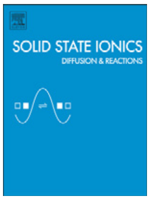
Solid State Ionics 292 (2016) 27–31

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Electrospun SiO_2/C composite fibers as durable anode materials for lithium ion batteries

YuRong Ren [a,b,*], Bo Yang [a,b], HengMa Wei [a,b], JianNing Ding [a,b,c,**]

[a] School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, China
[b] Jiangsu Province Cultivation base for State Key Laboratory of Photovoltaic Science and Technology, Changzhou University, Changzhou 213164, Jiangsu, China
[c] Micro/Nano Science and Technology Center, Jiangsu University, Zhenjiang 212013, China

ARTICLE INFO

Article history:
Received 16 December 2015
Received in revised form 4 May 2016
Accepted 6 May 2016
Available online 17 May 2016

Keywords:
Anode material
Electrospun
SiO_2/C fibers

ABSTRACT

Electrospun together with thermal treatment is proposed to synthetize reticular amorphous SiO_2/C composite fibers. The as-prepared fibers show carbon-coated SiO_2 nanoparticles and form a space network structure, which cannot only improve the electrical conductivity, but also buffer the volume change. The SiO_2/C fiber anode displays excellent performance, with an enhanced reversible capacity of 465 mAh/g at a current density of 50 mA/g up to 50 cycles, which is much higher than that of a pure SiO_2 anode even at the first cycle (113.8 mAh/g). Favorable rate property (~240 mAh/g at a current density of 500 mA/g) also exhibits in the further electrochemical test. The excellent electrochemical properties are attributed to the carbon coat and the unique structure. These results suggest that the fiber materials can be used as an anode for rechargeable lithium-ion batteries.

1. Introduction

Recently, Li-ion batteries (LIBs) have attracted a great deal of attention because of the broad prospects using in portable electronics, electric vehicles, and aerospace applications [1,2]. To improve the performance of LIBs, it is important to explore new electrode materials with high-energy capacity and long cycle life [3]. Graphite has been widely used as commercial anode material due to its advantages of long cycle life and low cost, but its low lithium-storage capacity has become a huge obstacle to apply in high power field [4–6]. Compared to other anode candidates such as Sn-based [7,8] and Fe-based [9] materials, Si-based materials are more attractive because of its abundant reserves and high theoretical capacity (4200 mAh/g). However, it shows a substantial volume change (400%) during the process of delithiation and lithiation, which results in pulverization and fast capacity fading [10–13].

As an oxide of silicon, SiO_2 has been considered as a promising material owning to its high theoretical capacity of 1965 mAh/g [14]. Since the Li_2O and/or Li_4SiO_4 generated during the initial lithiation helps buff the volume change, silicon oxide has good cycling stability [15,16]. Nevertheless, the poor electrical conductivity and strong Si–O bond in bulk crystalline SiO_2 prevent it from becoming an electrode material. Since now, much effort has been devoted to the practical use of silica, including films [17,18], hollow nanospheres [19], amorphous states [20] and so on [21–23]. Favors et al. [22] prepared SiO_2 nanotubes via a facile two step hard-template growth method, and they showed a highly stable reversible capacity of 1266 mAh/g after 100 cycles with minimal capacity fading. In addition, carbon coating is a cheap and effective way to improve the electrochemical performance [24–26]. Gong [26] succeeded in preparing SiO_2/C composites via a diazotization reaction and carbonizing treatment, which show good electrochemical performance.

More recently, electrospun has been recognized as a simple and low-cost method to produce 1D nanofibers from a few microns to 100 nm [27,28]. Using the electrospinning technique, a nonwoven thin film can be easily obtained by the deposition of nanofibers, without complex equipment or special substrates [29]. This has been adopted by a number of researchers for the development of electrode materials [30–33]. Carbon nanofibers (CNFs) containing graphene-wrapped silicon nanoparticles [34] were fabricated by electrospinning and subsequent thermal treatment, showing stable capacity retention. Core–shell structured nanofibers were reported by Hieu [35], which had a capacity of 1000 mAh/g and coulombic efficiency of 99% at the 100th cycle. If the Si nanoparticles are replaced by SiO_2 nanoparticles, better cycling stability will thus be achieved.

