Short communication

Growth of Si nanowires in porous carbon with enhanced cycling stability for Li-ion storage

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HIGHLIGHTS

- Solution-liquid–solid growth of Si nanowires in porous carbon.
- Porous carbon improve electrical conductivity and buffer volume change.
- Synergistic effect between porous carbon and Si nanowires enhances capacities.
- High reversible capacity of 1678 mAh g^{-1} during the 100th cycle at a current density of 420 mA g^{-1}.

ABSTRACT

Si nanowires are successfully grown in porous carbon by supercritical fluid-liquid-solid (SFLS) process, which show high specific capacities and charge–discharge cycling stability as anode materials for Li-ion storage. The enhancement capacity and cycling stability of the Si nanowires/porous carbon composite nanostructures is attributed to the porous carbon serving as a highly conductive framework and absorption of volume changes of Si nanowires during the lithiation/delithiation process. At optimized condition, the Si nanowires/porous carbon electrodes maintain reversible capacities of 1678 mAh g^{-1} for the 100th cycle at a current density of 420 mA g^{-1}, which is much better as compared to that of pure Si nanowires.

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1. Introduction

During the past decades, great efforts have been devoted to the preparation of new electrode with high capacity and good stability for lithium-ion battery due to its wide applications in portable electronics [1–5]. Among the various candidate materials for anode electrode, silicon has received extensive attention due to its highest known theoretical capacity (4200 mAh g^{-1} for Li$_{22}$Si$_5$) and abundance [6–10]. However, the large volume change (360%) during the discharge-charge reactions cause the loss of contact between silicon and the current collection, which leads to fast capacity fading with increasing cycles [11]. To overcome this problem, researchers have developed many silicon nanostructures as lithium-ion battery anode materials such as nanoparticles, nest-like nanospheres, nanotube, nanosheets and nanowires [3,10,12–16]. The advantage of using Si nanowires instead of other morphologies is that it

provides good electrical conductivity along the length of individual nanowires, short lithium ion diffusion distance and large interfacial area in contact with the electrolyte [10,17–19].

Recently, it was found that the stability of silicon electrode can be further enhanced by combining the nanostructures silicon with carbon material as a result of increased electrical conductivity, aggregation prevention and buffering volume changes [20–28]. For examples, silicon nanoparticles and nanowires coated with a thin carbon film [10,23] showed improved cycling stability. Combination of silicon with carbon nanotube or graphene displays high electrical conductivity which contributes the high cycling stability of the electrode [26,29]. Dispersing silicon nanoparticles in porous carbon matrix is also a good way to achieve high capacity and good stability. For instance, Magasinski et al. designed a chemical vapor deposition (CVD) synthesis process for robust porous carbon spheres loading with silicon nanoparticles as high-performance lithium-ion battery anodes [30].

In this paper, we report for the first time the solution growth of silicon nanowires in porous carbon (Si NWs/PC). The weight ratio of

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the Si NWs can be easily adjusted by changing the precursor ratio during the preparation. As anode materials for Li-ion storage, these materials showed improved specific capacities and charge–discharge cycling stability (e.g. delivering a reversible capacity of 1678 mAh g^{-1} during the 100th cycle at 0.1 C) as compared to that of pure Si NWs because the porous carbon provides better electronic pathways and also acts as a buffering phase for the volume changes of Si.

2. Experimental

2.1. Preparation of pure silicon nanowires

In a typical Si NWs synthesis, 0.1 mL of diphenylsilane (DPS) and Au seeds in the molar ratio of Au:Si being 1:150, were added to 20 mL of hexane in a glass beaker. The beaker was then placed in a high pressure high temperature (HPHT) reactor (Model: 4576, Parr Instrument Company), purged with argon gas for 10 min and then sealed up. The reaction mixture was heated in the reactor to 360 °C at a rate of about 10 °C min^{-1} and stand for 2 h. After cooling down, the as-synthesized Si NWs were rinsed with hexane and annealed at 650 °C in a tube furnace with Ar protection.

2.2. Growth of silicon nanowires in porous carbon

The synthesis of Si NWs in porous carbon is illustrated in Fig. 1. Firstly, gold seeds were prepared in porous carbon. Typically, 100 mg porous carbon (Vulcon XC 72) and 2 mL of 5 mM HAuCl$_4$ were mixed in 10 mL water. After 2 h, 1 mL of 0.1 M NaBH$_4$ was added and reacted for 1 h. The porous carbon–gold composite was separated by centrifugation and dried in vacuum oven. Si NWs were synthesized by thermally degrading diphenylsilane (DPS) in hexane at 360 °C. The gold/porous composite was put into the reactor, and then 20 ml hexane and diphenylsilane (with different amount) were added. The temperature was increased to 360 °C by the rate of 10 °C min^{-1} and stand for 2 h. After cooling down, the sample was rinsed with hexane and annealed at 650 °C in a tube furnace with Ar protection.

