Microstructural Characterization of Silicon/Carbon Nanofiber Composites for Use in Li-ion Batteries

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1. Introduction

This paper describes the microstructure of a Li-ion battery anode made of silicon/carbon nanofiber (CNF) composite at sub-nanometer level, and explains how its unique structure enables high cyclability and high efficiency.

Silicon is an attractive anode material for Li-ion batteries mainly because it has the highest known theoretical charge capacity at 4,200 mAh/g. However, bulk silicon anodes have limited applications because silicon's volume changes about 300% upon insertion and extraction of lithium, which results in pulverization and capacity fading. Recent work shows that nano-sized silicon can largely circumvent these issues as they can accommodate large strain without pulverization, provide good electronic contact and conduction, and display short lithium insertion distances [1]. However, the electrical conductivity of silicon is less than that of carbon. To take advantage of both silicon's high capacity and carbon's high conductivity, efforts have been made to use silicon/carbon composite particles for use as anode material [2]. A structurally more superior design is to develop silicon-coated hollow CNFs as the anode material for Li-ion batteries. Applied Sciences Inc. (ASI) has pioneered development of a high-performance Li-ion battery anode by depositing silicon-based materials onto low-cost CNF. Capacities in excess of 1000 mAh/g for 20 cycles and 500 mAh/g for 50 cycles (half-cell configuration) and near 1000 mAh/g (full cell configuration) have been achieved. The retention efficiency of these anodes has been measured in excess of 99.5% efficiency.

The performance of the anodic application of this Si/CNF composite is dictated by its microstructure, from the atomic-level and up. Of great interest is to find out 1) the crystallinity of the silicon, whether it is crystalline or amorphous; 2) size and distribution of silicon and the nature of the Si/C interface; and 3) if there is any oxygen present in the Si-layer.

2. Experimental procedures

A nanoscale layer of silicon was deposited onto a highly graphitic carbon nanofiber (Pyrograf-III, PR-25, Pyrograf Products, Inc.) through a chemical vapor deposition process. The source of silicon was silane gas (Custom Gas Solutions, LLC) blended in a non-reactive carrier gas. The silicon was deposited onto a powdered form of carbon nanofiber at elevated temperatures using either a horizontal bed reactor with a static target or in a fluidized reactor. The thickness, crystallinity, and morphology of the silicon are adjustable by controlling the deposition parameters [3].

The Si/CNF composites were analyzed 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 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-kα x-rays. Ar-ion sputter profiling was attempted as a way of showing changes in surface chemistry as a function of depth. The Avantage Software package (v. 4.44) was used for all data acquisition and analysis.

3. Understanding the Microstructure through Electron Microscopy and XPS Analysis

Electron microscopy was used in conjunction with energy dispersion spectroscopy to characterize the interface between the carbon nanofiber and the deposited silicon. Surface information of the composites was analyzed using XPS. The TEM bright field (BF) signals contain information of crystallinity (phase) and mass-thickness contrast. The Z-contrast (ZC) image, collected using a high-angle annular dark field detector, has a contrast proportionally to Z^2 (atomic number). Secondary electron micrographs (SEM) reveal topographical and morphological information. The Hitachi HF-3300 TEM/STEM is one of very few TEMs equipped with a scanning system for the detection of secondary electrons, enabling high-resolution micrographs to be recorded in BF, ZC, and SE modes from the same region of interest. The combination of the three electron signals allow a more complete understanding of the microstructures of the composites.

The as-produced CNF nanofibers are hollow with an outer diameter of 80-180 nm and an inner diameter of 20-65 nm. By adjusting the deposition parameters, silicon may form a complete or incomplete coating of both internal and external surfaces of the CNFs. In Fig.1, the SEM reveals an incomplete coverage as sub-20nm silicon nodules decorated the surfaces.
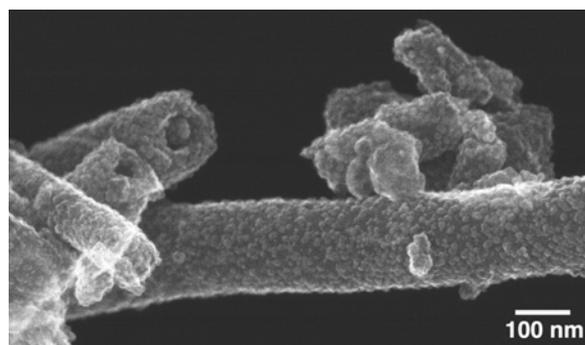

Fig. 1 An SEM image of the silicon/CNF composite showing the Si nodules on the surface of CNFs.

