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Electrospun silicon/carbon/titanium oxide composite nanofibers for lithium ion batteries

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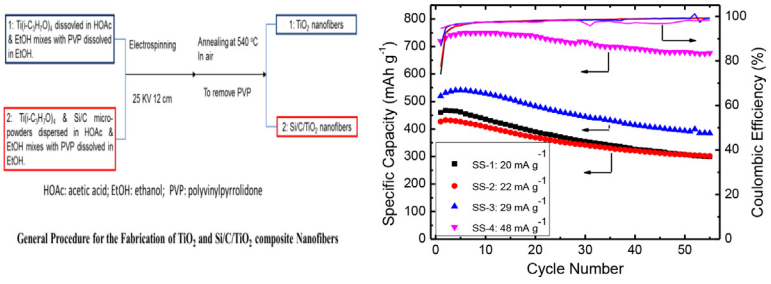
HIGHLIGHTS

- We fabricated silicon/graphite/TiO_2 composite nanofibers (NFs) via an electrospinning method.
- Stable TiO_2 shell is beneficial for enhancing the cycling performance of these electrodes.
- These NFs showed superior electrochemical performance as lithium ion battery anode.
- 94% of initial specific capacity (720 mAh g^{-1}) can be maintained after 55 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

$Si/C/TiO_2$ composite nanofibers have been prepared via a facile electrospinning method combined with a sol–gel chemistry, whose electrochemical performance as anode materials in lithium-ion battery was evaluated. As-prepared nanofibers (NFs) were characterized using scanning electron microscopy, energy dispersive spectroscopy, powder X-ray diffraction and thermogravimetric analyzer to identify their morphology, phase, crystallinity and compositions. Rutile phase TiO_2 nanofibers demonstrated a relatively low gravimetric specific capacity of ~83 mAh g^{-1} when discharged at 0.1C. In contrast, composite nanofibers possess a much higher gravimetric specific capacity. When the Si to C mass ratio is of 0.217, a specific capacity as high as 720 mAh g^{-1} can be attained, 94% of which can be maintained after 55 cycles. The enhanced cycling stability of micron silicon materials is attributed to the space confinement provided by the structurally stable TiO_2. These findings can provide a beneficial guidance for future lithium ion battery electrode development.

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1. Introduction

The utilization of green energy such as solar and wind power is believed to be one of the most promising approaches to support a more sustainable economic growth [1–4]. Lithium ion batteries (LIBs) have been widely viewed as one of the most promising energy storage technologies for renewable and intermittent energy sources [2,5]. However, several aspects including relatively high cost, low capacity and poor performance limit their broader applications [6,7]. Silicon is a promising candidate for lithium ion battery anode because of its high theoretical capacity (4200 mAh g^{-1}) and low operation voltage [8–10]. But the structure of Si is not stable during the lithiation/delithiation process, mainly due to the nearly 300% lattice volume variation and

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unstable solid electrolyte interphase (SEI) films, leading to pulverization, low cycling efficiency, and permanent capacity losses [10–12]. Recently, it has been found that nanostructured silicon as the anode material for LIBs possesses a much improved stability and gravimetric capacity [10,11,13]. It has been demonstrated that micro-sized Si–C composites composed of nanoscale primary building blocks are attractive anodes for lithium ion batteries [14,15]. To obtain high capacity (1200 mAh g^{-1}) and stable cycling performance (600 cycles), the size of Si building blocks should be smaller than 15 nm, and carbon coating can significantly improve the first cycle Coulombic efficiency and the rate capability [14,15]. However, the reduced volumetric energy density and increased fabrication cost could seriously hinder their commercial applications [11,15–17]. Titanium dioxide (TiO_2) as anode materials for LIBs possesses the advantages of low-cost, environmental benignity and easiness to process via sol–gel process [17]. Compared to conventional bulk material, the nanostructured TiO_2 has advantages like the large specific surface area and short diffusion length, and thus leading to a faster charging/discharging rate [18,19]. Among the fabrication approaches, electrospinning is one of the most promising methods to generate nanostructured TiO_2 in large scale with a relatively inexpensive cost and high specific surface area [20–23]. Noteworthy the theoretical capacity of TiO_2 is only ~335 mAh g^{-1}, which is much lower than the theoretic capacity of Si (4200 mAh g^{-1}) [8–10].

Herein, silicon/graphite (Si/C) micro-platelets embedded in TiO_2 nanofibers are fabricated via a facile electrospinning technique. After being thermally annealed in air, part of the graphite embedded in composite nanofibers can be oxidized to generate free space for volume expansion during the lithiation process of silicon. In addition, the titanium oxide shell is beneficial for creating stable SEI films which can further enhance Coulombic efficiency and cycling performance. This type of composite fibers as LIB anode possesses the advantages of high capacity, long cycle life and relatively low fabrication cost compared to other nanostructured silicon materials (nanoparticles, nanowires and nanotubes, as well as porous silicon).

