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High rate capacity anode of Si-C composite nanofiber wrapped with Cu foam for lithium-ion batteries

Xiaoqiang Tian, Gaoda Li, Leixin Meng, Wang Tian, Xin Gu, Yaqin Ding, Ruichao Zhang, Xiaofeng Jia, Yong Qin *

Institute of Nanoscience and Nanotechnology, Lanzhou University, Lanzhou 730000, China

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ABSTRACT

To resolve the huge volume expansion and poor electronic conductivity of silicon anode which restricts the cycling stability and rate capacity of lithium-ion batteries, a novel structure of copper foam wrapped silicon/carbon nanofibers (Si/CNFs-Cu) is successfully fabricated and applied as anode material in lithium ion battery. It exhibits excellent rate performance of 565.2 mAh g^{-1} at a high current density of 5 A g^{-1} and high cycling stability with the retention rate of 66.7% after 80 cycles at 0.5 A g^{-1}. The rate capacity is as 2.8 times as Si/CNFs and it is attributed to the framework structure of Si/CNFs-Cu which insures the faster electron transfer along the thickness direction of the anode material in charging/discharging processes. Furthermore, the complete wrapped electrode structure can avoid the separation of the composite fibers from the electrode during cycling substantially.

1. Introduction

Recently, increasing efforts have been devoted to the development of advanced lithium ion batteries (LIBs) on account of its superiority for excellent energy conversion efficiency, energy density and cycle life [1,2]. Silicon (Si) is one of the potentially attractive alloy-type anode materials for LIBs [3]. It exhibits a low discharge potential plateau below 0.5 V (*vs* Li^+/Li) and has the second-highest theoretical discharge capacity of 3579 mAh g^{-1}, next to metallic Li, forming $Li_{15}Si_4$ alloy phase at room temperature [4,5]. However, poor electronic conductivity and dramatic volume variation about 300% [6] for Si anode during Li insertion/extraction result in serious mechanical fracture/pulverization giving rise to the instability of solid electrolyte interphase (SEI), which subsequently causes the bad rate capability and sharp decay of specific capacity [7].

Embedding Si nanoparticles (Si NPs) in carbon nanofibers (CNFs) is considered an effective strategy to overcome the above-mentioned problems [8]. Among which, CNFs act as active materials, conductive additives, substrate to support Si NPs and mitigate the volume change of the entire electrode. However, the layered structures of Si/CNFs film by electrospinning suffer from inherently inferior electrical conduction along the thickness direction. Furthermore, poor mechanical stability tending to delaminate and separate from the electrode, which is resulting from the high stress field by the lithiation of Si NPs embedded in CNF and causing an incessant capacity fading with the increasing of cycle number [9].

In this work, a novel structure of Si/CNFs-Cu is fabricated to simultaneously improve the electronic conductivity, avoid the delamination of the CNFs layers and the separation of active material from electrode. As shown in Fig. 1a, the network structure of Cu foam wrapped Si-C composite nanofibers insures the fast electron transfer along with the thickness direction in charging/discharging processes and restricts the separation of the composite fiber from the electrode during the process of cycling, resulting in excellent rate performance and high cycling stability.

2. Experimental section

1.5 g Silicon nanoparticles (Si NPs, 80 nm) are soaked in 5% HF for 30 min to remove the intrinsic oxide layer and then dispersed in 10 g N, *N*-dimethylformamide with vigorously stirring. Meanwhile, 2.5 g polyacrylonitrile (PAN, M_W = 150,000) is dissolved in 15 g DMF with 10 h stirring. The above two solutions are mixed uniformly as the precursor for electrospinning. The electrospun sample (Si/PAN) is dried at 80 °C for 10 h, pre-oxidized at 280 °C in air, and then, carbonized at 850 °C for 180 min under Ar atmosphere with a heating rate of 5 °C min^{-1}. Eventually, the resulted sample (Si/CNFs film) is punched to wafer with a diameter of

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* Corresponding author.
E-mail address: qinyong@lzu.edu.cn (Y. Qin).

