



Superior cyclability of branch-like TiO₂ embedded on the mesoporous carbon nanofibers as free-standing anodes for lithium-ion batteries



Xianhua Li¹, Baoming Zhou¹, Wei Wang, Zhiwei Xu^{*}, Nan Li, Liyun Kuang, Cuiyu Li, Wei Mai, Hongjun Fu, Hanming Lv

State Key Laboratory of Separation Membranes and Membrane Processes, School of Textiles, Tianjin Polytechnic University, Tianjin 300387, China

ARTICLE INFO

Article history:

Received 23 December 2016
Received in revised form
18 February 2017
Accepted 20 February 2017
Available online 24 February 2017

Keywords:

Branch-like TiO₂
Mesoporous carbon nanofibers
Free-standing anodes
Lithium-ion batteries
Composite materials

ABSTRACT

For the poor capacity utilization and insufficient cyclability of TiO₂/C anodes for lithium-ion batteries, we synthesized branch-like TiO₂@mesoporous carbon nanofibers (TiO₂@MCNFs) as free-standing anodes via electrospinning technique, hydrothermal treatment and a subsequent carbonization process, where anatase TiO₂ branches were densely embedded on the mesoporous carbon nanofiber trunks. Due to the copious highly-exposed TiO₂ nanocrystal lattices on the branch except for the trunk support, the abundant intrinsic crystal channels for fluent Li⁺ transportation, and the interlaced carbon nanofiber framework with a high structural integrity and mechanical flexibility, the branch-like TiO₂@MCNFs composites presented a superior initial discharge capacity of 1932 mAhg⁻¹ and an excellent reversible capacity of ~617 mAhg⁻¹ after 100 cycles. And compared with those of the reported TiO₂/C electrodes, the initial discharge capacity and reversible capacity of the branch-like TiO₂@MCNFs composites increased by ~2 times and ~50%, respectively. Hence, the unique architecture of the branch-like TiO₂@MCNFs composites and their superior electrochemical performances may provide new insights for the development of better host materials for practical lithium-ion batteries.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Among various energy devices, lithium-ion batteries (LIBs) represent a dominant class of existing technology because of their safety, long cycle life and low cost. With the great demand of high capacity LIBs, plenty of efforts have been made to research for decades [1–4]. In view of this, to exploit new electrode materials, especially anode materials like TiO₂ are of great interest [5–9]. It is known that TiO₂ is widely used in lots of fields including environmental remediation, photocatalytic degradation and energy storage [10–12] owing to its abundance, safety and chemical stability. The volume expansion during lithiation and delithiation process of TiO₂ anodes for LIBs is about 3%, which enables a stable cycle life [13]. However, the low theoretical capacity (330 mAhg⁻¹) and poor cycling performance of TiO₂ greatly limit its practical use [14]. Hence, various approaches have been put forward to surmount this problem by improving the electron kinetics, which included

coating or combining TiO₂ with carbonaceous materials. Xia *et al.* investigated the effect of carbon coating on TiO₂ and concluded that the introduction of carbon could reinforce electronic conductivity and supply flexible space for preventing the large volume expansion during cycling [15]. The hierarchical mesoporous TiO₂/C nanospheres which showed a more stable cyclability and a higher rate performance has been synthesized by Wang *et al.* [16]. In addition, Zuniga *et al.* [17] has prepared TiO₂/carbon composite nanofibers with multichannel hollow structure, using a facile forcespinning method followed by subsequent thermal treatment. Although the electrochemical properties of the acquired anode materials enhanced, most of TiO₂/C composites reported so far had a limited reversible capacity less than 400 mAhg⁻¹, which still needed to be improved.

In this contribution, we reported a novel branched architecture prepared by the combination of electrospinning technique, hydrothermal reaction and carbonization process. The novel architecture consisted of TiO₂ branches and mesoporous carbon nanofiber trunks. And the composites were directly used as anodes of LIBs without adding any additional binder and conductive agent. By investigating the electrochemical performance of these free-standing anodes, direct evidences were gained to demonstrate

^{*} Corresponding author.

E-mail address: xuzhiwei@tjpu.edu.cn (Z. Xu).

¹ These authors contributed equally to this work.

the superiority of this architecture, suggesting that such novel composites could be used as ideal LIBs.

2. Experimental

2.1. Preparation of samples

Briefly, the PAN blend fibers were fabricated by optimizing the polyacrylonitrile (PAN) concentration (12%(w/w) in N,N-dimethylformamide and polyethylene glycol solution) via electrospinning technique. Then, the tetrabutyl titanate mixtures (8 g tetrabutyl titanate and a certain amount of n-Butanol were stirred for 1 h) and the dried PAN blend fibers were both heated at 180 °C for 12 h. The as-prepared fibers were washed with n-Butanol and distilled water under ultrasound, then dried at 60 °C under vacuum overnight. And the dried nanofibers were treated at 280 °C for 4 h with a heating rate of 2 °C min⁻¹ under air atmosphere in order to induce dimensional stability of the carbon nanofibers. Subsequently, the above pre-oxidated fibers were carbonized at 900 °C for 2 h with a heating rate of 2 °C min⁻¹ in a N₂ atmosphere tube furnace. The preparation process of TiO₂@MCNFs composites was illustrated in Fig. 1.

