



Hollow core–shell structured silicon@carbon nanoparticles embed in carbon nanofibers as binder-free anodes for lithium-ion batteries



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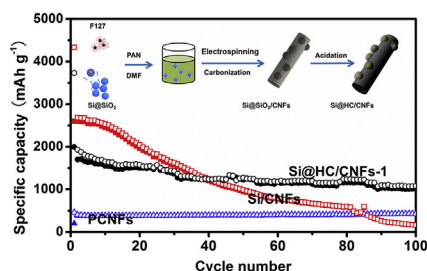
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HIGHLIGHTS

- Core-shell-structured Si@SiO₂ nanoparticles were prepared by a sol–gel method.
- The hollow core-shell structure was formed by electrospinning and an HF treatment.
- The void could accommodate the volume expansion of Si nanoparticles.
- A stable solid electrolyte interface film formed on the carbon shell surface.
- The structural integrity and cycle stability were significantly improved.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicon is regarded as one of the most promising candidates for lithium-ion battery anodes owing to its large theoretical energy density (about 4200 mAh g⁻¹) and low working potential (vs. Li/Li⁺). However, its practical application is limited by structure degradation and a comparatively poor capacity retention caused by large volume changes during cycling. In this study, we have prepared a novel nanofiber form of silicon/carbon with hollow core–shell structured silicon@carbon (Si@C) nanoparticles embedded in carbon nanofibers. Voids between the silicon nanoparticle (SiNP) core and carbon shell help to accommodate the volume expansion associated with the lithiation/delithiation process in a working electrode and allow formation of a stable solid electrolyte interphase (SEI) film. The obtained electrodes exhibited good cycle performance with a high reversible capacity of 1020.7 mAh g⁻¹ after 100 cycles at a current density of 0.2 A g⁻¹, and also delivered excellent cycling performance at a high current density of 3.2 A g⁻¹. The design of this new structure provides a potential method for developing other functional composite anode materials with high reversible capacities and long-term cycle stabilities.

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1. Introduction

The superior specific capacity of lithium-ion batteries (LIBs) makes them very attractive for use in many devices, such as portable electronics, hybrid electric vehicles, and plug-in hybrid electric vehicles [1–4]. Nowadays, LIBs successfully deployed in commercial applications commonly use graphite as the anode, which hosts lithium as LiC_6 in the fully charged state with a low capacity of 370 mAh g^{-1} [5,6]. The employment of non-carbonaceous materials that could store large amounts of lithium, such as tin-, silicon-, and metal-oxide-based anode materials, would boost the energy storage capacity of the anode [7–9]. Among these, novel silicon-based electrode designs for rechargeable lithium batteries have received considerable attention [10–12]. This interest can be attributed to the low working potential, abundance in nature, and the highest theoretical capacity (4200 mAh g^{-1}) of silicon, which is more than 10 times greater than that of commercialized graphite anodes [13]. However, the application of silicon-based materials in LIBs is far from practical owing to its low intrinsic electrical conductivity and severe volume change (greater than 300%), which results in serious pulverization of silicon particles, electrical contact loss, and rapid capacity fading upon cycling [14,15]. An effective method of alleviating the severe volume change uses a Si/C nanofiber (Si/CNF) design that combines the high capacity of silicon with the excellent stability of CNFs.

Electrospinning is a simple and low-cost approach for the fabrication of Si/CNF composites, through which silicon nanoparticles (SiNPs) are dispersed into CNFs. Moreover, the as-prepared fiber network could be directly used as the anode for lithium batteries, simplifying the cell preparation process. Silicon-carbon nanofibers (Si/CNF) by electrospinning have been applied by a number of researchers for LIB anode [15,16], but do not reach their performance potential owing to exposed SiNPs on the fiber surface caused by serious aggregation. Without protection, these exposed SiNPs come into direct contact with the electrolyte and suffer from serious fracturing and exfoliation during cycling, which leads to the formation of a thick solid electrolyte interface (SEI) film, inactivation of Si, and, eventually, rapid capacity loss. A design that provides additional protection to the Si/CNFs would allow these drawbacks to be overcome. In our previous study, an extra carbon layer was introduced as a maskant for the electrode, which helped to avoid exfoliation of SiNPs from the anode bulk and reduce electrical contact loss [17,18]. However, the carbon layer provided macroscale protection of the whole electrode on both sides of the nanofiber membrane, but could not prevent the exfoliation of SiNPs inside the electrode; thus, satisfactory electrochemical performance has not yet been achieved. Inspired by the hollow core-shell Si@C structure of Li [19] and the yolk-shell design of Cui [20], a sol-gel and electrospinning method assisted by an acid treatment step was used to provide additional protection to individual SiNPs (that is, to construct voids between the SiNPs and carbon shells that could accommodate volume expansion). In this structure, SiNPs are dispersed along the CNFs, and an appropriate interspace was built between the silicon core and carbon shell. The as-prepared nanofiber composite (Si@HC/CNFs) possessed the following advantages as a LIB anode: First, good electrical conductivity was obtained because the carbon shell is a good conductor for both electrons and ions. Second, the outer carbon shell did not rupture during cycling owing to the void between the silicon core and carbon shell, which helped accommodate the expansion and fracturing of SiNPs. This in turn suppresses exfoliation of SiNPs from the fiber surface and electrical contact loss, thus enhancing structural stability. Third, a stable SEI film was formed on the carbon shell surface because direct contact between the SiNPs and electrolyte is prevented. When used as a binder-free

