



Carbon-coated rutile titanium dioxide derived from titanium-metal organic framework with enhanced sodium storage behavior



Guoqiang Zou^a, Jun Chen^a, Yan Zhang^a, Chao Wang^b, Zhaodong Huang^a, Simin Li^a, Hanxiao Liao^a, Jufeng Wang^c, Xiaobo Ji^{a,*}

^a College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China

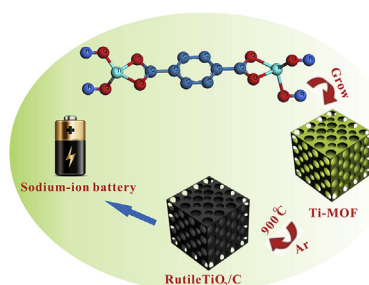
^b School of Energy Science and Engineering, University of Electronic Science and Technology of China, Chengdu, 611731, China

^c Zhengzhou Zhiqin Science and Technology Co., Ltd., Zhengzhou, 450002, China

HIGHLIGHTS

- The CRT was firstly utilized in the sodium-ion batteries as anode.
- This material showed stable structure and good electronic conductivity.
- Excellent storage performance for SIBs of $\sim 70 \text{ mAh g}^{-1}$ at 20 C after 2000 cycles.
- The CRT was prepared by an in-situ pyrolysis of Ti-MOF.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 March 2016

Received in revised form

2 June 2016

Accepted 3 June 2016

Keywords:

Carbon-coated

Rutile TiO_2

Sodium-ion batteries

Anode material

Electrochemistry

ABSTRACT

Carbon-coated rutile titanium dioxide (CRT) was fabricated through an in-situ pyrolysis of titanium-based metal organic framework ($\text{Ti}_8\text{O}_8(\text{OH})_4[\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2]_6$) crystals. Benefiting from the Ti–O–C skeleton structure of titanium-based metal organic framework, the CRT possesses abundant channels and micro/mesopores with the diameters ranging from 1.06 to 4.14 nm, shows larger specific surface area ($245 \text{ m}^2 \text{ g}^{-1}$) and better electronic conductivity compared with pure titanium dioxide ($12.8 \text{ m}^2 \text{ g}^{-1}$). When applied as anode material for sodium-ion batteries, the CRT electrode exhibits a high cycling performance with a reversible capacity of $\sim 175 \text{ mAh g}^{-1}$ at 0.5 C-rate after 200 cycles, and obtains an excellent rate capability of $\sim 70 \text{ mAh g}^{-1}$ after 2000 cycles even at a specific current of 3360 mA g^{-1} (20 C-rate). The outstanding rate capability can be attributed to the carbon-coated structure, which may effectively prevent aggregation of the titanium dioxide nanoparticles, accelerate the mass transfer of Na^+ and speed up the charge transfer rate. Considering these advantages of this particular framework structure, the CRT can serve as an alternative anode material for the industrial application of SIBs.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In the last decades, lithium-ion batteries (LIBs) have become one of the most important energy storage devices for portable electronics, electric vehicles (EVs), hybrid electric vehicles (HEVs), and other mobile power stations, due to their excellent energy density,

* Corresponding author.

E-mail address: xji@csu.edu.cn (X. Ji).

high rate capability and long cycle life [1–3]. Up to now, the electric power supply for portable electronic devices have been dominated by the LIBs to relieve the energy dependence on fossil fuels from the perspective of environmental protection [4]. Considering the increased demand for large scale applications of LIBs in future, the lithium resources might be exhausted by reason of the rather scarce and asymmetrical global distribution [5,6]. Therefore, the development of new alternative energy storage systems with wider distribution and lower cost is urgently needed for the future society. Recently, sodium-ion batteries (SIBs) have been regarded as one of the most promising alternatives to LIBs for the next generation of rechargeable batteries, owing to the earth abundance, low cost of sodium resources and similar electrochemical principle to that of LIBs [7–9]. The Na-ion volume, however, is 2.4 times larger than that of the Li-ion, as the Shannon's ionic radii of Na and Li are 1.02 Å and 0.76 Å, respectively, which brings about the difficulties to find active electrode materials for SIBs. Also, the electrolytes of SIBs still require newly designed materials different from that of the well-established LIB system [9,10]. Moreover, the storage mechanism of SIBs is not exactly the same as that of LIBs [11–13]. Even so, it is still highly hopeful for SIBs to replace LIBs in large-scale application, since nothing else can hold the advantages of both cost and availability as sodium species [9].

Recently, layered sodium transition-metal (vanadium, manganese, iron, cobalt) oxides and their compositions [14–19], poly-anionic compounds and NASICON-type sodium metal phosphates have been extensively explored as cathodes for sodium ion storage and showed excellent electrochemical performances [20,21]. So far, the exploration of new anode materials for SIBs has been considered as a big challenge with only a few relevant reports currently. It is found that the graphite anodes commercially utilized in LIBs are not suitable for SIBs, on account that the graphite interlayer spacing is not large enough to intercalate sodium ions [6,22,23]. Some promising anode materials have been utilized to satisfy the requirements for commercial applications of SIBs, but the performances of the batteries are still needed to be elevated. In the last three years, Sn, Sb, P and their derivative composites have also been considered as possible anode materials for their higher theoretical specific capacities for Na-ion storage [24–28]. These materials, however, undergo a great volume expansion during the uptake/release process of Na-ion, which seriously reduces the cycling life of the SIBs and hinders their potential applications.

