

RESEARCH ARTICLE

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# Electrochemical properties of the $\text{TiO}_2(\text{B})$ powders ball mill treated for lithium-ion battery application

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## Abstract

**Background:** Belt or wire shaped  $\text{TiO}_2(\text{B})$  particles were synthesized for lithium ion battery application by a hydrothermal and heat treatment process. In order to facilitate  $\text{TiO}_2(\text{B})/\text{C}$  composites fabrication, the synthesized  $\text{TiO}_2(\text{B})$  particles were crushed into smaller sizes by ball milling.

**Results:** Ball mill treated  $\text{TiO}_2(\text{B})$  particles of less than  $1.0\ \mu\text{m}$  with a fraction of anatase phase, compared to as-synthesized  $\text{TiO}_2(\text{B})$  particles with about  $24\ \mu\text{m}$  in average particle size, showed a significant improvement in the electrochemical properties. They showed a much improved stability in the charge–discharge cycles and irreversibility. They maintained about 98% of the initial capacity during 50 cycles while as-synthesized sample before ball mill treatment showed a gradual decrease in the capacity with the cycles. The irreversibility of 12.4% of as-synthesized sample was also greatly improved to 7% after ball milling treatment.

**Conclusions:** Our results indicate ball mill treatment can be an economical way to improve electrochemical properties of  $\text{TiO}_2(\text{B})$  anode materials for lithium ion battery application.

**Keywords:**  $\text{TiO}_2(\text{B})$ , Anode materials, Ball-milling, Lithium-ion battery, Hydrothermal method

## Introduction

Graphite has been extensively used as a negative electrode material due to its relatively high specific capacity and electrochemical stability [1-3]. However, several issues were brought about due to inherent electrochemical characteristics of graphite; electrodeposition of lithium at the surface of graphite during quick charging, and a solid electrolyte interface (SEI) layer formation by the secondary reactions between graphite and electrolyte. These problems deteriorated the performance of the graphite electrode, resulting in shorter lifetime and reduced capacity. Thus, an alternative electrode material has been actively explored to replace it. In particular, electric vehicles requiring fast charging need electrode materials not only experiencing little lattice distortions during charge–discharge cycles, but having a long

lifetime, high stability, and high discharging capacity, etc. And most of all, they need to be fabricated at a reasonably low cost.

Among the promising materials to replace the graphite electrode, nano-structured  $\text{TiO}_2$  polymorphs have attracted much attention due to their high capacity and microchanneled structure appropriate for intercalation and deintercalation of the Li ions during charge–discharge cycles [4,5]. The space existing between layers in the crystalline structure as well as within the  $\text{TiO}_2$  particles could facilitate the intercalation and deintercalation of  $\text{Li}^+$  ions during the process. Especially,  $\text{TiO}_2(\text{B})$  having relatively open structures compared to Rutile, Anatase, and Brookite has an obvious advantage for the intercalation and deintercalation of  $\text{Li}^+$  ions without severe lattice distortions [6,7]. The favorable structural characteristics of the  $\text{TiO}_2(\text{B})$  mentioned above are believed to improve the lifetime and performance of the battery [8-10]. In addition, the fabrication of  $\text{TiO}_2(\text{B})$  particles is relatively simple and easy to scale up for high volume production.

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In this study, we obtained belt or wire shaped  $\text{TiO}_2(\text{B})$  particles to use as a negative electrode by a hydrothermal and heat treatment process. Ball milling process was utilized to crush the synthesized  $\text{TiO}_2(\text{B})$  particles into smaller sizes to facilitate  $\text{TiO}_2(\text{B})/\text{C}$  composites fabrication. The effects of ball mill treatment on the electrochemical performance of the  $\text{TiO}_2(\text{B})$  particles were evaluated in terms of microstructure and phase changes.

