientation (horizontal, random, and vertical) was prepared by vacuum-drying or freeze-drying of electrophoretically deposited electrodes or via flocculation. For large-sized TiO$_2$(B)(300 nm) nanosheet electrodes, the orientation effect was not clear, suggesting that the kinetics is dominated by the Li$^+$ conductivity through the TiO$_2$(B) tunnel structure. By down-
sizing TiO$_2$(B) to 30 nm, the power capability was improved. A two times increase in rate performance was obtained for horizontally-aligned electrodes by downsizing, while for vertically- and randomly-aligned electrodes, higher capacity was obtained at the same C rate for TiO$_2$(B)(30 nm) nanosheets compared with TiO$_2$(B)(300 nm) nanosheets. The orientation of small-sized TiO$_2$(B) had a large influence on Li$^+$ storage kinetics. Vertically-aligned TiO$_2$(B) showed much faster Li$^+$ intercalation/de-intercalation behavior compared to horizontally aligned TiO$_2$(B) with the same mass loading.

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Supporting Information

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