Amongst various materials, titanium-based compounds, such as titanium dioxide with multiple polymorphs (amorphous, anatase, bronze and rutile) and sodium titanate family, appear as attractive candidates for SIBs anodes by virtue of their high safety, low cost, low sodiation/desodiation voltage, natural abundance, environmental friendliness and excellent structural stability during repeated charge–discharge process compared with other electrode materials [29–32]. Nevertheless, the pristine TiO_2 (B) showed relatively poor sodium storage performances with a rather low specific capacity about 80 mAh g^{-1} at a specific current of 50 mA g^{-1} and a specific capacity about 35 mAh g^{-1} at 400 mA g^{-1} , which could be attributed to its lower ion diffusion coefficients and worse electronic conductivity ($\sim 10^{-12} \text{ S cm}^{-1}$) [33]. It is found that the inferior electrochemical storage performance for SIBs of pristine TiO_2 is difficult to meet the requirement of practical energy storages [34]. In order to better use its advantages, lots of efforts have been taken to increase its electronic conductivity and avoid the agglomeration of TiO_2 nanoparticles. Zhang et al. employed rutile TiO_2 microspheres for sodium storage, and a high reversible capacity of 121.8 mAh g^{-1} was obtained after 200 cycles at 0.1 C-rate [35]. Meanwhile, Nb atoms were introduced into rutile TiO_2 nanoparticles to improve the electronic conductivity, which presents the first discharge capacity of $\sim 126 \text{ mAh g}^{-1}$ at 87 mA g^{-1}

[36]. Besides, Hong et al. employed the rutile TiO_2 mesocrystals as the negative electrode with a reversible discharge capacity of 188 mAh g^{-1} after 50 cycles [37]. Although certain progress has been achieved, the longing for new material with a high capacity has never stopped.

The MOFs family (Metal organic frameworks) are crystalline microporous materials, constructed by metallic ions that act as lattice nodes and are held in place by multidentate organic ligands. MOF have been largely explored in recent decades, with a focus on creating more thermally and chemically robust materials, which are highly desirable for their potential applications, including catalysis, molecular separations, gas storage and drug delivery [38–43]. Besides, MOFs have been deemed as a series of novel precursors or templates for preparing highly porous metal oxides and carbons with excellent electrochemical properties for LIBs and supercapacitors [44–46]. For example, a porous carbon-coated ZnO quantum dots have been prepared by Yang et al. with the metal–organic framework (MOF-5) as the precursor. The unique structure of the material can effectively prevent the aggregation of ZnO. When used as anodes for LIBs, it showed outstanding electrochemical performance of $\sim 1200 \text{ mAh g}^{-1}$ and $\sim 400 \text{ mA h g}^{-1}$ at a specific current of 75 mA g^{-1} and 3750 mA g^{-1} , respectively [47].

Herein, we prepared carbon-coated rutile TiO_2 (CRT) through the in-situ carbonization of titanium-based MOF ($\text{Ti}_8\text{O}_8(\text{OH})_4[\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2]_6$). The obtained CRT material possesses the advantages of unique pore structure (coexistence of micro/mesopores), higher specific surface area and superior electronic conductivity compared with pure rutile TiO_2 (RT), which can effectually increase the mass transfer process, prevent aggregation of the TiO_2 nanoparticles and accelerate electron transportation of the electrode material. To the best of our knowledge, the in-situ prepared carbon-coated rutile TiO_2 is first employed as anode material for SIBs and shows outstanding electrochemical performances, which provide a new potential way to prepare Ti-based anode materials from MOF.

2. Experimental section

2.1. Preparation of CRT

The Ti-MOF ($\text{Ti}_8\text{O}_8(\text{OH})_4[\text{O}_2\text{CC}_6\text{H}_4\text{CO}_2]_6$) was synthesized according to the solvothermal method reported by Serre et al. [48]. Typically, a mixture containing 3.0 mmol terephthalic acid (Alfa Aesar, AR), 2 mmol of TBOT ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) (Alfa Aesar, AR), 36 ml N,N-dimethylmethanamide (DMF) (Shanghai Titan Scientific Co., Ltd. AR), and 4.0 ml methanol was transferred to a 50 ml Teflon-lined stainless-steel autoclave and then heated for 24 h at 150°C under autogenous pressure. After cooling down to room temperature, the Ti-MOF was obtained by filtration and washed with acetone for three times, and then dried under vacuum at 80°C overnight. The CRT material was prepared by the in-situ carbonization of Ti-MOF under 900°C for 2 h with a temperature ramp of 5°C min^{-1} under Ar atmosphere. The obtained black powder was porous CRT. By contrast, the pure rutile TiO_2 (RT) material was gained in a similar way with air atmosphere instead of Ar atmosphere.

2.2. Materials characterization

The morphology of the CRT material was investigated by the SEM (FEI Quanta 200) and TEM (JEM-2100F instrument). While the structures and compositions of the samples were analyzed by the Raman (Jobin–Yvon Lab RAM HR-800), XPS characterization (ESCALab250), TGA (NETZSCH STA449F3), XRD (Rigaku D/max 2550), BET analysis (BELSORP-MINI), and FT-IR (FTIR (AVTA-TAR,

Download English Version:

<https://daneshyari.com/en/article/7727496>

Download Persian Version:

<https://daneshyari.com/article/7727496>

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