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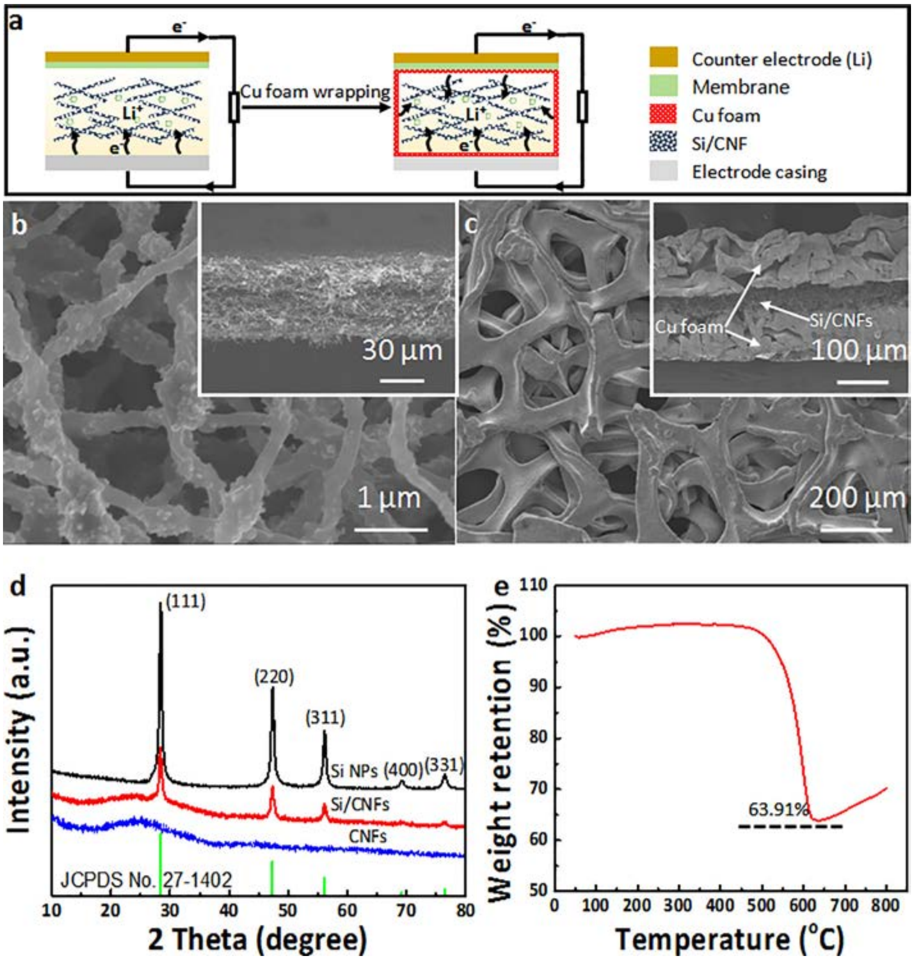

Fig. 1. The design of Si/CNFs-Cu (a). Morphology of Si/CNFs film (b) and Si/CNFs-Cu (c). XRD patterns of Si NPs, Si/CNF film and CNFs (d). TGA investigating of Si/CNFs (e).

10 mm and subsequently wrapped by Cu foam under a pressure of 2 MPa, and marked as Si/CNFs-Cu.

The electrochemical properties of the samples as anodes in LIBs are evaluated using CR 2032-type coin half cells. Si/CNFs-Cu and Si/CNFs films are directly utilized as working electrodes individually without conductive additives and binder material. Lithium foil is used as the counter and reference electrode. Polypropylene membrane is used as separator and 1 M $LiPF_6$ in ethylene carbonate and dimethyl carbonate mixture (V:V = 1:1) as the electrolyte. The galvanostatic charge/discharge and rate property of the assembled coin cells are investigated using a multi-channel battery tester within the voltage range of 0.01–1.20 V. The cyclic voltammetry (CV) test is performed at a scan rate of 0.1 mV s^{-1} and impedance analysis is carried out in the frequency range of 1 Hz–100 kHz.

3. Results and discussion

The fabricated Si/CNFs films is composed of uniform and continuous nanofibers, which form a network structure by interweaving, as shown in Fig. 1b. The cross-section image indicates the thickness of the film is 50 µm. The Si/CNFs films is further wrapped by Cu foam, which works as electrodes with a thickness around 100 µm, as shown in Fig. 1c. The network structure of Si/CNFs film is benefit for the electronic conductivity in charging/discharging processes, and exhibits a barrier-free quality for the migration of lithium ions. Furthermore, the complete wrapping of Si/CNFs film by Cu foam can restrict the separation of the composite fiber from the electrode during the cycling process.

