



Flexible binder-free silicon/silica/carbon nanofiber composites as anode for lithium–ion batteries



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ARTICLE INFO

Article history:

Received 21 January 2015

Received in revised form 30 March 2015

Accepted 7 April 2015

Available online 9 April 2015

Keywords:

Lithium–ion battery

Flexible electrode

Carbon nanofiber

Silicon

Chemical vapor deposition

ABSTRACT

High-capacity flexible electrode materials for high-energy lithium–ion batteries become critically important with technological improvements on portable and bendable electronic equipment such as rollup displays, implantable medical devices, active radio-frequency identification tags, and wearable devices. Although different types of bendable electrode materials have been introduced, it is very important to fabricate highly-flexible electrode materials with reasonable fabrication technique and high electrochemical performance similar to those of conventional high-capacity electrode materials. Herein, we introduced high-capacity, flexible Si/SiO₂/C nanofiber composite anode materials by simple electrospinning and subsequent heat treatment processes. To further improve the long-term cycling performance, additional nanoscale carbon coating of flexible Si/SiO₂/C nanofibers was performed by CVD technique. Electrochemical performance results showed that CVD carbon-coated flexible Si/SiO₂/C nanofiber composites exhibited high capacity retention of 86.7% and high coulombic efficiency of 96.7% at the 50th cycle. It is, therefore, demonstrated that CVD carbon-coated flexible Si/SiO₂/C nanofiber composites are promising anode material candidate for next-generation flexible and high-energy lithium–ion batteries.

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1. Introduction

With recent improvements in technologies of portable and bendable electronic equipment such as rollup displays, implantable medical devices, active radio-frequency identification tags, and wearable devices, flexible battery technologies become critically important to meet their energy requirements [1–3]. Flexible batteries are not only crucial for portable devices, but also an important power source for future electric and hybrid electric vehicles [4]. Although different types of flexible batteries have been introduced, it is very important to fabricate highly-flexible energy storage devices with high mechanical strength and reasonable electrochemical performance similar to those of conventional energy storage devices [5–7]. Compared to other existing battery technologies, lithium–ion battery is considered as one of the most preferred rechargeable batteries in recent years because of its superior properties, including high energy density, durable cycle life and good power performance. The development

of flexible, high-capacity electrode materials for high-energy lithium–ion batteries is crucial for technological improvements on portable electronics due to their advantages such as high mechanical strength, long cycle life, and high energy density [8,9]. Most of the current commercial lithium–ion batteries use graphitic materials in the anode. However, graphitic anode materials cannot meet the ever-growing capacity requirements of future portable electronics because of their low specific capacity of 372 mAh g⁻¹ [10–12]. Lithium storage capacities of alloy-type anodes, such as silicon (Si), tin, germanium, and their oxides etc., are much higher than those of commercially-used intercalation-type graphite anodes. Among all alloy-type anodes, Si gives the highest theoretical capacity of 4200 mAh g⁻¹, making it the most promising candidate for next-generation high-energy lithium–ion batteries [13,14]. However, similar to other alloy-type anode materials, the insertion of lithium ions into Si during cycling causes high volumetric change (up to 400%), which results in intense pulverization of active Si material and significant loss of electrical contact between Si and carbon conductor [15–17]. These drawbacks bring together the severe capacity fading of Si-based anodes during repetitive lithiation and de-lithiation processes [18]. Reducing the size of Si into the nanoscale range and dispersing

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it into carbon structures are some of the proposed effective methods for alleviating the volumetric change problem of Si-based anodes. Nano-sized Si/carbon (Si/C) composite anodes can potentially combine the advantageous properties of Si (high capacity) and carbon (excellent electronic conductivity and structural stability) [19,20].

Most of the reported Si/C composite anodes are not suitable for direct use in flexible lithium-ion batteries without adding electronically inactive materials such as polymer binder, conducting agent, and copper current collector [17]. The addition of these inactive materials considerably reduces the overall energy density of the battery. On the other hand, in a binder-free electrode design, the entire electrode structure is composed of electrochemically active materials, leading to higher useful electrode capacity. In this study, we report a novel binder-free, free-standing, and flexible silicon/silica/carbon (Si/SiO₂/C) nanofiber composite anode for lithium-ion batteries by the electrospinning and carbonization of a solution composed of Si nanoparticles, sol-gel tetraethyl orthosilicate (TEOS) solution, and polyacrylonitrile (PAN) polymer in *N,N*-dimethylformamide as the solvent. PAN can be converted to the carbon nanofiber matrix during carbonization while TEOS is the starting material for making SiO₂ structure [18,21]. To improve the interfacial stability and cycling performance, the resultant Si/SiO₂/C nanofibers can be coated with an amorphous carbon layer by the chemical vapor deposition (CVD) technique. These CVD carbon-coated flexible Si/SiO₂/C nanofiber composite anodes are expected to have excellent overall performance including high capacity, good cycling stability, and high coulombic efficiency because nanoscale CVD carbon coating enhances the carbon confinement of Si nanoparticles exposed on nanofiber surfaces and supports more stable SEI formation by preventing direct contact of the electrolyte with the active Si material.

