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TiO_2 Branched Nanostructure Anode Material Prepared by Seeding Method for High-performance Lithium Ion Batteries

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Abstract : We demonstrate rutile TiO_2 branched nanostructure (TiO_2-BN) electrodes synthesized by seeding method for enhanced lithium intercalation properties. The morphology and crystalline nature of the TiO_2-BN were clearly observed by field-emission transmission electron microscopy and fast Fourier transform pattern. The TiO_2-BN electrodes showed excellent capacity and high rate performance. The improved lithium-ion intercalation properties of the TiO_2-BN may be attributed to relatively large specific surface area and short transport distance of the branched nanostructure.

Keywords : Branched nanostructure, Lithium ion batteris, Rutile, TiO_2

1. Introduction

Lithium-ion batteries (LIBs) are essential portable power sources because of their high-energy density, high-power density, and long cycle life.[1,2] Typically, graphite-based materials have been a typical anode material to apply commercial LIBs. Because of several disadvantages of graphite anode materials such as initial capacity loss and structural deformation, it is urgently required to develop novel materials and structures with high-performance lithium intercalation.[3,4] As an alternative of graphite, titanium dioxide (TiO_2) utilized in a variety of applications such as photocatalytic activity,[5,6] catalyst supports,[7] and gas sensors[8] is regarded as a promising lithium insertion/extraction material with low production cost and high capacity.[9]

TiO_2 nanostructured materials such as nanorods, nanowires, and nanotubes have been studied in order to achieve excellent LIBs with high energy density, large capacity, rate performance and long cycle life.[10,11] Considerable efforts have been made to explore diverse synthetic methods ranging from vapor-phase techniques to solution-growth processes for the synthesis of nanostructure TiO_2.[12] In particular, it is well known that various types of TiO_2 nanostructures can be synthesized through strong acid treatment under hydrothermal or non-hydrothermal conditions.[13]

Herein, we synthesized rutile TiO_2 branched nanostructures (TiO_2-BNs) for LIBs via hydrothermal process without any surfactant and template. The structural characterization of the TiO_2-BNs was performed using high-resolution transmission electron microscopy (HR-TEM), fast Fourier transform (FFT), X-ray diffraction (XRD) analysis, and nitrogen sorption measurement. To analyze the performance for LIBs using the TiO_2-BNs as an anode, charge-discharge and rate cycling curves of the electrodes were measured using a lithium coin cell at room temperature.

2. Experimental

For the preparation of seeds of TiO_2-BNs, 8 mL of titanium(IV) isopropoxide (TTIP (97%), Aldrich) was dropped in 40 mL of 10 M hydrochloric acid (HCl (35%), Aldrich) with constant stirring at 25°C

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for 1 h and then kept at 120°C for 24 h. After the hydrothermal process, the resulting precipitates were cooled to room temperature, washed several times with ethanol and distilled water, and then precipitated using centrifuge at 10,000 rpm. The white TiO_2 seeds were obtained after drying at 50°C oven. The TiO_2-BN was synthesized by means of a seeding method with TiO_2 seeds. The seed-solution (12 wt%) was injected in 30 mL of 0.5 M HCl with constant stirring at 25°C and then kept constant for 15 min. After that, the 2 mL of TTIP as precursor was dropped in mixture solution and kept constant for 1 h and kept at 90°C for 4 h. The resulting precipitates were cooled to 25°C, washed several times with ethanol and distilled water, and precipitated using centrifuge at 8,000 rpm, and then dried at 50°C drying oven.

The morphology and size distribution of the samples were characterized by FE-TEM (a Tecnai G2 F30 system) operating at 300 kV. TEM samples were prepared by placing drops of powder suspension dispersed in ethanol on a carbon-coated copper grid. XRD analysis was carried out using Rigaku X-ray diffractometer with Cu K_α ($\lambda = 0.15418$ nm) source with a Ni filter. The source was operated at 40 kV and 100 mA. The 2θ angular scan from 20° to 60° was explored at a scan rate of 5° min^{-1}. The resolution in the scans was kept at 0.02°. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020. Before the adsorption measurements, all samples were outgassed at 473 K for 360 min in the port of the adsorption analyzer. The starting relative pressure was 0.995 P/P° and ending relative pressure was 0.01 P/P°.

