



Carbon-coated silicon nanotube arrays on carbon cloth as a hybrid anode for lithium-ion batteries



Wei Wang^a, Lin Gu^a, Haolei Qian^a, Ming Zhao^a, Xi Ding^a, Xinsheng Peng^b, Jian Sha^{a, **}, Yewu Wang^{a, *}

^a Department of Physics & State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou, 310027, PR China

^b State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, PR China

HIGHLIGHTS

- Carbon-coated silicon nanotube arrays on carbon cloth have been fabricated.
- The hybrid electrodes show high specific capacity and good cycling stability.
- The influence of the thickness of silicon shell has been studied.

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ABSTRACT

Silicon hollow nanostructure has been considered as one of the most promising material for commercial application in lithium-ion batteries due to its significant improvement of cycling stability. The fabricated hybrid structures, carbon-coated silicon nanotube arrays on carbon cloth substrate, with a high surface area and short electron collection pathway have been directly used as anode electrodes without any additional binder. The electrodes exhibit high capacity, excellent rate capability and good cycling stability. The discharge capacity of the hybrid electrode (the deposition time of silicon shell: 5 min) keeps stable, and after 100 cycles, the discharge capacities still remain 3654 mAh g⁻¹ at the rate of 0.5 C.

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1. Introduction

Rechargeable Lithium-ion batteries (LIBs) have been considered as one of most promising energy storage technology for next-generation electronic devices due to their high energy density, long cycle life and good safety features [1–3]. But the current commercial graphite anode has a relatively low specific capacity (372 mAh g⁻¹) [4], hardly meeting rapidly increasing energy demands. Various attempts have been made to seek for electrode materials with higher energy density. Among all of the possible anode materials, silicon is a most promising high capacity alternative to graphite [5–8]. Silicon has a high theoretical capacity (4200 mAh g⁻¹) [9], more than 10 times the value of the graphite

anodes and a low work potential (<0.5 V vs. Li/Li+) for safe use [10]. Additionally, silicon, the second abundant element on earth, is also the fundamental element of modern electronic industry [11]. But the dramatic volume expansions (>300%) during lithium insertion/extraction in silicon limit its practical applications [9]. This volume expansions cause silicon electrode pulverization and finally destroy the electronic connection between active materials and the electrode. Moreover, the repeated volume expansions would break the solid electrolyte interphase (SEI) repeatedly and then the formation of new SEI films will consume active materials, which finally lead to rapid capacity loss [12–14]. Therefore, alleviating the total mechanical stress of silicon electrodes and maintain the stability of SEI films are two main factors to improve silicon LIBs cycling performance [12].

Recently, various silicon hollow nanostructures have been reported for improving silicon LIBs cycling stability [12–18]. Usually, as the typical advantages of silicon nanostructures (nanowires [9,19], nanoparticles [20,21] and nanoporous films [22,23]), the

* Corresponding author.

** Corresponding author.

E-mail addresses: phyjs@zju.edu.cn (J. Sha), yewuwang@zju.edu.cn (Y. Wang).

strain in silicon electrode can be relaxed effectively when the material size is reduced to nanometer range. Furthermore, hollow nanostructure is offering inner free space to accommodate the volume expansions. In addition, deposition of a thick layer, which has little volume expansions during cycling, on the surface of the hollow nanostructure can force the electrode expands inward into the hollow space instead of out space, such as double-walled Si–SiO nanotubes [12], TiO₂, TiN or Al₂O₃-coated silicon nanotubes [24] and Si–SiC hollow nanospheres [25]. Hence the SEI films between silicon electrode and the electrolyte can maintain their shape during lithium insertion/extraction, minimizing the amount of silicon consume for forming SEI and finally improving the cycling stability. In this paper, carbon-coated silicon nanotube (Si NT) arrays on carbon cloth (CC) were fabricated and then directly used as the electrode of lithium-ion battery. The hollow inner space of silicon nanotube offers free space to accommodate the volume expansions, and the carbon coating forces the expansions to go towards the inner space. The carbon coating also improves the electrode conductivity. Moreover, CC has been considered as a practically promising substrate for LIBs or other flexible devices due to it is high surface area, good electrical conductivity and chemical stability, and high flexibility [26–28]. Therefore, the fabricated electrode exhibits high capacity, excellent rate capability and good cycling stability.