2. Experimental

2.1. Fabrication of Si/C/TiO_2 and TiO_2 nanofibers

First, 1 g Polyvinylpyrrolidone (1.3 M MW, Sigma Aldrich) was dissolved in 10 mL absolute ethanol. Meanwhile, 1 g Titanium (IV) isopropoxide (sigma Aldrich) and 0.1 g, 0.3 g, 0.5 g or 3 g Si/C microplatelets was mixed well with 3 mL glacial acid (HOAc, Sigma Aldrich) and 3 mL absolute ethanol by stirring and keeping under sonication for 10 min. Then these two solutions were mixed together and electrospun into nanofibers using a homebuilt electrospinning setup. The electrospinning working parameters were as follows: applied voltage is direct current (DC) 25 kV (Spellman P/N230-30R); distance between the syringe needle (16 gauge, Air-Tite Products Co.) containing the solution and the grounding collector (aluminum foil) is 12 cm; and pumping rate of syringe was 3 mL h^{-1}. The syringe pump was purchased from New Era Pump Systems Inc. (NE-1000). As-fabricated composite nanofibers were annealed at 540 °C in air for 12 h to remove organic polymers using a Lindberg Blue tube furnace, resulting in the formation of inorganic TiO_2 nanofibers (NFs). The general fabrication scheme for Si/C/TiO_2 composite nanofibers is listed in Fig. 1. The samples prepared using 0.1 g, 0.3 g, 0.5 g and 3 g silicon/graphite micro-platelets are named as SS-1, SS-2, SS-3 and SS-4 in this article, respectively. The fabrication method for TiO_2 nanofibers is similar to that of composite Si/C/TiO_2 NFs except that no Si/C micro-platelets were added.

2.2. Electrode preparation

The preparation of Si/C/TiO_2 and TiO_2 NF electrodes includes slurry making, casting, and drying. Typically, the active materials, Si/C/TiO_2 nanofibers, and carbon black were added into the solution of polyvinylidene difluoride (PVDF) dissolved in *N*-methy-2-pyrrolidone (NMP), with continuously stirring to make solid particles well dispersed in the slurry. The slurry was then coated onto Cu foil (current collector). Next, the electrode was dried at 75 °C for 4 h, followed by being dried at 75 °C in vacuum oven overnight. To completely remove the moisture, the electrodes were dried at 120 °C in the vacuum oven for at least 4 h before the cell assembly. The final solid electrodes are composed of 10 wt.% PVDF, 8 wt.% carbon black, 82 wt.% active materials. The NF electrodes were cut into disks of 1.6 cm^2, and then assembled in 2032-type coin cells using lithium metal as counter electrodes. The electrolyte solution containing 1.2 mol L^{-1} $LiPF_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3/7 by weight) was used in all cells.

2.3. Characterization of Si/C/TiO_2 and TiO_2 nanofibers

As-fabricated nanofibers were characterized using Field Emission Electron Microscopy (JEOL JSM-7600F) attached with OXFORD Energy Dispersive Spectroscopy (EDS) for elemental analysis. The samples were coated with a layer of thin gold film using Denton Desktop sputtering machine for SEM imaging. Samples were also characterized by powder X-ray diffractometer (XRD) using a Bruker D8 Advance diffractometer with Cu Kα radiation (=1.5406 Å) to identify the phase and elemental composition of these nanofibers. To collect information about the elemental composition, these nanofibers were also analyzed by Thermogravimetric Analyzer (TGA) using the thermal analyzer (NETZSCH STA 449 F3).

2.4. Electrochemical characterizations

Galvanostatic cycling tests of the Li/NFs electrode half-cells were conducted using a Maccor series 4000 potentiostat and applying constant currents at room temperature. Initially, 3 formation cycles with an approximated 0.1C current were applied to the cells to

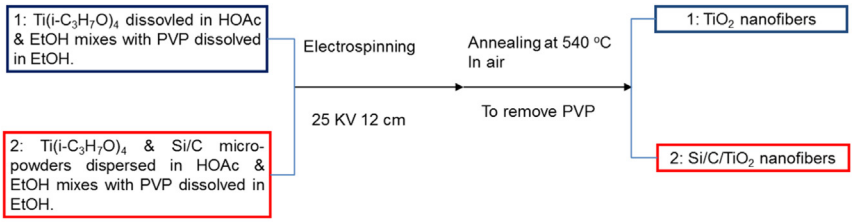

Fig. 1. The general fabrication scheme for pure TiO_2 nanofibers and composite Si/C/TiO_2 nanofibers.