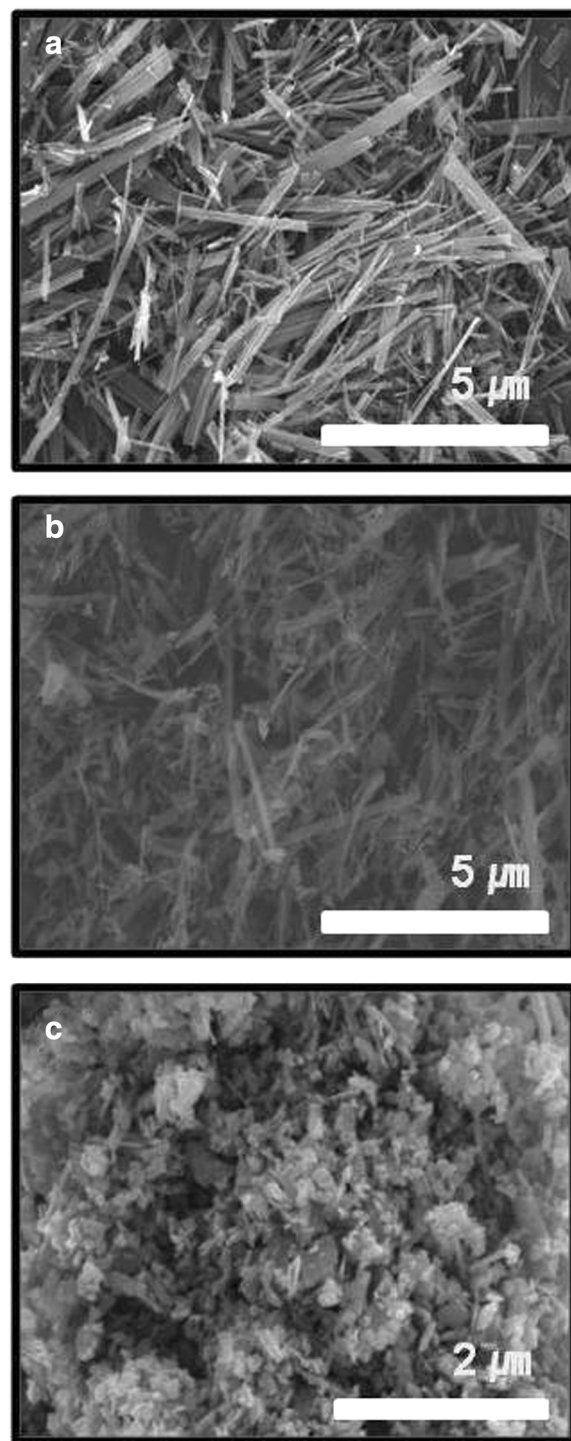
### Experimental details

For preparing  $\text{TiO}_2(\text{B})$  powder, 0.1 M P25 powder was at first put into 10 M aqueous NaOH solution, and then the solution was hydrothermally heated at  $180^\circ\text{C}$  for 24 hrs. The obtained particles were calcined at  $450^\circ\text{C}$  for 6 hrs in air, resulted in having  $\text{TiO}_2(\text{B})$  phase with nanobelt of thin and long length. After that ball-milling was conducted on  $\text{TiO}_2(\text{B})$ , materials and electrochemical characterizations were carried out using SEM (Scanning Electron Microscopy, S-4700, Hitachi), XRD (X-Ray Diffraction, D/MAX 2500, Rigaku) and Raman spectroscopy (Renishow, in via Raman Microscope). As the milling time increased, particle size of  $\text{TiO}_2(\text{B})$  powders decreased from  $24\text{ }\mu\text{m}$  to  $0.2\text{ }\mu\text{m}$  through a 300 rpm, 3 hrs ball-milling. Here, the size was measured using PSA (Particle Size Analyzer with laser scattering, Photal ELS-800, Otsuka electronics).

Electrochemical properties were measured with R2032 coin-type cells. A metal lithium foil was used as the anode. Composite electrodes were prepared by mixing 80 wt%  $\text{TiO}_2(\text{B})$  powders, 10 wt% conductive Super-P, 10 wt% SBR-CMC binder, and N-methylpyrrolidone (NMP) solvent to form uniform slurry. A solution of 1 M  $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 w/w) was used as the electrolyte. The cells were charged and discharged between 1.0 and 3.0 V by applying a constant current of  $50\text{ mA g}^{-1}$ .

