



Anatase TiO₂@C composites with porous structure as an advanced anode material for Na ion batteries



Xiaodong Shi, Zhian Zhang^{*}, Ke Du, Yanqing Lai^{**}, Jing Fang, Jie Li

School of Metallurgy and Environment, Central South University, Changsha 410083, China

HIGHLIGHTS

- Anatase TiO₂@C composites are derived from the precursor of MIL-125(Ti).
- Anatase TiO₂@C composites can exhibit a superior sodium storage performance.
- Carbon matrix can raise the conductivity and alleviate the volume change of TiO₂.

ARTICLE INFO

Article history:

Received 10 June 2016

Received in revised form

19 August 2016

Accepted 30 August 2016

Available online 3 September 2016

Keywords:

Metal organic frameworks

Anatase TiO₂

Disk shaped composites

Carbon matrix

Synergistic effect

Na ion batteries

ABSTRACT

In this paper, we propose a facile strategy to synthesize the porous structure TiO₂@C composites through a two-step method, in which the precursor of MIL-125(Ti) was firstly prepared by solvent thermal method and then calcined under inert atmosphere. When employed as anodes for Na ion batteries, TiO₂@C composites can exhibit a superior cyclability with a reversible sodium storage capacity of 148 mAh g⁻¹ at the current density 0.5 A g⁻¹ after 500 cycles and an excellent rate performance with a capacity of 88.9 mAh g⁻¹ even the current reached to 2.5 A g⁻¹ due to the dispersion of anatase TiO₂ throughout amorphous carbon matrix and the synergistic effect between the anatase TiO₂ nanocrystals and carbon matrix, which can availably enhance the electric conductivity and alleviate the volumetric variation of TiO₂ during the insertion/extraction process of Na⁺.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Na ion batteries (NIBs) have aroused enormous considerations as the next generation of energy storage and conversion system for the low price and widely geological distribution of sodium resources [1,2]. However, the relatively larger ionic radius of Na⁺ restrict the choice of suitable host materials, which can permit Na ions insert/extract reversibly. Therefore, seeking advanced anode materials with high reversible capacity for NIBs to achieve superior electrochemical performance is urgently desirable but remains a great challenge [3–5].

Titanium dioxide (TiO₂) possesses the advantages of excellent chemical stability, abundant resources, nontoxicity and environmental friendly, making it a particularly attractive electrode material for Na ion batteries (NIBs). Though various morphologies of

TiO₂ materials have been synthesized and employed as anode materials for NIBs, such as nanocubes [6], nanotubes [7,8], microspheres [9,10], nanorods [11], nanoarrays [12] and so on, its practical large scale applications are still hindered by the poor rate capability [13–17] and fast capacity decay [18–20] owing to its low electric conductivity and volumetric change during the electrochemical cycling process. Generally, to effectively improve the conductivity and enhance the electrochemical properties of TiO₂, a beneficial strategy is to combine titanium dioxide with carbon substrates, which can not only provide abundant growth sites and restrict the aggregation of TiO₂ nanocrystals, but also buffer the variations of volume and enforce the diffusion rate of electrons/ions at the interface of active materials and electrolyte to raise the rate capability during cycling. Actually, varieties of carbon materials have been served as protective layers and/or support frameworks [11,17,21–30] for TiO₂. Myung et al. [11] adopted pitch as a carbon source to synthesize carbon coated TiO₂ nanorods by a carbonization process under Ar flow, which respectively delivered 104, 82 and 53 mAh g⁻¹ under the current of 3.3, 10 and 33 A g⁻¹ with the

^{*} Corresponding author.

^{**} Corresponding author.

E-mail address: zhangzhian@csu.edu.cn (Z. Zhang).

existence of carbon layer, while the raw TiO₂ nanorods only displayed about 38 mAh g⁻¹ at the current of 3.3 A g⁻¹. Jiao and her co-workers [29] made TiO₂ nanoparticles grown on the surface of reduced graphene oxide (rGO) nanosheets by the way of ultrasonic and reflux. When the hybrid material was served as anodes for NIBs, it displayed a reversible capacity of 186.6 and 112.2 mAh g⁻¹ at 0.1 and 1 A g⁻¹, respectively. According to the synthetic routes of these TiO₂/C hybrids, it can be found that the previous reported TiO₂/C composites are mainly fabricated through separate and multistep synthesis procedures, which always need to add additional carbon sources, leading to the relatively poor internal connection between TiO₂ and carbon. Therefore, it is urgently needed to prepare TiO₂/C hybrids through a more facile and convenient approach.

Metal organic frameworks (MOFs) assembled by metal ions and organic ligands have been widely applied into catalyzers [31], detections [32], biomedicines [33], gas adsorption and separation [34], photochemical [35] and electrochemical [36] energy storage devices due to their tunable open framework structure. To take full advantage of the open channels and abundant cavities, MOFs also have been employed as the templates or precursors to prepare hierarchical porous metallic oxides [37,38] (MOs) and carbon matrices [39,40], in which metal ions can be fully translated into MOs without long range atomic migration as a result of the periodically atomic level alignment of metal and oxygen atoms inside of MOF crystals and inherit a certain extent of permanent porosity structure. In contrast with conventional approaches, the MOs derived from MOFs can not only further simplify the preparation process, but also weaken the destructive effect of template removal on product morphology to possess a relatively stable structure.