Herein, a combination of electrospun and carbonization at 700 °C under nitrogen was used for the fabrication of SiO_2/C composite fibers. In this way, the carbon shell can wrap tightly around the SiO_2 core, thereby buff the volume change and improve the conductivity of SiO_2.

---

[*] Correspondence to: Y.R. Ren, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, China.
[**] Correspondence to: J.N. Ding, Micro/Nano Science and Technology Center, Jiangsu University, Zhenjiang 212013, China.
E-mail address: ryrchem@cczu.edu.cn (J. Ding).

http://dx.doi.org/10.1016/j.ssi.2016.05.002
0167-2738/

The electrochemical measurements revealed that the SiO_2/C fibers had a good electrochemical performance with higher specific capacity and better cyclic performance.

2. Experimental

2.1. Preparation of precursor solution for electrospinning

2.0 g PVP (Mw = 1,300,000) was dissolved in 20 ml anhydrous ethanol to form a solution as the carbon fiber precursor. Then 0.3 g SiO_2 nanoparticles were added into the solution with a 24 h magnetic stirring and a 1 h ultrasonic dispersion. We named it as SiO_2/C fibers. Pure SiO_2 nanoparticles were used as contrast samples.

2.2. Preparation of SiO_2/C composite fibers

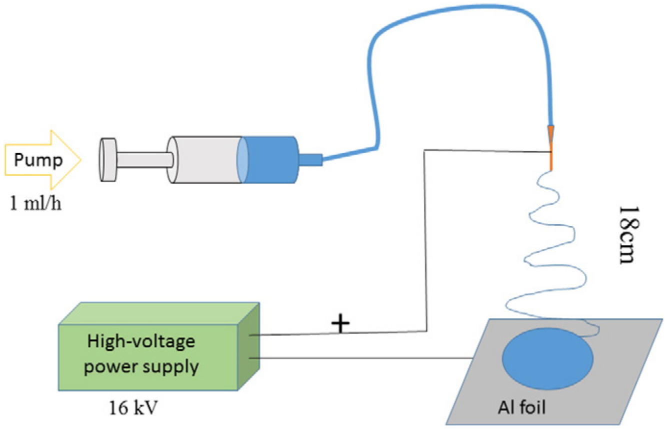
The static spinning precursor solution was added into a 5 ml syringe, whose needle diameter was 0.8 mm, and the injection speed was 1 ml/h for electrospinning, as is shown in Scheme 1. The spinning voltage was 16 kV, and the receiving distance was 18 cm. The obtained spinning precursor was firstly pre-oxidated for 1 h at 250 °C in air, and then carbonized for 4 h at 700 °C in nitrogen to form the final product of SiO_2/C composite fibers.

2.3. Material characterization

Transform infrared (FTIR) spectra were recorded on Nicolet Avatar 370 using a KBr pellet technique. The phase structures of the synthesized samples were characterized by X-ray diffraction (XRD, D/max 2500 PC) with Cu Kα radiation (λ = 1.5406 Å, operating at 40 kV × 40 mA). The morphologies were observed by field emission scanning electron microscopy (FESEM, SUPRA55). The microstructure and distribution of the composites were examined by using transmission electron microscopy (TEM, JEM-2100). Thermogravimeric analysis (TGA) measurement was performed with TG 209 F3 by heating in air to 850 °C at a rate of 10 °C/min.

2.4. Electrochemical measurements

Electrochemical performances were measured using two-electrode 2032 coin-type cells. The working electrodes were prepared by mixing active material, carbon black (Super-P), and sodium carboxymethyl cellulose (CMC) at a weight ratio of 80:10:10 and then pasted on thick copper foil. Pure lithium foil was used as a counter electrode. The cells were assembled in an Ar filled glove box, with a 1 M $LiPF_6$ solution in a mixture of ethyl carbonate (EC), dimethyl carbonate (DMC) and ethyl carbonate (EMC) (1:1:1, v/v) as the electrolyte. The cells were tested in the voltage range of 0.01–3 V on a LAND battery tester.