As illustrated by the XRD patterns (Fig. 1d), the crystalline Si NPs keeps and undesired silicon carbide is absent in the carbonizing process, The broad peak between 20° and 25° in Si/CNFs is attributed to the amorphous carbon. The Si:C ratio is analyzed and shown in Fig. 1e, the weight is stable over 50–450 °C and decrease abruptly between 450 and 620 °C, which is due to the thermal decomposition of C. According to this data, the mass percent of Si NPs in Si/CNFs is 63.91%. Based on this, the theoretical capacity of the fabricated Si/CNFs-Cu is deduced as ~2422 mAh g^{-1}.

The charging/discharging profiles of Si/CNFs and Si/CNFs-Cu at 0.5 A g^{-1} for the first cycle are shown in Fig. 2a. Compared with Si-C, the Si-C/Cu electrode possesses a longer charging potential platform, which indicates the introduction of Cu can enhance the electrochemical reversibility by improving the electronic conductivity and mechanical stability. As shown in Fig. 2b. The reversible capacity of Si/CNFs-Cu decays from 1400 mAh g^{-1} to 814 mAh g^{-1} after 80 cycles. It gives a retention rate of 66.7%, which is 2.74 times of the Si/CNFs' retention rate. Considering that the coulombic efficiency of designed Si/CNFs-Cu electrode is higher and more stable during the cycling process and reaches as high as 99.3% after 80 cycles under 0.5 A g^{-1} (Fig. 2c), it is supposed that the enhanced electronic conductivity and mechanical stability are responsible for the Si/CNFs-Cu's higher cycling performance.

The rate capacity of Si/CNFs-Cu is also evaluated. As shown in Fig. 2d, the designed electrode has the reversible capacity of 565.2 mAh g^{-1} at the current density of 5.0 A g^{-1} with an outstanding reversibility. This excellent rate capacity is better than that of previous reported Si/CNFs-based anode (514 mAh g^{-1}) at the same

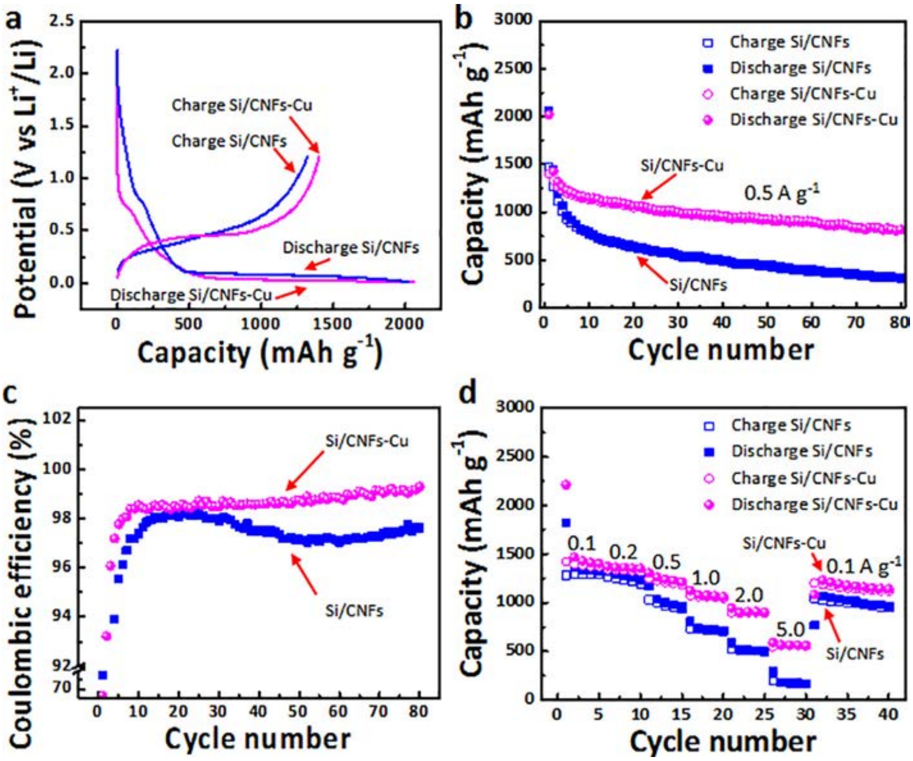

Fig. 2. Charging/discharging profiles (a), cycle performance (b), the corresponding coulombic efficiencies (c) and rate performance (d) of Si/CNFs-Cu and Si/CNFs, respectively.

current density, which is achieved by 3D Si/CNF-graphene structure [10]. Remarkably, compared with Si/CNFs, an approximate 1.8 times enhancement of reversible capacity for Si/CNFs-Cu at 5.0 A g^{-1} can be attributed to the increase of electronic conductivity and barrier-free Li$^+$ transferring.

