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Boron-doped TiO_2 anode materials for high-rate lithium ion batteries

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ABSTRACT

Boron(B)-doped TiO_2 (BT) materials are synthesized through a simple one-pot process using a sol–gel method, and are employed as anode materials in Li-ion batteries. The increase of B-dopant concentration up to 10.4 wt% in BT samples increases the interplanar spacing between TiO_2 lattices from 3.33 Å to 4.33 Å, and the BET surface area from 27.7 $m^2\ g^{-1}$ to 90.6 $m^2\ g^{-1}$. Additionally, the BT sample containing a relatively large amount of B possesses cylindrical pores that are favorable for lithium-ion transfer, leading to the highest diffusion coefficient. Consequently, the BT anodes with high B-dopant concentration exhibit significantly-improved cyclic capacities at 100 cycles: 166.9 mA h g^{-1} at 1 C and 119.4 mA h g^{-1} at 10 C, whereas the non-doped BT sample, TiO_2, exhibits 107.7 mA h g^{-1} at 1 C and 19.9 mA h g^{-1} at 10 C at 100 cycles.

1. Introduction

Rechargeable Li-ion batteries (LIBs) have attracted attention as one of several promising electrochemical energy storage devices for electronic vehicles, due to their high energy density, long cycling life and zero emission [1,2]. Graphite, a typical LIB anode material, can be cycled at high C-rates. However, it is unfavorable because of such disadvantages as low power density, low C-rate and safety concerns [3,4]. Recent research in the field of electric vehicles has focused on developing new active anode materials with high power density [3–5].

Titanium dioxide (TiO_2) has garnered considerable interest among the new anode materials being considered for next-generation LIBs due to advantages such as fast Li insertion at low voltage and low volume variation (<4%) during the charge/discharge processes [6–8]. TiO_2 is also an inexpensive and environmental-friendly material [9,10]. Generally, TiO_2 exists in the phases of rutile [8], anatase [9] and brookite [10]; the anatase phase can be considered a host material for electroactive Li-insertion [11–13]. A crucial disadvantage of anatase-structure TiO_2, however, is low electric conductivity owing to its wide band gap energy (E_g = 3.0–3.4 eV), a significant hindrance in LIB anode materials, resulting in dramatic performance decreases at high C-rates in the charge/discharge process [11–15]. Methods studied to overcome this challenge include changes in crystallinity, crystallite size, and specific surface area of the TiO_2 [14–17]. In particular, TiO_2 with large internal surface area is able to enhance lithium storage capability and reaction kinetics due to a short diffusion pathway [11–14]. The internal surface area is usually related to the mesoporosity, interplanar spacing and specific surface area of TiO_2. A doping technique is considered an efficient means of increasing the internal surface area and electrical conductivity [11–13]. Doping with cationic or anionic dopants contributes to the formation of more open channel and active sites for Li-ion transport via the expanding interplanar spacing of TiO_2 lattices. Boron(B)-doped carbon anode materials have been investigated in many studies [18–20], demonstrating that B-doped graphite has a larger lattice constant value, a_0, and a smaller d_{002} distance than ideal graphite, due to replacement of the carbon atoms with boron [18], leading to increases in both the crystallinity and electronic property of carbon as a Li-host material. Yin et al. [19] reported that B-doped graphite exhibited a higher discharge capacity, which was attributed to higher amounts of enhanced graphitization than non-doped graphite. Fujimoto et al. [20] also reported that both the discharge capacity and Coulombic efficiency of LIBs were enhanced by B-doping in graphite. In the present work, a simple one-pot process using a sol–gel method will synthesize B-doped TiO_2, and the resultant anode material with high-rate capability for the high-power application of LIBs will be compared with non-doped TiO_2. While there have been few studies on the LIB performance of B-doped TiO_2, the B-doped TiO_2 has been mainly studied to the application of photocatalysts [21–28]. Boron doping in TiO_2 significantly enhanced photocatalytic activity due to various beneficial effects such as large adsorption of visible light, a shift in the conduction band, and the formation of Ti^{3+} induced by oxygen vacancy.

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2. Experimental

The B-doped TiO_2 (BT) was synthesized using boric acid (H_3BO_3, Oriental Chem. Co., Korea) and titanium isopropoxide ($Ti[OCH_2(CH_3)_2]_4$, Junsei Chem. Co., Japan) as the precursors for B-dopant and TiO_2. The precursors were used to obtain B-dopant to Ti ratios of 2, 5 and 10 wt% in the BT samples, which are notated as BT2, BT5 and BT10, respectively. To manufacture the BT2 sample, 0.11 g of boric acid dissolved in 20 ml of isopropyl alcohol was mixed with 5.93 g of titanium isopropoxide dissolved in 30 ml of isopropyl alcohol. The mixture was vigorously stirred for 10 min, followed by the addition of 5 ml of de-ionized water; the final solution was ultrasonicated for 90 min to accelerate hydrolysis. The resultant was filtered and washed with a mixture of de-ionized water and ethanol, dried at 80 °C for 12 h in a convection oven, and finally heat-treated under air at 450 °C for 5 h. The TiO_2 sample was synthesized via the same method, without boric acid.

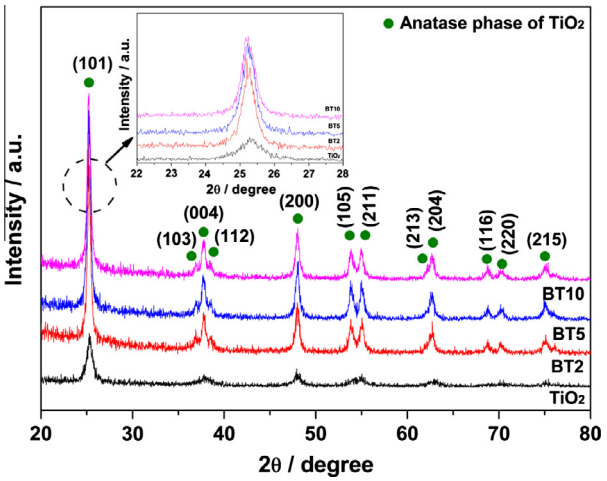

Fig. 1. (a) XRD patterns for TiO_2 and the BT samples.