The electrodes were prepared by mixing 70 wt% TiO_2-BN as an active material, 20 wt% acetylene black as a conducting agent, and 10 wt% poly-vinylidene fluoride (PVDF) as a binder. In order to obtain the slurry, several drops of N-methyl-pyrrolidone were added into the mixture of TiO_2-BN with acetylene black and PVDF. The prepared slurry was homogenized by stirring and then coated uniformly on ~11 μm thick copper foil substrates. The electrode dried in an oven at 80°C for 12 h and then cooled down to room temperature. The cells were assembled in a high purity argon filled glove box using the TiO_2-BN as the working electrode and lithium foil as the counter and reference electrodes and a separator that was saturated with the electrolyte solution that consisted of 1.1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of EC/DMC = 1:1.

The lithium intercalation properties of the assembled cells were recorded with charge/discharge curves between 3.0 and 1.0 V. The charge/discharge tests were galvanostatically cycled between 3.0 and 1.0 V for 100 cycles at a current rate of 1 C. After charge/discharge tests for 5 cycles at a current rate of 0.5 C, rate cycle performance tests were also carried out at various current rates from 0.5 to 20 C in order to confirm the rate capability. All of the lithium intercalation measurements were completed at room temperature.

3. Results and Discussion

As shown in Fig. 1(a) and (b), the TiO_2-BNs obtained by a seeding method seem to be a three-dimensional structure with branches grown along one-dimensional backbones. The diameter and length of the TiO_2-BNs are ~20 and ~110 nm,

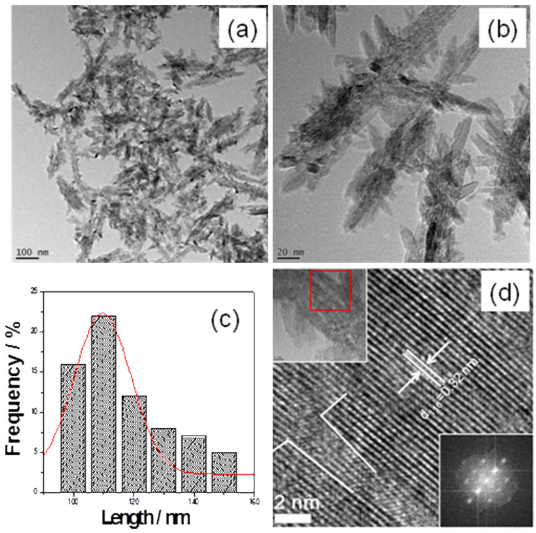

Fig. 1. (a), (b) TEM images of TiO_2-BNs; (c) Size-distribution histogram of TiO_2-BNs; (d) HR-TEM image of TiO_2-BNs (The insets indicate a TEM image of TiO_2-BNs and the corresponding FFT pattern.).

respectively (Fig. 1(c)). As shown in Fig. 1(d) of high-resolution TEM image, the TiO_2-BN was exposed to (110) plane corresponding to *d*-spacing of 0.32 nm. The FFT pattern of the inset in the Fig. 1(d) indicates the (101) and (110) plane of rutile phases. Fig. 2 shows the XRD pattern of the TiO_2-BNs representing rutile phase with tetragonal crystal structure ($a = b = 0.452$ nm, $c = 0.294$ nm, space group $P4_2/mnm$). According to the reference (JCPDS No. 88-1175) of the TiO_2 rutile phase, the

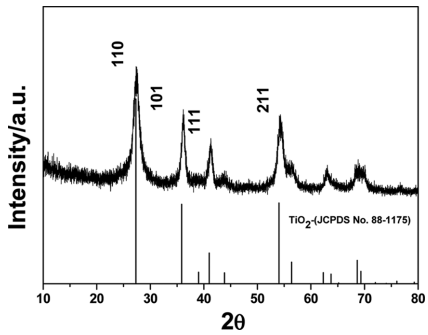

Fig. 2. Wide-angle XRD pattern of TiO_2-BNs.