Herein, we design a facile strategy to fabricate the porous structure anatase TiO₂@C composites derived from the precursor of MIL-125(Ti), which do not need to add any additional carbon sources during the preparation process. Meanwhile, the crystal structures, morphologies and sodium storage properties of TiO₂@C composites have been investigated through different material characterization and electrochemical test techniques. As the anode materials for NIBs, TiO₂@C composites display a superior cycling performance and an outstanding rate performance as a result of the dispersion of TiO₂ nanocrystals throughout amorphous carbon framework and the synergistic effect between TiO₂ and carbon matrix, which can availably improve the conductivity and alleviate the volume changes of TiO₂ during the insertion/extraction reaction process.

2. Experimental section

2.1. Preparation of MIL-125(Ti)

MIL-125(Ti) was prepared by a modified solvent thermal method reported in previous literature [41]. 1.5 mmol tetra-*n*-butyl titanate (Ti(OC₄H₉)₄) (Aladdin, AR) and 6 mmol terephthalic acid (H₂BDC) (Aladdin, AR) were added into a component solvent containing 18 ml dimethylformamide (DMF) (Sinopharm Chemical Reagent Co.,Ltd, AR) and 2 ml MeOH (Sinopharm Chemical Reagent Co.,Ltd, AR). The above mixture was kept stirring state for 0.5 h and then transferred into a Teflon-lined stainless steel autoclave and heated at the temperature of 160 °C for 20 h. Subsequently, the resultant suspensions were filtered and washed several times with DMF and methanol, respectively. The final white solid products were obtained after drying at 80 °C in a vacuum oven for 12 h.

2.2. Preparation of porous structure TiO₂ and TiO₂@C composites

To prepare the TiO₂@C composites, the as-synthesized MIL-

125(Ti) was firstly pre-carbonized at 200 °C for 3 h under argon atmosphere, and then further carbonized by elevating the carbonization temperature to 600 °C with a heating rate of 5 °C min⁻¹ and kept for 5 h under Ar atmosphere. Finally, the black powder of TiO₂@C composites were collected, labeled as TiO₂@C in the whole manuscript. As a comparison, MIL-125(Ti) was carbonized under air atmosphere at the same temperature for the same time with the same heating rate to obtain the bare TiO₂ and the resultant sample was denoted as TiO₂.

2.3. Materials characterizations

Both scanning electron microscopy (SEM, Nova NanoSEM 230) and transmission electron microscopy (TEM, TecnaiG2 20ST) were employed to investigate the microstructures, particle sizes and morphologies, while the lattice structure was examined through high resolution TEM (HRTEM) and the element distribution on the surface of the samples were detected by Energy Dispersive X-ray spectroscopy (EDX). Meanwhile, the crystalline phase features of the samples were determined by the X-ray powder diffraction (XRD, Rigaku3014) and X-ray photoelectron spectroscopy (XPS, Thermo-Fisher ESCALAB250xi). Additionally, The carbon content in the TiO₂@C composites was determined by Thermogravimetric analysis (TGA, SDTQ600) and nitrogen adsorption/desorption measurements were implemented by Quantachrome instrument (Quabrorb SI-3MP) to characterize the porous structure, including the BET surface area and pore size distribution.

2.4. Electrochemical tests

To manufacture the electrode, active material was mixed with conductive carbon agent of Super P (TIMCAL) and binder of sodium alginate (SA) (Aladdin, AR) into distilled water under the mass ratio of 8:1:1 to form evenly black slurry. Then, black slurry was spread on the rough surface of copper foil and dried for 12 h in a vacuum oven at 60 °C. Finally, the electrode was cut into pellets with a diameter of 10 mm and dried at 60 °C for another 6 h. With metal sodium plates (Aladdin) as reference electrode and Celgard 2400 membrane as the separator, 2025-type coin cells were fabricated in a glove box filled with argon. 1 M NaClO₄ (Aladdin, AR) dissolved in the mixture of ethylene carbonate/propylene carbonate (EC:PC = 1:1 in volume) was chosen as the electrolyte system. Cyclic voltammogram (CV) was conducted by a Solartron 1470E/1400 system with a scan rate of 0.2 mV s⁻¹ from 3.0 to 0.01 V. Meanwhile, electrochemical impedance spectroscopy (EIS) measurement was investigated from 100 kHz to 10 mHz and galvanostatic charge/discharge tests were carried out by a LAND CT2001A battery testing system within 0.01–3.0 V. All the electrochemical capacities of TiO₂@C composites in this paper were calculated based on the whole mass of TiO₂@C in electrode.

3. Results and discussion

3.1. Structural characterizations

The morphologies and particle sizes of MIL-125, TiO₂ and TiO₂@C hybrids were characterized by SEM and TEM. Fig. 1a–b represent that the SEM images of raw MIL-125 samples displays a typical disk shape with submicrometer diameters and a relatively rough surface, which can be further confirmed by the TEM images (Fig. 1c). According to SEM images of TiO₂ and TiO₂@C composites shown in Fig. 1d–e and g–h, respectively, it can be determined that both of them could well maintain the initial morphology of MIL-125 in spite of undergoing different calcination treatment processes. Furthermore, it is clearly detected from their TEM images

Download English Version:

<https://daneshyari.com/en/article/5150237>

Download Persian Version:

<https://daneshyari.com/article/5150237>

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