anode in LIBs, the as-prepared novel Si@HC/CNF composite exhibited high electrochemical performance.

2. Experimental

All chemicals were of analytical grade and used without further purification.

2.1. Preparation of Si@SiO₂ particles

SiNPs (200 mg, ~50 nm, 98%, Alfa Aesar) were dispersed in a 400 mL mixture of ethanol and water (v:v = 4:1) by ultrasonication, followed by the addition of concentrated ammonium hydroxide (4.0 mL). Tetraethoxysilane (2.0 g, TEOS, Aldrich) was added to the dispersion dropwise with vigorous stirring, and the reaction was left at room temperature under stirring for 12 h. Then, the SiNPs coated by SiO₂ (Si@SiO₂) were collected by centrifugation (10,000 r/min) and washed three times with ethanol.

2.2. Fabrication of Si@HC/CNFs

A mixture of Si@SiO₂ nanoparticles, pluronic F127 (Sigma-Aldrich) as a surfactant, and polyacrylonitrile (PAN, Mw ~150,000, J&K) with a mass ratio of 1:1:2 was dispersed in *N,N*-dimethylformamide (DMF, purity ≥ 99.5%) by stirring for 24 h at 60 °C and ultrasonication for 1 h at room temperature to form a homogeneous solution. Then, electrospinning was carried out at a high voltage of 15 kV and a flow rate of 0.7 mL h^{-1} to generate continuous composite nanofibers. A self-made electrospinning device was used, which consisted of a high voltage supplier, an injection pump, and a receiver. The as-prepared yellow membrane was collected on an aluminum foil positioned 15 cm from the needle tip and then carbonized at 700 °C to obtain Si@SiO₂/CNFs. Finally, the as-prepared nanofibers were immersed in a 2 wt% HF solution for 0, 0.5, 1, and 2 min to remove the SiO₂ layer. The corresponding products are denoted Si@HC/CNFs-0, Si@HC/CNFs-0.5, Si@HC/CNFs-1, and Si@HC/CNFs-2.

2.3. Characterization

The morphological appearance of the samples was examined using field-emission scanning electron microscopy (FE-SEM, Carl Zeiss SMT Pte Ltd.) at an operating voltage of 3.0 kV. Transmission electron microscopy (TEM) observations were carried out using a JEM-2100 microscope with 0.23 point resolution. The crystal structure was characterized by X-ray diffraction (XRD) using a Thermo ARL XTRA system, with a scanning rate of 3° min^{-1} . Compositional analysis was performed using energy dispersive X-ray spectroscopy (SEM/EDX, JSM-5610LV, JEOL), and the surficial silicon content change was determined by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific).

2.4. Electrochemical measurements

LIR2032 coin-type half-cells were assembled with metallic lithium counter anodes for the electrochemical measurements. The as-prepared Si@HC/CNFs membranes were punched into circular discs, followed by drying at 180 °C under vacuum overnight. The cells were assembled in an argon-filled glovebox with Celgard 2300 as the separator membrane. The electrolyte consisted of a 1 M LiPF₆ solution in a mixture of ethyl methyl carbonate, dimethyl carbonate, and ethylene carbonate (1:1:1, v/v/v). After standing for 24 h, the cells were subjected to a galvanostatic charge/discharge test at a current density of 0.2 A g^{-1} on a LAND-CT2001A battery-testing system in the potential range of 0.01–3.0 V. Cyclic voltammetry

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