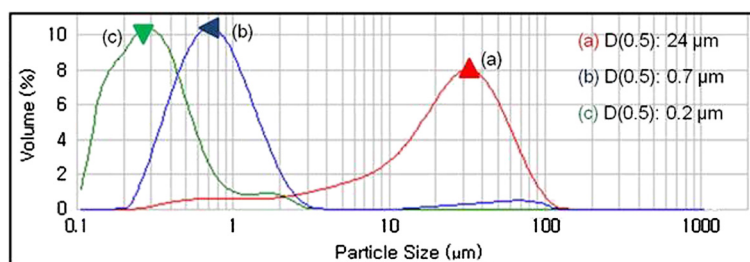
### Results and discussion

$\text{TiO}_2(\text{B})$  powders were synthesized by the heat treatment of the rod or belt-shaped H-titanate powders at  $450^\circ\text{C}$  for 6 hrs, which had been prepared by a hydrothermal process. The combined process of the hydrothermal and heat treatment has been used for the synthesis of  $\text{TiO}_2(\text{B})$  powders [11,12]. The synthesized  $\text{TiO}_2(\text{B})$  powders were ball milled using a planetary type ball mill at a fixed rotation speed of 300 rpm for up to 3 hrs to make them smaller sizes. The changes of morphology and size of the powders with the milling time were observed under SEM as shown in Figure 1. The as-synthesized  $\text{TiO}_2(\text{B})$  powders were observed from Figure 1(a) to be long rod or belt shaped. The powders were broken



**Figure 1** SEM images for planetary-milled  $\text{TiO}_2(\text{B})$  powders with 300 rpm and various milling times. (a) as-prepared  $\text{TiO}_2(\text{B})$ , (b) 1 hr ball-milled  $\text{TiO}_2(\text{B})$ , and (c) 3 hrs ball-milled  $\text{TiO}_2(\text{B})$ .

into smaller sizes after 1 hr ball milling (Figure 1(b)). However, they became severely agglomerated after ball milling for 3 hrs as can be seen in Figure 1(c). The size



**Figure 2** Particle size distribution of planetary-milled  $\text{TiO}_2(\text{B})$  with milling times by laser scattering (PSA) shown in Figure 1: (a) as-prepared  $\text{TiO}_2(\text{B})$ , (b) 1 hr ball-milled  $\text{TiO}_2(\text{B})$ , and (c) 3 hrs ball-milled  $\text{TiO}_2(\text{B})$ .

distribution of the  $\text{TiO}_2(\text{B})$  powders with the milling time was graphed in Figure 2. As-synthesized  $\text{TiO}_2(\text{B})$  powders with an average of  $24 \mu\text{m}$  became broken into smaller sizes of  $0.7$  and  $0.2 \mu\text{m}$  after ball milling for 1 and 3 hrs, respectively.

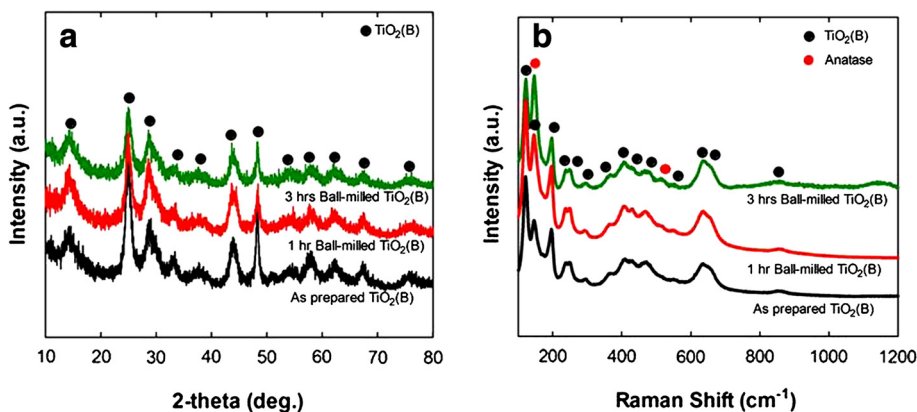
Figure 3 shows the XRD patterns and Raman spectra for the samples of as-synthesized and ball milled for up to 3 hrs. Typical peaks for  $\text{TiO}_2(\text{B})$  phase were observed from all the samples as in Figure 3(a). It was also noticed that the intensity of the main peak at  $24.979^\circ$  was gradually decreased but the FWHM was increased with the milling time, indicating the particles were becoming smaller sizes. These results were found to be consistent with the SEM observations in Figure 1 for the size changes of the particles with the milling time.