2. Experimental

2.1. Nanofiber preparation

Tetraethyl orthosilicate (TEOS, 99%), polyacrylonitrile (PAN, $M_w = 150,000$ g/mol), and *N,N*-dimethylformamide (DMF), hydrochloric acid (HCl, 37%) were purchased from Sigma-Aldrich. Si nanoparticles (diameter: 30–50 nm) were purchased from Nanostructures & Amorphous Materials, Incorporated. All chemicals were used without further purification.

PAN solution (10%) in DMF was prepared at 60 °C and mechanically stirred for 24 h. TEOS solution (20%) was prepared by dissolving TEOS in DMF, followed by adding HCl (37%). In this solution, TEOS was used as silica precursor while HCl was added to catalyze the sol-gel transition process. During that process, sol-gel

silica solution was formed by hydrolysis and condensation reactions between TEOS, solvent DMF and catalyst HCl [21,22]. Because of the precipitation of PAN in ethanol, TEOS solution was prepared with DMF instead of using ethanol, since DMF was already reported as an effective solvent to stimulate the polymerization rate during sol-gel process [23]. The TEOS solution was stirred at room temperature for 3 h and was then gradually added to the PAN solution, followed by stirring for additional 3 h. The molar ratio of the components in the mixed TEOS/PAN solution was TEOS: PAN: DMF: HCl = 1:0.00275:62.14:0.04. Si nanoparticles (20 wt.% with respect to PAN) were added into the as-prepared TEOS/PAN solution and stirred at room temperature for 24 h, followed by ultrasonic treatment for 1 h to obtain a homogenous dispersion. The as-prepared Si/SiO₂/PAN dispersion was then electrospun into nanofibers with a flow rate of 0.75 ml/h, a voltage of 16 kV, and a tip-to-collector distance of 25 cm.

Electrospun Si/SiO₂/PAN nanofibers were stabilized in air environment at 280 °C for 5.5 h with a heating rate of 5 °C min⁻¹ and then carbonized at 700 °C for 2 h in argon atmosphere with a heating rate of 2 °C min⁻¹, during which PAN was pyrolyzed to carbon. The resultant Si/SiO₂/C nanofiber composite was coated with amorphous carbon by the CVD method using acetylene (C₂H₂) as the carbon precursor gas. CVD carbon coating was applied at 700 °C for 1 h with 600 sccm flow rate of acetylene while the system was settled at 20 torr. Fig. 1 illustrates schematically the entire nanofiber fabrication approach.

For comparison, flexible SiO₂/C nanofibers and inflexible Si/C nanofibers were also prepared from TEOS/PAN/DMF solution and Si/PAN/DMF solution, respectively, using the same electrospinning and thermal treatment procedures.

2.2. Structure characterization

The morphology of composite nanofibers was examined by field emission scanning electron microscope (FE-SEM, JEOL 6400F) and transmission electron microscope (TEM, JEOL JEM-2000FX). The structure of composite nanofibers was investigated by Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 470) and wide angle X-ray diffraction (WAXD, Rigaku Smartlab). Compositions of the flexible nanofiber composites were examined by TGA (Perkin-Elmer Pyris 1) and elemental analysis (Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer).

2.3. Mechanical testing

For mechanical property characterization, both tensile and compressive tests were conducted. Tensile testing was operated by using a MTS-30G load frame at a crosshead speed of 2 mm min⁻¹ and the gage length was 10 mm. For each sample, 5 specimens

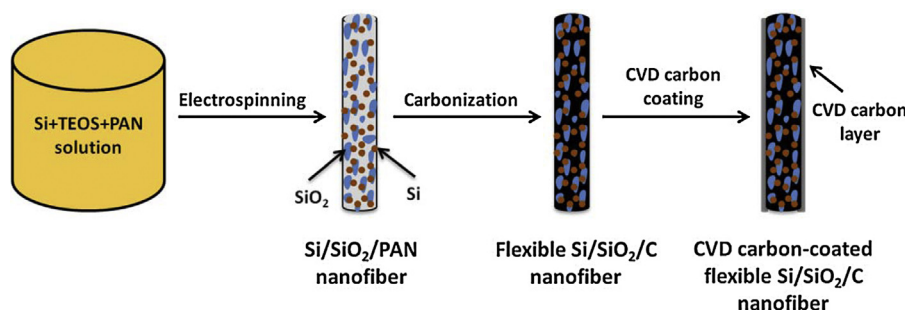


Fig. 1. Schematic illustration of the fabrication process of flexible Si/SiO₂/PAN nanofibers, flexible Si/SiO₂/C nanofibers, and CVD carbon-coated flexible Si/SiO₂/C nanofibers.

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