



Improving microstructure of silicon/carbon nanofiber composites as a Li battery anode

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HIGHLIGHTS

- ▶ We report an interfacial study of a silicon/carbon nanofiber (Si/CNF) anode for Li-ion batteries.
- ▶ Amorphous Si layers were uniformly coated on both the exterior and interior walls of the hollow CNF.
- ▶ After cycling, more Si had fallen off from the outer wall than from the inner wall of CNF.
- ▶ Computer modeling suggests a higher interfacial strength at the Si/C interface at the inner wall.
- ▶ We proposed several interfacial engineering approaches to optimize the microstructure.

ARTICLE INFO

Article history:

Received 6 March 2012

Received in revised form

12 July 2012

Accepted 10 August 2012

Available online 21 August 2012

Keywords:

Silicon–carbon composite

Nanomaterial

Anode

Lithium-ion batteries

ABSTRACT

We report the interfacial study of a silicon/carbon nanofiber (Si/CNF) nanocomposite material as a potentially high performance anode for rechargeable lithium ion batteries. The carbon nanofiber is hollow, with a graphitic interior and turbostratic exterior. Amorphous silicon layers were uniformly coated via chemical vapor deposition on both the exterior and interior surfaces of the CNF. The resulting Si/CNF composites were tested as anodes for Li ion batteries and exhibited capacities near 800 mAh g⁻¹ for 100 cycles. After cycling, we found that more Si had fallen off from the outer wall than from the inner wall of CNF. Theoretical calculations confirmed that this is due to a higher interfacial strength at the Si/C-edge interface at the inner wall than that of the Si/C-basal interface at the outer wall. Based upon the experimental analysis and theoretical calculation, we have proposed several interfacial engineering approaches to improve the performance of the electrodes by optimizing the microstructure of this nanocomposite.

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1. Introduction

Carbon materials, usually in the form of graphite, are commonly used as the negative electrodes in secondary lithium ion batteries owing to their high cycle life and low cost. However, carbon negative electrodes have a theoretical capacity of 372 mAh g⁻¹, a typical practical energy capacity of ~300 mAh g⁻¹ [1]. To boost the capacity of negative electrodes to meet the goals of the automotive industry for lithium ion batteries, researchers are investigating materials, which form alloys with lithium to generate

negative electrodes that have specific capacities an order of magnitude higher than graphite. Silicon is an attractive negative electrode material for Li-ion batteries mainly because it has a very high theoretical charge capacity exceeding 3500 mAh g⁻¹ [1]. However, the use of crystalline silicon as negative electrodes has been limited because silicon goes through large volume change and becomes amorphous after the first charge/discharge cycles. Recent work by Liu et al. [1] shows that pure silicon does collapse upon de-intercalation of lithium ions; this rapid volume change induces mechanical stress and fracturing (pulverization) of the Si particles, resulting in loss of electrical connection to the negative electrode structure and capacity fade.

In order to overcome these technical barriers, researchers have tried several approaches to combine the advantage of silicon's high capacity with carbon's high electrical conductivity and mechanical

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strength. These approaches include: (1) producing nano-sized Si negative electrodes, either in particulate [2,3] or aligned nanowire form [5,6]; (2) making silicon/carbon composites in particulate form [3–7]; (3) coating tubular-forms of carbon with silicon [8–10,12]; and (4) putting a carbon coating on silicon nanowires [11]. These research efforts demonstrated that nanoscale silicon/carbon composites are able to accommodate larger strains than the bulk silicon and thus reduce the extent of pulverization, provide good electronic contact and conduction, and display short lithium insertion distances.

A structurally superior design would be to develop silicon-coated hollow carbon nanofibers as the negative electrode material for Li-ion batteries. The attractive properties of catalytically grown carbon nanofibers (CNF) have been known for decades [13,14]. They can be mass-produced inexpensively, have excellent mechanical strength, and high thermal and electrical conductivity [15]. The CNF produced by Applied Sciences Inc. (Cedarville, OH) has a water hose-like morphology. About 30–100 μm in length, it has an outer diameter of 100–200 nm and a hollow core typically about 1/3–1/2 of the total fiber diameter. To make a Si/CNF composite, Applied Sciences Inc. uses chemical vapor deposition of nano-scale coatings of amorphous silicon on both the interior and exterior surfaces of the hollow CNF. Battery tests have shown that capacities about 800 mAh g^{-1} for 100 cycles in half-cell and full cell configuration have been achieved. The Coulombic efficiency of these negative electrodes has been measured to be 99% after SEI formation being stabilized in several cycles. In this paper, we report the failure analysis of the Si/Carbon nanofiber nanocomposite as a negative electrode material after cycling; and further provide pathways for improving the cycling performance based upon the unique microstructures of these Si/CNF composites.