Scheme 1. The figure of electrostatic spinning device.

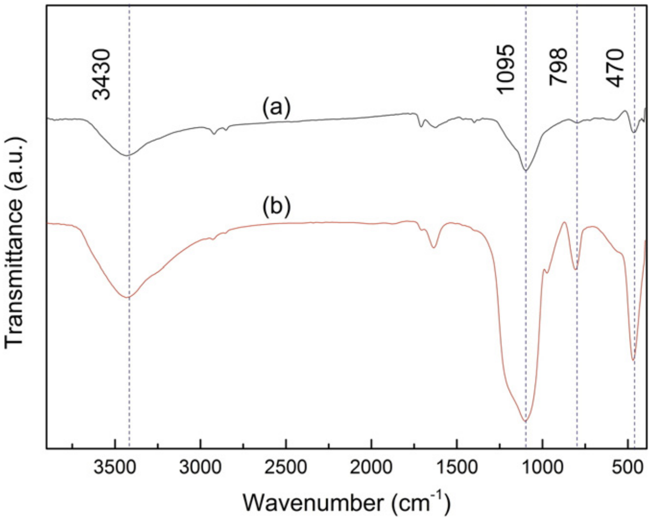


Fig. 1. FT-IR spectra of (a) pure SiO_2, (b) SiO_2/C fibers.

3. Results and discussion

Fig. 1 is the FTIR spectra of as-prepared samples. For pure SiO_2 nanoparticles in Fig. 1(b), the peaks at 470 cm^{-1}, 798 cm^{-1}, 1095 cm^{-1} and 3430 cm^{-1} are assigned to O–Si–O bending vibration, Si–O–Si symmetric stretching vibration, Si–O–Si unsymmetric stretching vibrations and O–H stretching vibration, respectively. Compared to Fig. 1(b), SiO_2/C fibers in Fig. 1(a) show almost the same peaks at the same positions, but the intensity of the peaks has weakened a lot. Fig. 2(a) shows the XRD pattern of pure SiO_2 nanoparticles. The broad band indicates that the structure of SiO_2 is amorphous. Fig. 2(b) gives the XRD pattern of SiO_2/C fibers. The wide peaks at about 22° (0 0 2), 43° (1 0 0) are attributed to the carbon layer coated on pure SiO_2 nanoparticles, which correspond to the PVP carbonation peak [36], and the composite fibers also have an amorphous structure. No silicon peak can be found in the pattern, which proves that the SiO_2 is not reduced after high temperature carbonization. It was reported that SiO_2 cannot be reduced to glass-like compounds such as SiO_2-δ or Si–C–O by carbon at 1000 °C [37]. In order to confirm the content of amorphous SiO_2 nanoparticles in SiO_2/C fibers, the TGA data of them is collected and shown in Fig. 3. The prominent weight loss between 420 °C and 700 °C is related to the oxidization of carbon. Based on the curve, the SiO_2 content in them can be gotten out of 44.1 wt.%. There is no gradually regained mass above 700 °C,

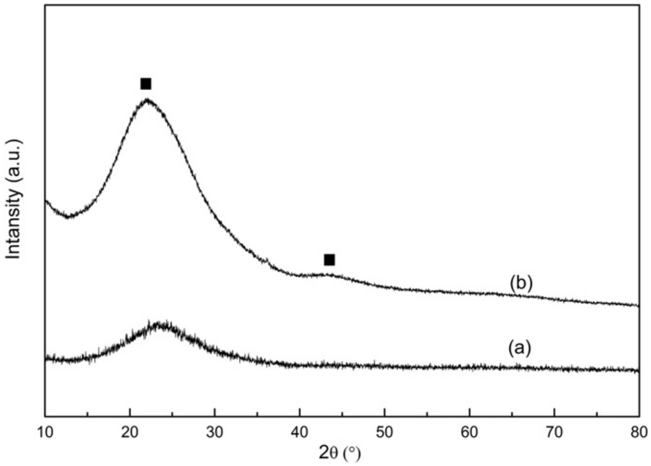


Fig. 2. XRD pattern of (a) pure SiO_2 and (b) SiO_2/C fibers.