Materials Letters 231 (2018) 205–208

Contents lists available at ScienceDirect

Materials Letters

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

Facile fabrication of hollow structured Si-Ni-C nanofabric anode for Li-ion battery

Qianru Liu [1], Yan Gao [1], Pinggui He, Chao Yan, Ying Gao, Jianzhi Gao, Hongbing Lu, Zhibo Yang *

School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710119, China

ARTICLE INFO

Article history:
Received 25 May 2018
Received in revised form 24 July 2018
Accepted 8 August 2018
Available online 9 August 2018

Keywords:
Functional
Microstructure
Silicon
Energy storage

ABSTRACT

Hollow structured Si-Ni-C composite nanofabric was fabricated by electrospinning combined with thermal treatment. The hollow structure was obtained by calcining the precursory Si-NiO-C nanofabric under Ar atmosphere without using any sacrificial material. The resultant hollow structure could accommodate the volume effect of Si during Li-ion insertion and extraction. The NiO was reduced to Ni simultaneously with the calcination, which could increase the conductivity of the nanofabric. The hollow Si-Ni-C nanofabric formed a freestanding conductive structure which can be directly used as electrode for Li-ion batteries. The obtained self-supported anode delivered a capacity of 622 mAh/g after 100 cycles. The anode also presented a stable rate performance at 2000 mA/g.

1. Introduction

Among all the new generation of anode materials for Li-ion batteries (LIBs), Si is considered as the most promising one due to the high theoretical capacity and low discharge platforms [1–3]. However, huge volume-effects during Li-ion insertion and extraction severely constrains the cycling life of Si based anodes. Fortunately, numerous results have proved that nanostructured Si materials with enough free spaces could effectively accommodate the volume effect [2–5]. On the other hand, for Si nanoparticles, the conductivity between the nanoparticles is essential for the rate performance of LIBs. Conductive coatings are usually used to enhance the conductivity between Si based nanoparticles, but such methods are always complicated and high costs [5–7].

In this work, we designed a facile way to fabricate hollow structured Si-Ni-C composite nanofabric. By calcining the electrospinning obtained Si-NiO-C composite nanofabric under Ar atmosphere, the NiO was reduced to Ni, and the hollow structure was formed simultaneously. The obtained hollow Si-Ni-C composite nanofabric formed freestanding conductive membrane that can be directly used as anodes for LIBs without adding conductive and binding additives. The experimental results proved that the obtained Si based anode could deliver an improved lithium storage performance.

2. Experimental

Hollow structured Si-Ni-C composite nanofabric was fabricated by electrospinning combined with thermal treatment. Typically, 0.1 g Si nanoparticles (average dimeter of 50 nm) and 1.2 g $Ni(CH_3COO)_2{\cdot}4H_2O$ were firstly dissolved in 10 mL N,N-dimethylformamidel (DMF) solution with a vigorous stirring for 3 h. After that, the solution was ultrasonic treated for another 1 h. Then, 0.8 g polyacrylonitrile (PAN) and 0.4 g polyvinyl pyrrolidone (PVP) were added into the above solution and stirred at 60 °C for 1 h. Subsequently, the precursory solution was stirred at room temperature over night to obtain a homogeneous mixture for electrospinning. The electrospinning was conducted under a voltage of 15 kV with a precursory solution flow rate of 1 mL/h. Then, to obtain the Si-Ni-C composite nanofabric, the collected nanofabric were stabilized under air atmosphere at 280 °C for 2 h and continuously carbonized under Ar atmosphere at 700 °C for another 2 h.

The structural and morphological information of the resultant materials were characterized by X-ray diffraction (Rigaku, D/Max-2400, Cu Ka radiation), micro-Raman spectrometer (Jobin-Yvon, Lab RAM HR800, 532 nm radiation), field emitting scanning electron microscopy (FEI, Nova Nano SEM 450) and transmission electron microscopy (FEI, Tecnai G2 F30). The component information was obtained by a simultaneous thermal analyzer (Netzsch, STA 449 F5, air atmosphere).

CR 2032 coin type cells were assembled in an argon-filled Glove box (Mikrouna, Super1220) and used for electrochemical characterization. The obtained Si-Ni-C composite was directly used as work electrode. Celgard 2320 and Li foil were used as the separator

---

* Corresponding author.
E-mail address: yangzhb15@snnu.edu.cn (Z. Yang).

[1] These authors contribute equally.