2. Materials and experimental procedures

2.1. Fabrication of Si/CNF nanocomposites

A nanoscale layer of silicon was deposited onto a highly graphitic carbon nanofiber (Pyrograf[®]-III, PR-25-Xt-PS and HHT, Pyrograf Products, Inc., Cedarville, OH) through a chemical vapor deposition process. The source of silicon was a silane gas blended in a non-reactive carrier gas. The silicon was deposited onto a powdered form of carbon nanofiber at elevated temperatures (400–700 $^{\circ}\text{C}$) using either a horizontal bed reactor with a static target or in a fluidized bed reactor. The thickness, crystallinity, and morphology of the silicon are adjustable through alterations in the coating parameters. For this research, the silicon to carbon ratio (by weight) of 1:3 was targeted to provide a specific negative electrode capacity of about 900 mAh g^{-1} .

2.2. Half-cell and full-cell battery tests

Electrodes were produced from a thick slurry paste that contained 80 wt% silicon coated CNF powder as the active material, with 15 wt% PVDF (polyvinylidene fluoride) binder dissolved in NMP (N-Methyl Pyrrolidone) and 5 wt% conductive carbon black. The mass of conductive carbon black was excluded while calculating the capacity. A 20-micron thick coating of the paste was applied to a 10-micron thick copper foil using a doctor blade draw-down technique. The electrodes were pre-dried inside a well-ventilated hood and then transferred to a hot antechamber (110 $^{\circ}\text{C}$) of a dry box and evacuated for at least 4 h. The dry sample was transferred to the inside of the dry box that was filled with argon, with less than 1 ppm of oxygen and moisture. Disks were cut from the coated copper foil and inserted into the coin cells.

Half and full cells were manufactured with the silicon coated carbon nanofibers. The half cells were constructed with the Si–CNF powder as the cathode and lithium metal as the negative electrode. The half cells were cycled from 2.5 V to 0.010 V. Full cells were constructed with the Si–CNF product as the negative electrode and LiCoO_2 as the cathode. Full cells were cycled from 4.3 V to 2.7 V. The performance of the carbon–silicon negative electrode was measured at different C rates ranging from C/15 to 1C. All cells used an electrolyte consisting of a multi-blend solvent (a combination of dimethyl carbonate and ethylene carbonate with a vinylene carbonate additive) containing 1 M LiPF_6 .

2.3. Materials characterization of the Si/CNF composites

The Si/CNF composites were analyzed before and after the coin cell tests using electron microscopy, energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). For the microscopy study, the Si/CNF composite specimens were dispersed onto a lacey carbon film supported on a 200-mesh Cu grid without using any dispersing agent, then analyzed using a Hitachi HF-3300 TEM/STEM equipped with a Thermo Noran Si(Li) EDS detector at 300 kV. The XPS study, with samples mounted on the stainless steel sample carrier using double-sided tape, was carried out by a Thermo Fisher Scientific K-Alpha XPS using monochromatic Al K- α x-rays. Ar-ion sputter profiling was attempted as a way of showing changes in surface chemistry as a function of depth. Profiles were generated by intermittently sputtering the sample surface with 3 kV Ar-ions and then collecting a set of core level data. The Avantage Software package (v. 4.44) was used for all XPS data acquisition and analysis.

3. Results and discussions

3.1. Electrochemical evaluations

Half-cell performance data – Samples of the silicon coated carbon nanofiber were converted into an electrode and countered with lithium metal in a coin cell. The cell was cycled from 2.5 V to 0.010 V at rate of C/2 with no formation cycle performed to intentionally create an SEI layer. Fig. 1 contains the delithiation-capacity, showing that the initial specific capacity of the composite material was 1100 mAh g^{-1} and decayed to 750 mAh g^{-1} after 100 charge/discharge cycles. We attribute the irreversible capacity to the initial breakdown of the Si/CNF composite and the formation of the SEI layer. The Coulombic efficiency was measured to be 99% after SEI formation being stabilized in several cycles. Post cycling analysis of the composite material was performed to

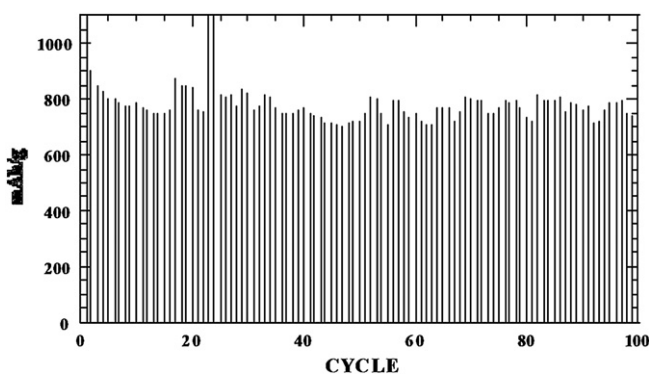


Fig. 1. Specific capacity of silicon coated carbon nanofiber against Li metal in coin cell (Delithiation of the Si/CNF in half-cell configuration).

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