2. Experimental section

2.1. Synthesis of carbon-coated silicon nanotube arrays on CC

Silicon nanotubes were fabricated by using ZnO nanowire as a sacrificial template [18]. Typically, CC substrates (WOS1002, Phychemi Company Limited) were cut into small pieces (1–2 cm²), and then cleaned by sonication sequentially in acetone and alcohol for 10 min, respectively. The cleaned CC was then soaked in 0.0025 M zinc acetate dihydrate alcohol solution for 5 min and annealed in oven for 20 min at 300 °C to form a ZnO seed layer. A precursor 150 ml solution was prepared with 0.04 M zinc acetate dihydrate, 0.04 M hexamethylenetetramine and 0.009 M poly(ethylene imine). After preheating the precursor solution for 1 h at 95 °C, the seeded CC substrates were dipped into the solution for another 4 h and finally ZnO nanowire arrays were grown on the substrates. Subsequently, the substrates with ZnO nanowires were cleaned by deionized water and transferred into a chemical vapor deposition chamber to deposit a silicon shell. The deposition of silicon shell was achieved at 500 °C for several min with passing 4 sccm SiH₄ and 20 sccm Ar at a pressure of 100 Pa. To form a carbon coating on the surface of silicon shell, another deposition process was carried out at 650 °C for 90 min with passing 4 sccm C₂H₂ and 20 sccm Ar at a pressure of 500 Pa. Finally, the core ZnO nanowires were selectively removed via a reduction process at 600 °C for 12 h with 20% H₂ in N₂ at 600 Pa, leaving a carbon-coated Si NT. For comparison, the sample of Si NT arrays/CC was prepared without carbon deposition process.

2.2. Characterizations and electrochemical measurements

The morphology and microstructure of the as-prepared Si NT arrays/CC were investigated by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL 2010). Electrochemical properties of the products were measured using CR2025-type half coin cells assembled in the Ar-filled glove box. The as-prepared carbon-coated Si NT arrays/CC was directly used as the working electrode without any additional binder. Test cells were assembled with the metallic lithium foil as counter electrodes, 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl

carbonate (DMC) as the electrolyte and Celgard 2400 as the separator. The cells were tested by EQ-BST8-WA battery-test system after 24 h aged at room temperature. The galvanostatic charge–discharge performances were tested in the voltage range of 0.01–2.0 V under a constant current density of 0.025 C for the initial two cycles and other rates for the following cycles. Electrochemical impedance spectroscopy (EIS) was measured using a CHI 660D electrochemical station by applying an alternating voltage of 10 mV in the frequency range of 0.01–100,000 Hz.

3. Results and discussions

The fabrication process of carbon-coated Si NT arrays/CC includes three steps: ZnO nanowire growth, silicon and carbon shell deposition, and ZnO nanowire removal, as shown in Fig. 1. ZnO NWS were first synthesized on CC via a hydrothermal process. Then the silicon and carbon films were coated on the surface of ZnO NWS via a two-step CVD, respectively. Finally, the ZnO NWS were reduced to Zn by H₂ and evaporated at high temperature, leaving a hollow carbon-coated silicon nanotube. Fig. 2(a) shows the low magnification SEM pictures of carbon-coated Si NT arrays/CC, displaying the well-established texture structure. ZnO NWS with diameters of 25–50 nm are randomly distributed on the surface of CC, as shown in Fig. 2(b) and (c). The inset in Fig. 2(b) is the cross-section of ZnO NW arrays/CC, indicating the ZnO NWS have a length of about 4–5 μm. The detailed morphology of carbon-coated Si NT arrays/CC is shown in Fig. 2(d)–(f). It clearly shows the nanowire shape of carbon-coated Si NTs, which are grown almost vertically with respect to the substrate, are well maintained after inner ZnO NWS have been etched away. The length of them was typically also 4–5 μm and the diameter ranged from 100 nm to 150 nm, as shown in Fig. 2(e) and (f), respectively. The microstructural characterizations of the carbon-coated Si NTs were performed by TEM, which clearly indicate that the Si NTs have a straight morphology with rough surface, as shown in Fig. 3(a) and (b). The thickness of Si shell is about 20–30 nm for the deposition time of 7 min Fig. 3(c) shows the uniform coverage of carbon film around Si NTs. The magnified TEM image of the edge reveals the amorphous carbon shell with a

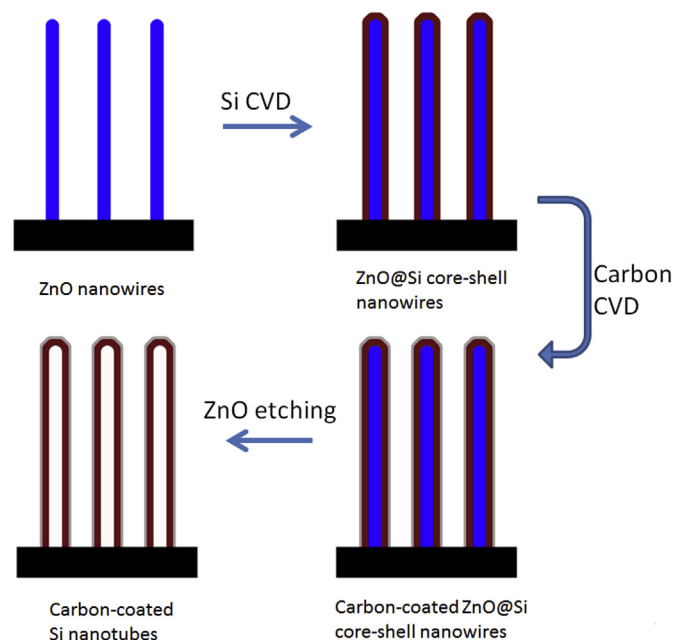


Fig. 1. Schematic illustration of the fabrication process of carbon-coated silicon nanotube arrays on CC.

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