



ELSEVIER

Contents lists available at ScienceDirect

Materials Letters

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

Facile synthesis of silicon/carbon nanospheres composite anode materials for lithium-ion batteries



Yu Zhou, Huajun Guo*, Yong Yang, Zhixing Wang, Xinhai Li, Rong Zhou, Wenjie Peng

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

ARTICLE INFO

Article history:

Received 28 October 2015

Received in revised form

16 December 2015

Accepted 2 January 2016

Available online 4 January 2016

Keywords:

Lithium-ion batteries

Silicon

Microstructure

Carbon materials

ABSTRACT

Silicon/carbon nanospheres composite has been prepared by a facile chemical method followed by heat treatment. The Si particles are coated by an amorphous carbon layer that suppresses agglomeration of pristine Si. Carbon spheres accommodate large volume expansion of silicon during cycling. The unique carbon frameworks enhance transmission capability of the composite by offering a large surface area and a short diffusion distance. By electrochemical characterizations, the silicon/carbon nanospheres composite exhibits initial reversible specific capacity of 888.6 mAh g^{-1} at current density of 200 mA g^{-1} . After cycling up to 50 cycles, the electrode still delivers charge capacities of 610.7 mAh g^{-1} . Notably enhanced rate capability is attained, with a reversible specific capacity of 811.4, 747.3, 395.5, 289.9 mAh g^{-1} at the current density of 0.5, 1, 3 and 5 A g^{-1} , respectively.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries (LIBs) are the widely used in energy storage systems due to their unmatched combination of high energy and power density. In order to meet the increasing demand of higher energy density and long term cycle life for LIBs, new anode materials should be developed to substitute the current commercial electrode materials [1–3]. Silicon (Si) has been extensively explored as anode material because of its natural abundance, low discharge voltage (vs. Li/Li^+), and extremely high theoretical capacity ($\sim 4200 \text{ mAh g}^{-1}$) [4]. However, the alloying reaction of Si with lithium causes significant volume expansion and results in particle fracture and loss of capacity with cycling. Si nanostructures and Si/carbon hybrids have been explored to address these problems [5]. The key design Si-based composite is to have free volume around nanostructures so that the silicon can expand without breaking. Many strategies for the preparation of hollow carbon or Si nanostructure have been described. Hollow nanostructure provides an enhanced surface to volume ratio and reduced transport lengths for both mass and charge transport [6,7]. The general approach is confined to the use of removable or sacrificial templates. However, hollow structures prepared from template routes usually suffer from disadvantages related to high cost, tedious and harsh synthetic procedures [8].

Here, we report a facile process to prepare silicon/carbon nanospheres composite. The Si particles coated by an amorphous

carbon layer that suppressed agglomeration of pristine Si. Graphene cover the surface of Si@carbon particles via chemical reduction. After further dispersion and thermal treatment, the Si@carbon particle is separated from the carbon framework. The obtained silicon/carbon nanospheres composite show a good electrochemical performance as anode materials for lithium-ion.

2. Experimental

0.2 g nano-Si powder ($\sim 80 \text{ nm}$) and 0.1 g phenolic resin were dispersed in 15 mL acetone. After magnetic stirring and drying at $50 \text{ }^\circ\text{C}$, the solid blend precursor was sintered at $800 \text{ }^\circ\text{C}$ for 2 h under argon atmosphere. Subsequently, the obtained Si@carbon composite were dispersed in 200 mL graphene oxide suspension (1 mg mL^{-1}). After the suspension was ultrasonic stirred for 1 h, ammonia was dropped to increase the pH value of the solution to 10. 0.2 g hydrazine hydrate (hydrazine/GO = 7:10) was added and the solution heated in oil bath at $95 \text{ }^\circ\text{C}$ for 3 h. The graphene gradually coated on the surface of Si@carbon particles and precipitated out as a black solid. After being high speed centrifuged for 10 min and then washed with deionized water for five times, the graphene was separated from the Si@carbon particles. In order to reinforce this structure, the blended precursor was heated to $500 \text{ }^\circ\text{C}$ for 2 h in argon atmosphere. The proportion of Si in the prepared composite is about 29.5%.