https://doi.org/10.1016/j.matlet.2018.08.044
0167-577X/

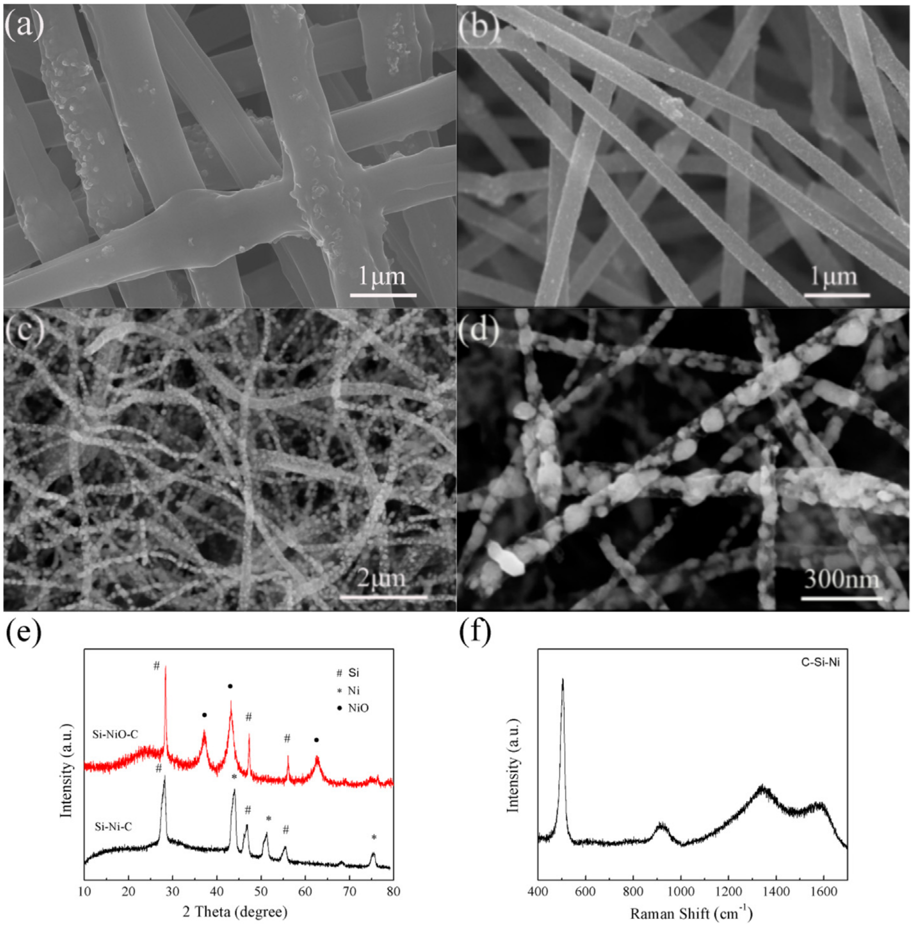

Fig. 1. Scanning electron microscopy (SEM) images of the (a) contrast Si-C nanofabric, (b) precursor Si-NiO-C nanofabric, (c) and (d) Si-Ni-C nanofabric under different magnification, (e) X-ray diffraction spectra of the as-prepared Si-NiO-C and Si-Ni-C nanofabric, (f) Raman spectra of the Si-Ni-C nanofabric.

and counter electrode, respectively. The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbonate and diethyl carbonate (1:1 in volume). Galvanostatic cycling was carried out on a multi-channel cell test instrument (Neware, BTS-610). Cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) were measured using an electrochemical workstation (Metrohm, Autolab302N). The voltage cut-off window for galvanostatic cycling was set in the range of 0.02–2.0 V. CV was tested at a scan rate of 0.1 mV/s over the voltage range from 0.02 V to 2.0 V. The active mass was evaluated base on the whole Si-Ni-C nanofabric through an analytical balance (Mettler, XS105, accuracy of 0.01 mg). The mean mass density was about 2.1 mg cm^{-2}.

3. Results and discussion

Fig. 1a is the SEM image of the contrast Si-C nanofabric which was prepared by the same experimental condition but without addition of Ni source. It can be seen that the dimeter of the nanofiber is about 700 nm and the aggregation of Si nanoparticles is obvious. Fig. 1b is the morphology of the precursory Si-NiO-C nanofabric. The surface of the Si-NiO-C nanofiber is smooth and all the nanoparticles is well covered by carbon coating. At the same time, the dimeter of the Si-NiO-C nanofiber was decreased when compared with the Si-C nanofiber. Fig. 1c and d clearly showed that the thickness of carbon shell was decreased and some parts of the nanofiber presented a transparent state. Fig. 1c and d also indicated that all the nanoparticles is evenly distributed inner the nanofibers. The XRD patterns showed in Fig. 1e is belongs to the nanofabric before and after thermal treatment, respectively. The XRD results directly proved that the Si (JCPDS 27-1402)-NiO (JCPDS 47-1049) composite is in-situ reduced to Si (JCPDS 27-1402)-Ni (JCPDS 04-0850) composite after the thermal treatment. From the Raman spectra illustrated in Fig. 1f, it can be seen that no signal of NiO was detected, which further proved the reduction of NiO. The Raman spectra also indicated that the Si nanoparticles have a high crystallinity and the carbon shell was mainly constituted by amorphous carbon. From the above information, it can be concluded that NiO was reduced to Ni by carbon during the calcination process and a certain amount of carbon was consumed at the same time, which formed the hollow structure.

The detailed structural information was investigated through TEM. Fig. 2a clearly shows that all the nanoparticles are well covered by the carbon shell and the smaller nanoparticles are distributed between the bigger ones. It can be seen that the dimeter of the bigger nanoparticles is about 45–50 nm and that of the smaller nanoparticles is about 10–20 nm. HRTEM images showed in Fig. 2b and c revealed that the bigger and smaller nanoparticles were Si and Ni, respectively. The Ni nanoparticles existed between Si nanoparticles could greatly increase the conductivity of the whole nanofabric anode. Thermogravimetric analysis under air atmosphere was applied to evaluate the constituent ratio of the Si-Ni-C nanofabric. From Fig. 2d, it can be seen that the weight of the nanofabric is no longer changed after 500 °C, which indicated that the carbon was totally consumed and the residual was Si and NiO. The residual was then reduced under hydrogen