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Copper nanorods supported phosphorus-doped silicon for lithium storage application

Zhibo Yang, Desheng Wang, Fei Li, Hongwei Yue, Dequan Liu, Xiuwan Li,
Li Qiao, Deyan He *

School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China

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ABSTRACT

Functional Cu nanorods supported P-doped Si anode was designed to improve the performance of lithium-ion batteries for high-power applications. The binder-free anode consists of an electrochemical etched Cu nanorod network coated with P-doped Si. The obtained electrode exhibits excellent rate capability and superior cyclability. At a rate of 2 A/g, the anode presents a capacity of 2010 mA h/g even after 80 cycles with a capacity retention of above 80%. The anode also presents a stable rate performance even at a high rate of 10 A/g. The enhanced performance can be mainly ascribed to the Cu nanorod network which could result in a nanocable structure on the micro-level and play a role of scaffolding on the macro-level, as well as the nature of high conductivity and amorphism of the heavy P-doped Si coating.

1. Introduction

Recently, lithium-ion batteries (LIBs) with high power density and energy density are urgently desired as a result of the ever increasing attention for electrical vehicles and portable electronic devices with ultra long work period [1,2]. Si is considered as a promising candidate for anode of LIBs because of its high theoretical specific capacity at room temperature (3579 mA h/g) [3]. However, bulk Si commonly undergoes a severe volume change during Li-ion insertion and extraction, which results in pulverization of the electrode [3]. Fabrication of nanostructured amorphous Si materials is seemingly a promising solution to solve the above issues due to its high mechanical strength, short diffusion path of Li-ions and good strain accommodation [3,4]. Among them, hybrid nanocable-structured Si anodes such as Si/C and Si/Si_xNi_y nanocables exhibit improved cyclability and rate capability due to high conductivity and mechanical intensity of the nanorod core and thin film nature of the Si shell [5,6]. However, the areal mass loading of the nanocable anodes are always limited by the low tap density of nanocables and the thin shell thickness, which has hindered the development of such anodes. Thicker shell could increase the areal mass loading, but normally make it unstable and result in a poor cyclability.

Herein we report a Cu nanorod network supported P-doped Si as an anode for LIBs. The areal mass loading and the electrochemical performance of the anode was enhanced by thickening the thickness of Si coating and interconnecting the nanocables with each other, which could result in a three-dimensional net-structure. The conductivity and structural integrity of the electrode were further improved through heavily P-doping in Si coating [7]. The electrode exhibits a capacity of 1790 mA h/g over 80 cycles at 4 A/g.

2. Experimental

The anode was prepared by directly depositing P-doped Si onto the electrochemical-etched Cu nanorod network. The Cu nanorod network was fabricated by a galvanostatic-anodization of Cu plate followed by a thermal reduction process, as described in our earlier publication [8]. Briefly, the anodization was carried out at a current density of 1.5 mA/cm^2 in a 0.8 M NaOH aqueous solution at room temperature for 12 min. Then the anodized Cu plate was heated to 300 °C in hydrogen atmosphere for 60 min. Si was coated onto the fabricated Cu nanorod network by plasma enhanced chemical vapor deposition (PECVD) using an excitation frequency of 81.36 MHz. The depositions were performed at a pressure of 60 Pa with a substrate temperature of 200 °C. The source gas was 10% silane mixed with 5% phosphine diluted in hydrogen with a flow rate of 52 sccm in a flow ratio of 25:1.

The morphologies of the samples were characterized by a Hitachi S-4800 field-emission scanning electron microscope (SEM). Raman spectra were obtained by a Jobin-Yvon Horiba HR800 spectrometer with a 532 nm-wavelength excitation. X-ray diffraction (XRD) measurements were performed on a Rigaku D/

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* Corresponding author. Tel.: +86 931 8912546; fax: +86 931 8913554.
E-mail address: hedy@lzu.edu.cn (D. He).

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Max-IIIC X-ray diffract meter using Cu $K\alpha$ radiation (0.15406 nm). The active mass of Si coating was obtained by measuring the mass difference before and after Si deposition via a Mettler XS105 analytical balance. The mean mass loading of Si coating is 0.33 mg/cm^2.

CR2032 coin-type half-cells were assembled using the prepared Cu nanorods supported P-doped Si as the working electrode and lithium metal as the counter and reference electrode. The electrolyte was 1 M lithium hexafluorophosphate dissolved in ethylene carbonate and dimethyl carbonate (1:1 by vol.). The galvanostatic discharge–charge cycling was tested in the voltage range from 0.05 to 1.50 V. Cyclic voltammetry testing was performed at a rate of 0.1 mV/s.

3. Results and discussion

Fig. 1a shows XRD patterns of the $Cu(OH)_2$ nanorod precursor and the reduced Cu nanorod network, which are consistent with the data of JCPDS 13-0420 and JCPDS 04-0836, respectively. It indicates that the product of the anodization of Cu is $Cu(OH)_2$, and $Cu(OH)_2$ is totally reduced to Cu after reduction process. From the Raman spectra shown in Fig. 1b, it can be seen that the Raman-shift of the P-doped Si film is located at 480 cm^{-1}, which indicates that the film is amorphous. However, the undoped Si film deposited under the same experimental conditions shows Raman-shifts at 480 and 520 cm^{-2}, which means that the film is partly crystallized. It could be concluded that heavy P-doped Si film is not only more conductive than undoped one, but also prefers to form amorphous structure which is benefit to the insertion/extraction of Li-ions.