The crystal structure of the as-prepared composite was characterized by X-ray diffraction (XRD, Rint-2000, Rigaku) using $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) in the range of $2\theta = 10\text{--}80^\circ$. Raman spectra from 180 to 3500 cm^{-1} were obtained from WiTec

* Corresponding author.

E-mail address: hjguo_csu@163.com (H. Guo).

Alpha300 system applying 632.8 nm laser light. The microstructure of the composite was examined by a Tecnai G12 transmission electron microscope (TEM).

Electrochemical performances were measured in a CR2025 coin-type cell. The working electrodes were prepared by mixing the active material, Super P and 5 wt% LA-132 binder (Chengdu Indigo Power Sources Co., Ltd, China) in a weight ratio of 70:15:15. Lithium foil was used as a counter electrode. A polypropylene micro-porous film as the separator and 1 M LiPF₆ in EC:EMC:DMC (1:1:1, v/v/v) as the electrolyte. The cells were charged and discharged using a Neware battery tester (Neware, Shenzhen) with a potential range of 0.01–2.00 V at room temperature. Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy were carried out with a CHI660A electrochemical analyzer.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction pattern of the prepared Si/carbon nanospheres. All peaks are similar to that of pure silicon phase, implying that the silicon particles in the composite are still kept its own crystalline structure. A broad diffraction peak is observed at around $2\theta=26.4^\circ$, corresponding to the peak of graphite (002), which may be due to the deterioration of graphene after the thermal treatment. As seen in Fig. 1(b), the peaks located at 263, 500 and 911 cm^{-1} are associated with the spectrum of nano-Si. Two peaks are observed at ~ 1355 and ~ 1602 cm^{-1} , which correspond to the A_{1g} mode of disordered carbon and E_{2g} mode of the graphitic carbon lattice vibration, respectively. The I_D/I_G ratio of 0.846 reveals the existence of graphene in the composite [9,10]. In Fig. 2(a), it can be clearly seen that the Si particles are homogeneously distributed into the carbon frameworks. A typical carbon nanosphere was clearly shown by the amplifying figure insert on the right side of Fig. 2(a). Silicon nanoparticles are individually encapsulated by amorphous carbon shell, which provides a buffer during the insertion/extraction of lithium ions. Fig. 2(b and c) are local magnified images of the Si/carbon nanospheres particles. The obtained carbon frameworks exhibit spherical shape and are nanometer in diameter. The carbon shell can be seen from the ruined nanospheres. Fig. 2(d) shows the microstructure of the contrast composite, which was prepared following the similar method without chemical reduction with hydrazine hydrate. No carbon nanospheres can be observed in the particles. The formation of the carbon nanospheres can be described as follows. The Si particles play as template, which encapsulated by amorphous

carbon layer. Graphene is further encapsulated the Si@carbon particles by reduction with hydrazine hydrate [11,12]. In Fig. 3(a and b), HRTEM image and the fast fourier transform (FFT) image reveal the existence of crystalline Si and amorphous carbon layer. The surface of Si particles in Si@carbon and Si/carbon nanospheres are well encapsulated by an amorphous carbon layer around 4–5 nm. As shown in Fig. 3(b), the outermost layer of the particle is surrounded by another carbon layer, which may be the remaining of the graphene. The carbon nanospheres function as a conducting framework and the carbon layer function as an electrolyte blocking layer [12]. Thus, the electrochemical properties of the composite have been significantly improved.