The morphology, crystal structure and surface area of the BT samples were characterized via transmission electron microscopy (TEM, Jeol, JEM-2100F), X-ray diffractometry (XRD, Rigaku, RAD-3C) with Cu Kα radiation (λ = 1.541 Å), and a Brunauer, Emmett & Teller (BET) analyzer (Micromeritics, ASAP 2010). In addition, the chemical-bonds and element compositions in the BT samples were analyzed via Fourier transform infrared spectroscopy (FT-IR, Nicolet IR 200, Thermo Fisher Sci.) with KBr pellets, and X-ray photoelectron spectroscopy (XPS, Escalab 250, Thermo Fisher Sci.) with an Al Kα ($h\nu$ = 1486.6 eV) source, respectively.

The electrochemical properties of the samples were evaluated via 2016-type coin half-cells with BT samples as working electrodes and lithium foil as a counter electrode. The working electrode was composed of 80 wt% BT, 10 wt% super-P as a conductive additive, and 10 wt% polyvinylidene fluoride (PVDF, Solef 5130, Solvey Plastic Co., Belgium) binder dissolved in n-methyl-2-pyrrolidinone. The mass loading of the working electrodes was approximately 1.0 g cm^{-3} on the copper current collector. The electrical conductivity of the electrodes was measured using a four-point probe (CMT-100M, AIT Co.) method. The coin cells were assembled in an argon-filled glove box with the electrolyte, a solution of 1 M $LiPF_6$ (Panaxetec Co., Korea) in ethyl carbonate/dimethyl carbonate/ethyl methyl carbonate (1:1:1, vol.%). A galvanostatic charge/discharge cycling test was performed in the voltage window of 1–3 V using the WBCS3000 system (Wonatech Co., Ltd.) at 0.1 C for the first 2 cycles, and 1 C, 5 C or 10 C for the next 100 cycles. Cyclic voltammetry (CV, Biologis, VSP) was performed in the voltage range of 1–3 V at various scan rates from 0.1 mV s^{-1} to 10 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was also measured in the frequency range of 100 kHz to 0.01 Hz.

3. Results and discussion

The XRD patterns of the TiO_2 and BT samples shown in Fig. 1 reveal that the TiO_2 crystals are indexed to an anatase phase with an *I*41/*amd* space group and a body-centered tetragonal (BCT) structure. It is clear that addition of B atoms increases crystallinity of TiO_2. Li et al. [21] reported that the increase in the crystallinity of B-doped TiO_2 was due to the reduction in the grain boundaries and amorphous regions acting as charge-carrier recombination centers. In addition, the increase in the concentration of B slightly shifts the (101) crystal planes of the BT samples compared to that

Table 1
Summary of the physical properties of TiO_2 and the BT samples. The average particle size was calculated from the XRD date in Fig. 1 using the Scherrer's formulas.

Samples	Average particle size (nm)	Pore diameter (Å)	BET's surface area ($m^2\ g^{-1}$)	Surface resistance ($\Omega\ sq^{-1}$)	Diffusion coefficient ($\times 10^{-11}$) $cm^2\ s^{-1}$
TiO_2	11.3	13.41	27.7	26.3	0.25
BT2	18.3	4.27	55.5	14.2	0.54
BT5	19.3	3.64	64.8	3.1	5.27
BT10	19.8	3.26	90.6	1.3	6.06

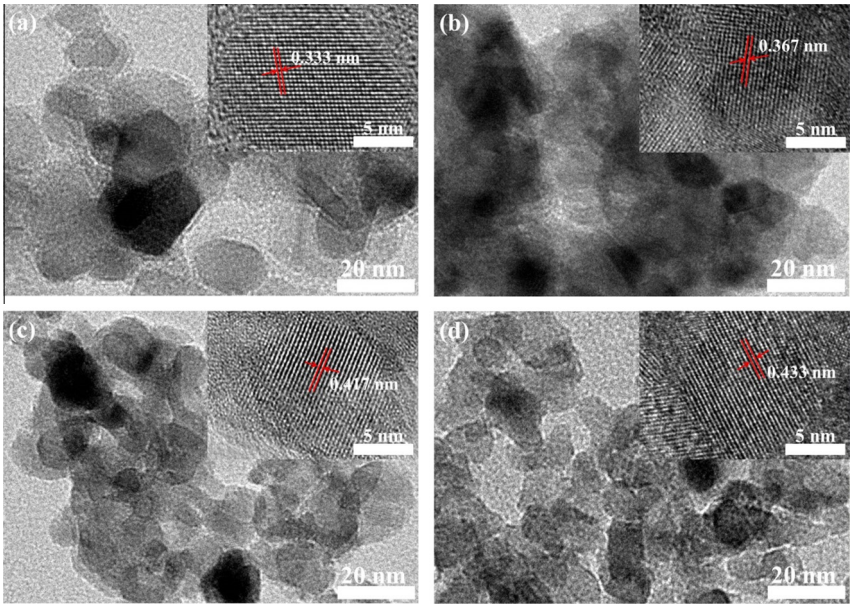

Fig. 2. HR-TEM images of (a) TiO_2, (b) BT2, (c) BT5 and (d) BT10 samples.