Fig. 2a shows that the diameter of the as-etched $Cu(OH)_2$ anorods is 150–200 nm, and the nanorods are straight and interconnected. Fig. 2b shows the SEM image of the Cu nanorod network, it can be seen that the Cu nanorods are fallen and intertwined, forming a Cu nanofabric. The insets in Fig. 2a and b indicate that, after reduction treatment, the Cu nanorod becomes curve and uneven, but the diameter is not apparently changed. Fig. 2c shows that the Cu nanorod network is fully covered with Si, which exhibits a film-like structure in panoramic view. As shown in Fig. 2d, Si film is conformal coated on each Cu nanorod and its thickness is about 150 nm.

The cyclic voltammogram (CV) of the obtained Cu nanorods supported P-doped Si anode is shown in Fig. 3a. One cathodic peak between 0.05 and 0.37 V in the first discharge can be observed, corresponding to the lithium-ion insertion and the formation of solid electrolyte interphase. And four cathodic peaks around 0.05, 0.20, 0.32 and 0.43 V shown in the subsequent cycles correspond to Li-ion insertion to form different phases of Li–Si alloy. After the 2nd cycle, the cathodic peaks at 0.05 and 0.43 V has a decline, meanwhile the cathodic peaks at 0.20 and 0.32 V are ascended. These variations could be related to the activation of the anode, and there is no substantial change in the following cycles [9]. Only one anodic peak at 0.48 V in all the scans is observed, which could be ascribed to the delithiation of Li–Si alloy.

Cyclability of the electrodes at current densities of 2 and 4 A/g (the initial three cycles were performed at 0.5 A/g) is illustrated in Fig. 3b. An undoped Si film on planar Cu plate was used as contrast, which was cycled at 0.1 A/g. The contrast undoped Si film anode shows higher initial capacity but decreases quickly from 2686 to 393 mA h/g after 80 cycles. In comparison, the Cu network supported P-doped Si anode is able to operate at higher rates and deliver a better cyclability. At a rate of 2 A/g, the first discharge and charge capacities were 2678 and 2628 mA h/g, respectively. A reversible capacity of 2442 mA h/g is obtained in the 2nd cycle, which maintains at 2010 mA h/g after 80 cycles. The first reversible capacity at 4 A/g is 2141 mA h/g, and decreased slowly to 1790 mA h/g after 80 cycles.

The rate performance of the Cu nanorods supported P-doped Si anode at rates from 0.5 to 10 A/g is presented in Fig. 3c and d. As the rate increasing, the voltage of discharge plateau declines slightly, while that of the charge plateau has a rise. This could be ascribed to the kinetic effects of the electrode materials [1,2]. The rate capacity is illustrated in Fig. 3d, it is apparent that the nanostructured P-doped Si anode presented a stable rate performance at all the test rates. Notably, the anode manifests a specific capacity of about 1260 mA h/g at a rate of 10 A/g.

The enhanced rate performance and cyclability could be attributed to the unique configuration of the electrode. First, the Si–Cu nanocable structure could provide short Li-ion diffusion path and high conductivity, and largely accommodate the volume change, which make the lithiation reaction could occur more efficiently, and is beneficial to the structural integrity. Second, the Cu nanorod network is directly connected to the substrate, the adhension and electrical contact between active material and current-collector are greatly improved, which is crucial for high rate performance. More importantly, the conductivity and structural integrity of the electrode is greatly enhanced through P-doping and the formation of the interconnected Cu network scaffolding [7,10].

4. Conclusion

We have synthesized P-doped Si coating with Cu nanorod network as the scaffolding for Li storage application. The nanostructured Si anode displays an improved cyclability and rate capability. Specific

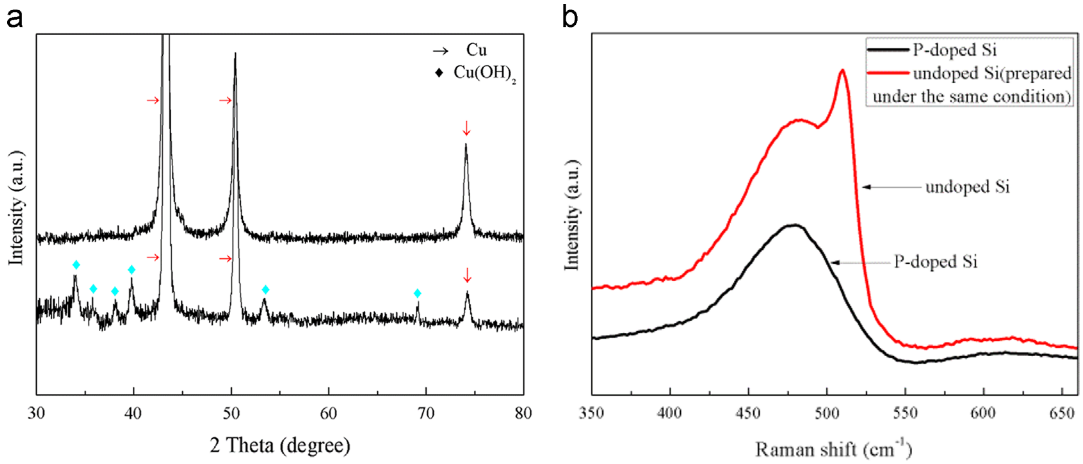

Fig. 1. (a) XRD patterns of $Cu(OH)_2$ and Cu nanorods, (b) Raman spectra of P-doped Si and undoped Si films deposited under the same condition.