Raman spectra showed that as-synthesized sample was composed of primarily  $\text{TiO}_2(\text{B})$  with the minor phase of anatase as seen in Figure 3(b). However, intensity of the anatase became stronger with the ball milling time, resulting in a dominant phase after ball milling for 3 hrs.

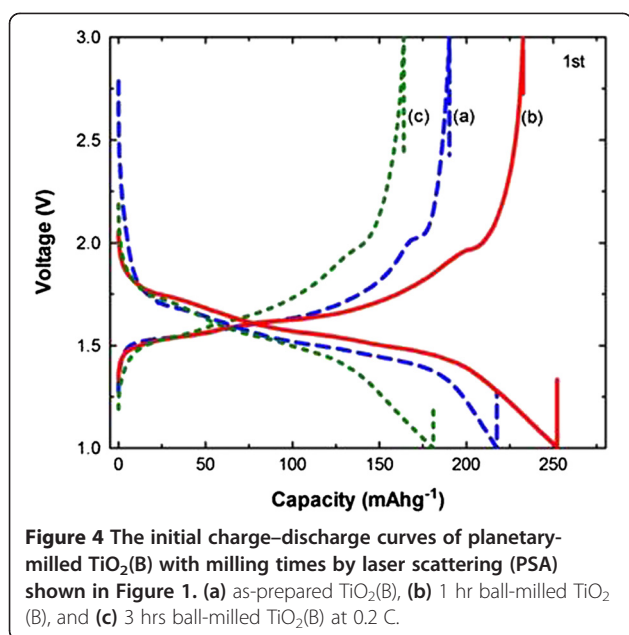
Figure 4 shows the initial charge–discharge performance for the  $\text{TiO}_2(\text{B})$  samples measured in the range

of  $1.0 - 3.0 \text{ V}$  with a lithium foil as a counter electrode. As-synthesized  $\text{TiO}_2(\text{B})$  sample had the charging capacity of about  $217 \text{ mAh/g}$ , discharging capacity of  $190 \text{ mAh/g}$ , and the resultant irreversibility of about  $12.4\%$ . Meanwhile, the sample ball milled for 3 hrs was measured with the charging capacity of about  $180 \text{ mAh/g}$ , discharging capacity of  $164 \text{ mAh/g}$ .

The reduced charge–discharge capacity of the 3 hrs ball milled sample seemed to be caused by the presence of the strong anatase peaks identified with Raman spectra in Figure 2. Similar to our results,  $\text{TiO}_2$  anode materials with anatase or rutile phase were reported to have a relatively low charging capacity of about  $150 - 200 \text{ mAh/g}$  [13,14]. It is also well known that charge–discharge capacity is much affected by the particle size of the electrode materials; smaller particles show better performance [15,16]. On the other hand,  $\text{TiO}_2(\text{B})$  sample ball milled for 1 hr was measured to have a high charging capacity of  $250 \text{ mAh/g}$  and discharging capacity of  $232 \text{ mAh/g}$ , and irreversibility of  $7\%$ . Based on the results with 1 hr and 3 hrs ball milled samples, the performance was found to be affected positively by the smaller scale of particles, but negatively by the presence



**Figure 3** XRD patterns (a) and Raman spectra (b) of the planetary ball-milled  $\text{TiO}_2(\text{B})$  samples used in Figure 1.



of anatase phase; the presence of anatase phase with a strong intensity in the 3 hrs ball milled sample even with smallest particles deteriorated the performance.