In Fig. 2, silicon forms complete layers on the external and internal surfaces. The presence of silicon on the inner surface of hollow CNF was clearly revealed in the Z-contrast image of Fig. 2b, as the high-Z silicon was bright. Chemical composition of the Si/CNF was obtained from the EDS line scan across the fiber. The profile in Fig. 2d showed a Si-rich outer surface which does not contain carbon, suggesting the presence of a continuous *pure* silicon outer layer. The regions corresponding to the inner surface also has a high concentration of Si. In order to positively identify the presence of pure inner Si layer, we compared the structural features of the outer and inner layers in the high-resolution BF image (Fig. 3): both are amorphous and bear similar features. The EDS line scan shows oxygen to be near or below the detection limit. From both EDS line scan profiles and ZC or BF images, we can measure the thickness of the silicon layers. In Fig. 2, the inner layer is about 15 nm and an outer layer about 10nm. The SEM image revealed the granular nature of the silicon coating. It was further confirmed by the XPS analysis that oxygen was mainly adsorbed onto the surfaces of silicon.

We are still in the process of analyzing the Si/CNF after battery cycling to try to understand the relationship of Si size and distribution to the performance of batteries.
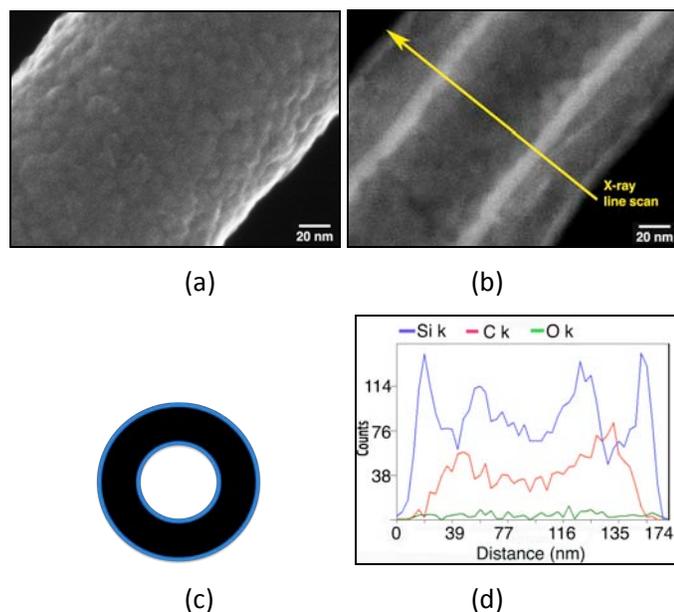
(a)

(b)

(c)

(d)

Fig. 2. Continuous silicon layer over the internal and external surfaces of a CNT: (a) SEM image; (b) Z-contrast image where the silicon coatings are bright; (c) a schematic of the cross-sectional view of a Si/CNF; and (d) the EDS line-scan across the fiber revealing the concentration and distribution of Si, C, and O.
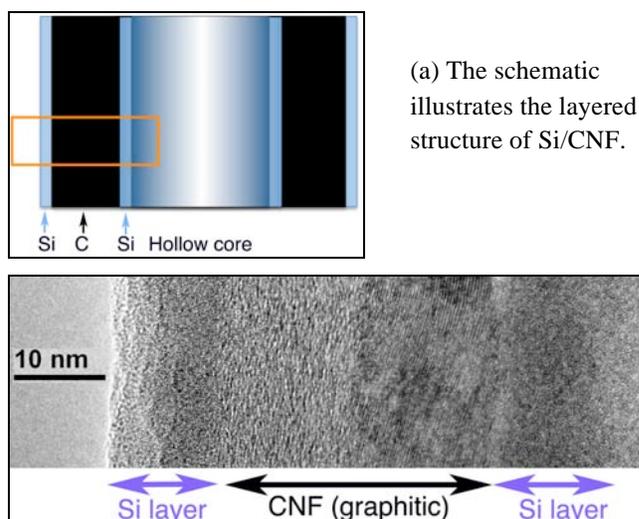
(a) The schematic illustrates the layered structure of Si/CNF.

Fig. 3. Bright-field TEM reveals the amorphous Si on both inner and outer surfaces of CNF of an area as in (a).

4. Conclusions

We found that the Si/CNF composites have amorphous silicon coatings on both internal and external surfaces of the hollow CNFs. Depending on the deposition conditions, silicon may form a complete coverage about 12nm thick, or, it forms sub-20nm nodules that partially cover the surfaces.

The Si/CNF composite described in this paper has many unique features that, we believe, lead to the high cycling performance. First, having silicon coatings on both inner and outer surface of a hollow carbon nanofiber maximizes the efficiency of the Si/CNF composite during cycling. Nano-size channels provide fast mass transport of Li ions whereas the graphite core offers high electric conductivity. The Si/CNF structure contributes to weight reduction. Such structure may also be effective in slowing down the growth of the SEI layer. Second, the process provides a controllable size and distribution of silicon. Finally, the integrity of the anodic material is preserved largely due to the mechanical strength of the carbon nanofiber.

References

[1] Kim H, Seo M, Park M-H, Cho J. A critical size of silicon nano-anodes for lithium rechargeable batteries. Angew. Chem. Int. Ed. 2010; 49,2146-2149.
[2] Jang SM, Miyawaki J, Tsuji M, Mochida I, Yoon SH. The preparation of a novel Si-CNF composite as an effective anodic material for lithium-ion batteries. Carbon 2009;47 (15):3383-3391.
[3] US Patent Application 20080261116, Oct. 23, 2008.