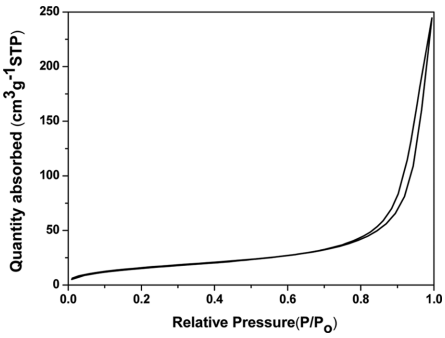

Fig. 3. Nitrogen adsorption/desorption isotherm curve of TiO_2-BNs.

TiO_2-BNs show the similar intensity ratio of the principal XRD peaks to that of the reference. As shown in Fig. 3. The BET specific surface area of the TiO_2-BNs is ~60.3 $m^2 g^{-1}$ and is much larger than that of the typical rutile TiO_2 nanoparticles.[9)]

Fig. 4(a) shows 1st and 2nd discharge-charge curves of the TiO_2-BNs at a current density of 1 C. At the cycling rate of 1 C, the first charge capacity of the TiO_2-BNs is 300 $mAh \cdot g^{-1}$ and much larger than that of the typical rutile TiO_2 electrode.[9)] Furthermore, the TiO_2-BNs as a rutile TiO_2 electrode exhbit an irreversibility between 1st and 2nd cyle and two plateaus due to phase transition from rutile to spinel and then rock salt.[14,15)] The cycling performance and coulombic efficiency of the TiO_2-BNs at a current rate of 1 C for 100 cycles are indicated in Fig. 4(b). The TiO_2-BNs exhibit the reversible capacity of ~190 $mAh \cdot g^{-1}$ and high coulombic efficiency of ~92.5% up to 100 cycles. To investigate rate cycling performance of the TiO_2-BN electrode, the discharge-charge rates were increased stepwise from 0.5 to 20 C as indicated in Fig. 4(c), the specific charge capacities of TiO_2-BNs are 215 $mAh \cdot g^{-1}$ at 0.5 C; 119 $mAh \cdot g^{-1}$ at 5 C; 43 $mAh \cdot g^{-1}$ at 20 C. This represents that even at high current rates from 5 to 20 C, TiO_2-BNs can display an excellent rate cycling performance. The remarkably large capacity of 216 $mAh \cdot g^{-1}$ can be obtained when the current rate is returned to 0.5 C after 60 cycles at different current rates. The improved lithium-ion intercalation properties of TiO_2-BNs may be attributed to large specific surface area, short transport distance of nanostructure, and freedom for volume change accompanied by lithium-ion intercalation.[16)]

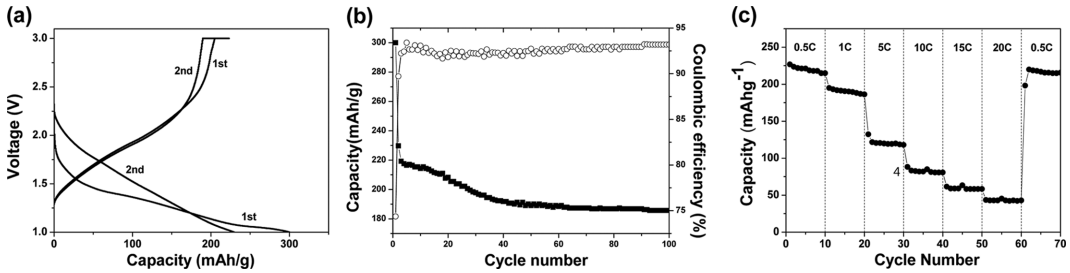

Fig. 4. (a) 1st and 2nd discharge-charge curves of the TiO_2-BNs at a current density of 1 C; (b) The cycling performance and coulombic efficiency of the TiO_2-BNs at a current rate of 1 C for 100 cycles; (c) Rate capability of the TiO_2-BNs from 0.5 C to 20 C.

4. Conclusions

In summary, using seeding method in hydrothermal process without any surfactant and template, we have prepared three-dimensional TiO_2-BN anode materials. The TiO_2-BNs showed large capacity, high coulombic efficiency, and excellent high rate cycling performance in lithium intercalation properties, and the facilitating lithium ion motion in the nanostructure electrode.

Acknowledgments

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