To further understand the enhanced Li-storage performance, electrochemical impedance spectra of each electrode are obtained at different states. Based on the equivalent circuit (Fig. 3a), the rising values from 55 to 370 Ω after 50 cycles in Fig. 3b suggest that the Si/CNFs electrode is unstable during electrochemical reactions, an increasing number of nanofibers are separating from the electrode and the SEI are getting thicker because of the polarization effect due to the deteriorated electronic conductivity. However, a relatively smaller value of about 70 Ω is obtained from Si/CNFs-Cu after 50 cycles (Fig. 3c). There is an inconspicuous change compared with the pristine state (~67 Ω), which is attributed to the promotion of the electrochemical and mechanical stability benefiting from the framework structure.

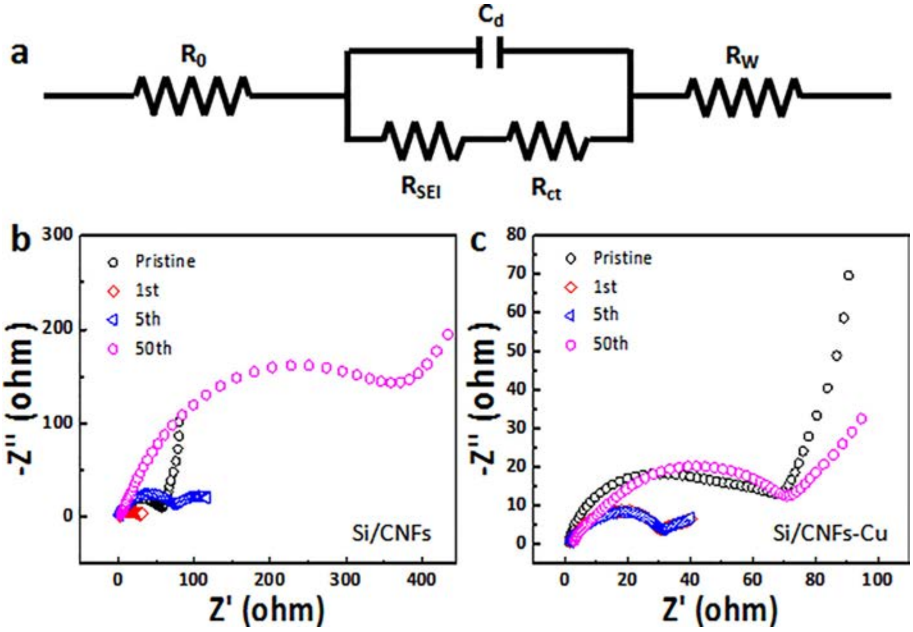

Fig. 3. Equivalent circuit (a), Where the R$_0$, R$_{SEI}$, R$_{ct}$ and R$_W$ are ohmic resistance, SEI membrane resistance, charge transfer resistance and Warburg impedance, respectively, C$_d$ is double layer capacitance. Nyquist plots of the electrochemical impedance spectra of Si/CNFs (b) and Si/CNFs-Cu (c).

4. Conclusions

We designed and developed a kind of Si/CNFs-Cu anode material for lithium ion battery. The excellent electrical conductivity and the structural integrity of Si/CNFs film with Cu foam greatly enhanced the performance of LIBs. The reversible capacity reaches 565.2 mAh g^{-1} at a high current density of 5.0 A g^{-1} and outstanding cycling stability with the high capacity retention of 66.7% is achieved after 80 cycles at 0.5 A g^{-1}. It is significant for the designed Si/CNFs-Cu electrode to improve the cycling performance for long life span. Furthermore, the incorporation of electrospinning nanofiber film and foamy conductive metal is favorable for the energy storage material to realize the larger power density.

CRediT authorship contribution statement

Xiaoqiang Tian: Conceptualization, Methodology, Software, Investigation, Data curation, Writing - original draft. **Gaoda Li:** Writing - review & editing, Formal analysis. **Leixin Meng:** Writing - review & editing, Project administration. **Wang Tian:** Investigation, Software. **Xin Gu:** Investigation, Software. **Yaqin Ding:** Data curation. **Ruichao Zhang:** Data curation. **Xiaofeng Jia:** Formal analysis. **Yong Qin:** Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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