The CV curves of and pure Si and Si/carbon nanospheres electrode are shown in Fig. 4(a). In the first cycle, there is an obvious reduction peak located at 0.7 V, which can be attributed to the formation of solid electrolyte (SEI) film on the electrode surface. The cathodic peaks located in 0.2 V and 0.01 V correspond to the alloying process. The anodic peaks at 0.35 and 0.5 V are associated with the successive transitions from highly lithiated Si to less lithiated Si, and to Si [10]. Fig. 4(b) displays the initial three discharge/charge curves of the Si/carbon nanospheres electrode at current density of 200 mA g^{-1} . The initial discharge and charge capacities are 1713.7 mAh g^{-1} and 888.6 mAh g^{-1} , respectively, with a first cycle coulombic efficiency of 51.85%. Low initial coulombic efficiency may be associated with the high specific surface area of carbon nanospheres. A plateau at 0.7 V is assigned to the formation of a SEI layer, which disappears in the following cycles. This is in accordance with the CV curves and relates to an initial irreversible capacity loss. Fig. 4(c) shows the cycling performances of Si/carbon nanospheres electrode. After cycling up to 50 cycles at 200 mA g^{-1} , the electrode retained discharge and charge capacities of 636.6 and 610.7 mAh g^{-1} , respectively. The rate capability of the composite was investigated by increasing current densities from 0.1 A g^{-1} to 5 A g^{-1} (Fig. 4d). It can be seen that the Si/carbon nanospheres electrode can exhibit large reversible specific capacity of 811.4, 747.3, 629.6, 395.5, 289.9 mAh g^{-1} at the current density of 0.5, 1, 1.5, 3 and 5 A g^{-1} , respectively. When the current density switches back from 5 to 0.1 A g^{-1} , the reversible capacity recovers to 649.3 mAh g^{-1} . The good performance of the Si/carbon nanospheres composite is attributed to the internal hollow structure, which can accommodate significant volume expansion and reduce the lithium ion diffusion path during the charge/discharge processes. AC impedance spectra measurements were also carried out to verify the good electrochemical performance of the Si/carbon nanospheres electrode. As shown in Fig. 4(e), the diameter of the semicircle for the Si/carbon nanospheres electrode is

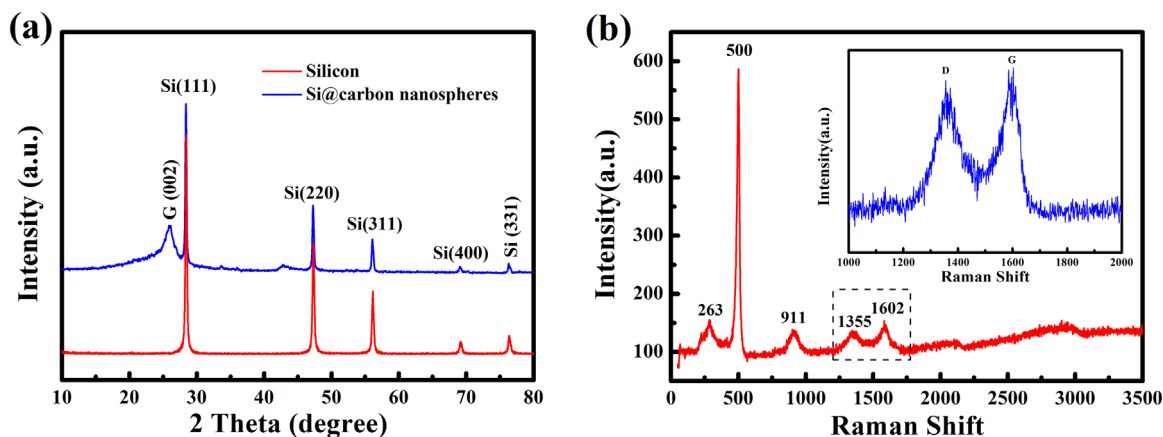


Fig. 1. (a) XRD patterns and (b) Raman spectra of Si/carbon nanospheres composite.

Download English Version:

<https://daneshyari.com/en/article/1641828>

Download Persian Version:

<https://daneshyari.com/article/1641828>

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