Cyclic stability of charge–discharge capacity and capacity variation as a function of C-rate was compared among the samples in Figure 5. As can be seen in Figure 5(a),  $\text{TiO}_2(\text{B})$  sample ball milled 1 hr showed a high degree of cyclic stability. About 98% of the initial discharge capacity was maintained even after 50 cycles; initial capacity of 232 mAh/g was reduced only to 227 mAh/g. On the other hand, as-synthesized sample and 3 hrs ball milled sample showed a gradual decrease of the capacity with the cycle suggesting smaller particle size without anatase phase in  $\text{TiO}_2(\text{B})$

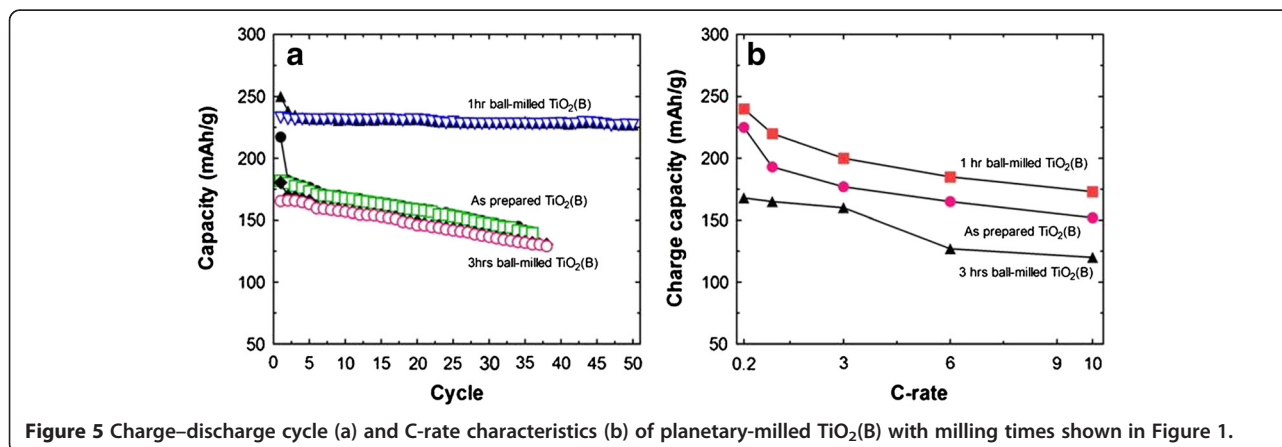
was an optimum condition for the high electrochemical performance. Discharging capacity was gradually decreased with the C-rate regardless of the sample types as compared in graph Figure 5(b). But the gaps in the initial capacity among the samples were observed to be kept during the whole measurements in the C-rate range of 0.2 – 10 C.

## Conclusions

$\text{TiO}_2(\text{B})$  particles were synthesized for lithium ion battery application by a hydrothermal and subsequent heat treatment processes. They were rod or thin belt shaped of about 24 microns in average size. For the efficient fabrication of  $\text{TiO}_2(\text{B})/\text{C}$  composite anode materials, the  $\text{TiO}_2(\text{B})$  particles were crushed into smaller sizes by ball milling process. Prolonged ball milling for up to 3 hrs produced particles with the average size of less than 1.0  $\mu\text{m}$ . However, 3 hrs ball milled sample showed the anatase phase with a strong intensity by Raman spectra observation. Similar to other research results, the sample with the strong anatase peaks was measured to have a relatively low reversible capacity of 165 mAh/g compared to 190 mAh/g of as-synthesized sample. On the other hand, the sample ball milled for 1 hr, consisting of less than 1.0  $\mu\text{m}$  particles with weak anatase peaks, showed much improved reversible capacity of 232 mAh/g.

$\text{TiO}_2(\text{B})$  sample ball milled for 1 hr also showed a very high stability during charge–discharge cyclic tests. : It maintained about 98% of the initial discharge capacity during 50 cycles while as-synthesized and 3 hrs ball milled samples showed a gradual decrease in the capacity with the cycles.

Our results suggest that the electrochemical performance of  $\text{TiO}_2(\text{B})$  as a negative electrode material can be significantly improved with a simple and economical way of ball milling treatment.



#### Competing interests

The authors declare that they have no competing interests.

#### Authors' contribution

BRK has carried out the experiments for the study, collected the data and analyzed them and has written the manuscript. KSY and HJJ have been involved by contributing their intellectual content for the research work. STM and SCJ have made their intellectual contributions in revising the manuscripts with their knowledgeable suggestions. WK and SJK were involved in interpretation of the data, drafting the manuscript, analyzing the results and critically revising it for intellectual content. The final manuscript has been read and approved by all the authors.

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