2.3. Characterization

Transmission electron microscopic (TEM) observations were carried out under a JEOL-2010 electron microscope after the dilute dispersions of the particles were dropped onto carbon coated copper grids. The morphologies of the composites were investigated by using a JEOL JEM-7600F field emission scanning electron microscope (FESEM). X-ray diffraction (XRD) patterns were acquired on a Shimadzu X-ray diffractometer (Cu Kα). Electrochemical experiments were performed by assembling two-electrode coin cells in an argon-filled glove box with Li foil as the counter electrode and 1 M LiPF$_6$ in EC/DEC as the electrolyte. For Si NWs/PC, the electrodes were prepared by mixing 90 wt% of the active materials and 10 wt% of poly(vinylidene fluoride) binder and then coating on copper foil. For pure Si NWs, the electrodes were prepared by mixing 80 wt% of the active materials 10% super P carbon black and 10 wt% of poly(vinylidene fluoride) binder and then coated on copper foil. The obtained electrodes were dried under vacuum at 50 °C for 12 h. The cells were charged and discharged within the voltage window from 0.005 to 1.5 V. Cyclic voltammetry and electrochemical impedance spectroscopy (EIS, frequency range: 0.001–10^5 Hz, amplitude: 5 mV) analysis were performed with an electrochemical workstation (CHI 660C).

3. Results and discussion

3.1. Structure and morphology

The typical sample preparation process is described in the scheme displayed in Fig. 1. Gold nanoparticles were firstly embedded in porous carbon matrix, which is confirmed by TEM and HRTEM images (Fig. 2). The particles size is typically in the range of 10 nm–20 nm with polycrystalline phase. These gold nanoparticles served as seeds for the further growth of Si NWs by supercritical fluid-liquid-solid process (SFLS) [31]. During the SFLS process, the precursor (DPS) was decomposed into silicon atom and then dissolving into the melting gold seeds. As more Si dissolves, the gold droplets become saturated and expel Si in the form of crystalline nanowires. After the reaction, the Si NWs grow in porous carbon while the hexane solutions remain clear. Fig. 3 shows TEM and FESEM images of the Si NWs/PC composite. A large quantity of nanowires was obtained. Although it is hard to clearly observe all the Si NWs in porous carbon in the TEM image (Fig. 3a) due to the three dimensional structure, the magnified TEM image (Fig. 3c) of a single Si NW shows the Si NW is surrounded with carbon. It can be seen clearly from the FESEM images (Fig. 3b) that the Si NWs are embedded in the porous carbon with diameters of 30–70 nm, which is much smaller than the Si NWs prepared by etching Si wafer [32]. The diameter of the Si NWs is larger and broader than that of the gold seeds which is due to the aggregation of the seeds during the SFLS process [31]. The lattice fringes of the Si NW in porous carbon are also observed in the HRTEM image in Fig. 3d, which shows d-spacing of 3.12 Å, corresponding to the (111) plane. And the XRD patterns (Fig. 4) of Si NWs/PC show the signature peaks of cubic Si (JCPDF 89-5012). In addition, diffraction peaks corresponding to the (111) plane of the cubic gold phase (JCPDF 89-3697) and copper (JCPDF 89-2838) were also observed, which are from the gold seeds and Cu substrate. The Cu substrate serves as the current collector for the electrochemical measurements.
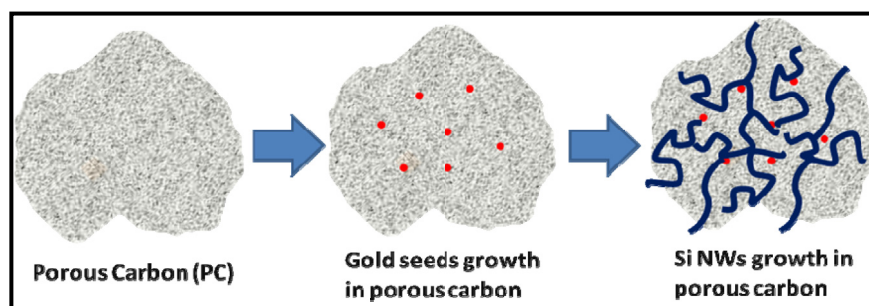

Fig. 1. Schematic illustration of the synthetic process of Si NWs/Porous carbon composite. Gold seeds were embedded in the porous carbon, and then the silicon nanowires were grown in the porous carbon by supercritical fluid-liquid-solid (SFLS) process.