2.2. Characterization

The morphology of branch-like TiO₂@MCNFs composites was examined by field emission scanning microscope (FESEM) and transmission electron microscopy (TEM, JEM-2100). The Brunauer-Emmer-Teller (BET) specific surface area and average pore size were characterized by N₂ adsorption-desorption isotherms with Micromeritics Analytical Services. The crystal structure of as-prepared composites was determined by X-ray diffraction (XRD, Bruker D8 Discover) with Cu K α radiation ($\lambda = 1.54059 \text{ \AA}$) with a scanning speed of 5° min⁻¹ from 3 to 80° and Raman spectrum on RENISHAW in Via Raman Microscope with an excitation wavelength of 514 nm and a power of 5 mW. Thermo-gravimetric analysis (TGA) was conducted with a Netzsch TG209F1 under air atmosphere with a heating rate of 5 °C min⁻¹ to calculate the content of TiO₂.

2.3. Electrochemical tests

The electrochemical performance of the branch-like TiO₂@MCNFs composites was estimated by using them as

working electrodes without any additional binder and conductive agent in CR2032 coin-type cells. And the digital photos of anodes were shown in Fig. S1, indicating that the toughness of composites was superior. In addition, the packing density of anodes was 1.76 g cm⁻³ (thickness and active mass was 0.019 mm and 6.12 mg, respectively). The lithium foil worked as the counter electrode and 1 M LiPF₆ dissolved in ethyl carbonate, dimethyl carbonate and diethyl carbonate mixture (1:1:1,v/v/v) worked as the electrolyte. And Celgard 2400 membranes were used as separators. The package of batteries was conducted in a glovebox and measured after aging for 24 h. Electrochemical impedance spectroscopy was also tested on the CHI660D electrochemical workstation in the frequency range between 100 kHz and 0.01 Hz. The charge-discharge performances were evaluated by Land testing system at 100 mA g⁻¹. Cyclic voltammograms were collected at a scan rate of 0.5 mV s⁻¹ by a CHI660D electrochemical test-station. The rate property was measured at the current density of 100, 200, 500 and 1000 mA g⁻¹.

3. Results and discussion

Fig. 2a showed FESEM micrographs of the branch-like TiO₂@MCNFs composites and presented that the composites mainly consisted of a large quantity of branched TiO₂ architectures onto the carbon nanofiber trunks. It could be observed from the high-magnification FESEM image that the composites possessed rough and well-aligned surfaces, which were derived from compactly irregularly shaped TiO₂ nanorods [18]. During the carbonization process, polyethylene glycol would be decomposed and rapidly volatilized. The outward diffusion of some gas generated a force to compress the TiO₂ nanostructures [19]. In this case, it was imaginable that the interface layer between the TiO₂ and carbon nanofibers would change due to the pressure and high temperature (low heating rate), which could alter the structure of TiO₂. That was branch-like TiO₂ structures. In addition, the composites contained 45.4% anatase nanorods and 54.6% carbon nanofibers from TGA measurement (Fig. S2), indicating that the ratio of TiO₂ and MCNFs was about 1:1. The relevant N₂ adsorption-desorption isotherm curves of the branch-like composites were shown in Fig. 2b, presenting a type IV isotherm with typical adsorptive behaviours such a monolayer adsorption, suggesting the mesopores existed within the branch-like composites [20]. And the calculated BET specific surface area of the composites was 216.1 cm² g⁻¹. Compared with the CNFs prepared at the same conditions as

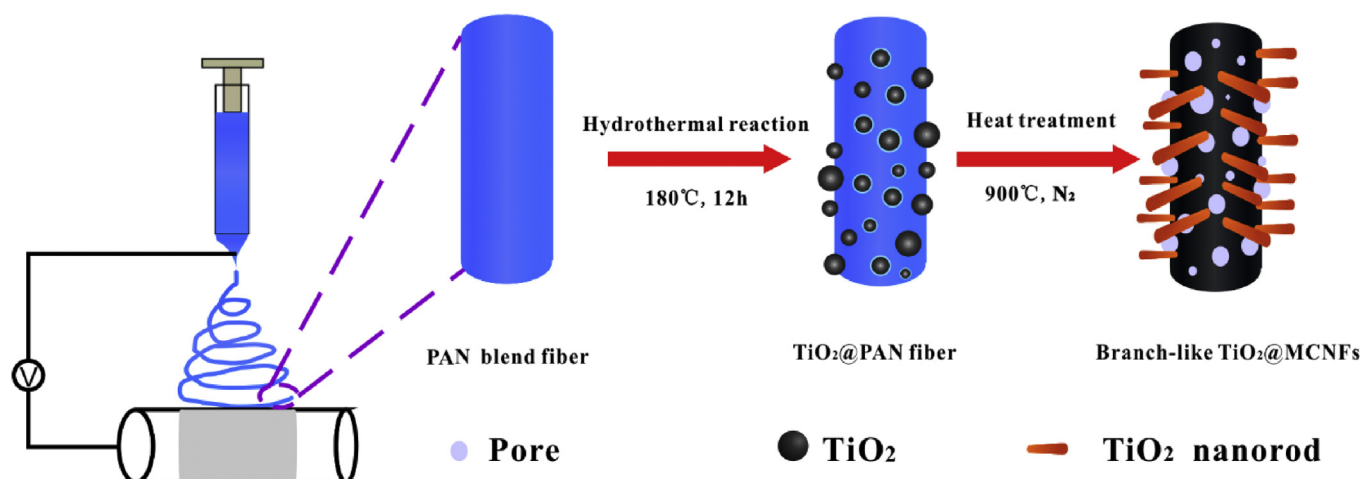


Fig. 1. Schematic diagram for the preparation of branch-like TiO₂@MCNFs composites.

Download English Version:

<https://daneshyari.com/en/article/5461191>

Download Persian Version:

<https://daneshyari.com/article/5461191>

[Daneshyari.com](https://daneshyari.com)