



Silicon thin film anodes coated on micron carbon-fiber current collectors for lithium ion batteries



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ABSTRACT

Si thin films have been sputter deposited on vapor grown carbon-fibers and used as the anode materials for lithium ion batteries. A common issue for the Si anodes is the volume expansion during charge–discharge, leading to severe capacity fading. In this study, micron carbon-fibers (MCFs) are used as the current collectors to ease the volume-change induced stress, and significantly improve the cycling stability. The MCFs were fabricated using thermal chemical vapor deposition on stainless steel substrates. The Si films can be coated on MCFs as characterized by field emission scanning electron microscopy. The electrochemical properties of Si thin film anodes with various Si/MCFs ratios were investigated. The larger quantity of MCFs, the higher specific capacities can be obtained after 200 cycles for a given amount of Si. The cycling stability is enhanced under low Si/MCFs ratios. After 200 charge–discharge cycles, the Si anode deposited on suitable amount of MCFs shows a well rounded surface with very few cracks. The results indicate that the combination of Si anodes and MCFs current collectors can effectively reduce the volume-change induced stress, and enhance the cycling stability.

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1. Introduction

Lithium ion batteries are nowadays the primary power supplies of portable electronic devices [1] because of their high energy density. However, as more and more functions are required in the limited volumes of the portable devices, batteries with higher specific capacities are ever demanded. Therefore, new materials for high capacity lithium ion batteries have been of great interest. Conventional graphite anodes for lithium ion batteries possess a limited capacity less than 400 mAhg⁻¹, and therefore many researches have been focused on searching for alternative high capacity anode materials.

One of the alternative anode materials is Si, which has a theoretical capacity (4200 mAhg⁻¹) nearly 10 times more than that of conventional graphite anodes. Si is not only inexpensive but also abundant in earth's crust [2,3]. However, similar to other alloy-type anode materials, a common issue of Si related electrodes is the volume expansion (>300%) during charge–discharge process by lithium alloying and de-alloying [4], leading to severe capacity fading, poor electrical contact, secondary formation of solid electrolyte interface (SEI) and poor cycle stability [4]. In order to address the above mentioned issues, carbon–silicon composites as the anode materials have attracted considerable attention recently. There are many reported approaches, such as core–shell structured particles [5–8], chemical vapor deposition (CVD) [9–12], and electro-deposition [13,14].

In this study, micron carbon-fibers (MCFs) have been synthesized by thermal chemical vapor deposition (TCVD), followed by radio frequency (RF) magnetron sputter deposition of Si. MCFs provide conductive and three-dimensional current collectors for Si thin film anodes. These three-dimensional carbon–silicon structures have been found to be able to buffer the stress, while maintaining the electrochemical activity of Si. Using this simple method, we have demonstrated a Si/MCFs anode with high cycling stability, high specific capacity and no any binder additives.

2. Experimental

MCFs were directly synthesized on 304 stainless steel (SS) substrates (1.33 cm²) using TCVD. The SS substrates were pre-annealed with a heating rate of 14 °C/min, and kept at 850 °C for 30 min. The furnace was then cooled to 700 °C for MCFs growth. Various weights of MCFs were obtained by depositing under different acetylene flow rates of 10–50 sccm and constant hydrogen flow rate of 100 sccm. After TCVD process, the specimens were transferred to a sputter chamber, and Si was deposited on the synthesized MCFs by RF magnetron sputtering under 99.99% pure argon with constant pressure of 1 × 10⁻² Torr and gas flow of 15 sccm. The schematic representation of the Si/MCFs electrodes with three-dimensional structures after the TCVD and sputtering steps is shown in Fig. 1. The masses of Si and MCFs were weighed by a Sartorius (Sartorius, ME and SE models) microbalance with an uncertainty of 0.01 mg. Si/MCFs composite samples, with Si to MCFs weight ratios of 0.1, 1, 2 and 7, were prepared and

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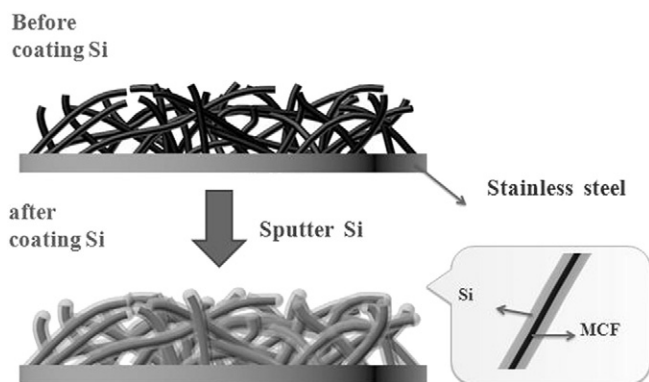


Fig. 1. Schematic representation of Si/MCFs electrode with a three-dimensional structure.

denoted as R0.1, R1, R2, and R7, respectively. Pure Si films and MCFs were also prepared as mass and thickness monitors for comparison. The surface morphologies were observed by a field-emission scanning electron microscope (FE-SEM), and crystal structures of the Si/MCFs electrodes were characterized by X-ray diffraction with Cu K α radiation, with 2-theta degree of 10° to 60° and θ glancing angle of 3°, and the crystalline phases of Li–Si alloy were determined by x'pert highscore plus program (based on JCPDS Cards) equipped in the diffractometer. The interfacial contact resistances (ICR) of the MCFs grown SS sheets and the bare ones were measured by clamping the samples with graphite sheets under 20 psi and collecting the resistance values using Agilent 4338B milliohm meter.

For electrochemical characterization, the Si/MCFs electrodes (as working electrodes) and Li foils (as counter and reference electrodes) were packed in 2032 coin cells with 1 M LiPF₆ in ethylene carbonate and ethyl methyl carbonate mixed solution (volume ratio 1:2) as the electrolyte. All cells were assembled in an Ar-filled glove box (H₂O < 0.1 ppm, O₂ < 0.1 ppm) to avoid environmental influence. The charge–discharge cycles of the cells were carried out on an electrochemical station (Arbin-BT2000, Arbin Instrument Inc) under current densities of 250 μAcm^{-2} , 500 μAcm^{-2} , 750 μAcm^{-2} , 1250 μAcm^{-2}

and 3750 μAcm^{-2} in the potential window of 0.01–1.5 V. To verify the cycling stability, 200 charge–discharge cycles at 750 μAcm^{-2} were tested for each type of cells. The redox reactions of the pure MCFs and Si/MCFs electrodes were analyzed by plotting the differential capacity versus potential using the charge–discharge curves.

3. Result and discussion

The SEM images of MCFs electrodes and Si/MCFs electrodes with R values are shown in Fig. 2. The pure MCFs directly grown on SS substrate are of fiber-like morphology, which can act as three-dimensional current collectors. The spaces in between the fibers also provide more reactive area for the coated Si. It should be noted that the area might change during molding in the cell fabrication process. The MCFs are around 5–20 μm in length and 0.3 μm in diameter. Sputter deposition of Si films on the MCFs can be obtained (R2 and R0.1). For sample R2, the morphology is still composed of fibers, but with much larger diameters of around 3–5 μm due to deposition of Si on the MCFs. With less amount of Si coating (R0.1), the diameters of the fibers are finer than R2 and only slightly greater than pure MCFs. The results show that either thick or thin Si films can be sputter deposited on TCVD grown MCFs. With the increase of R ratios, the deposited Si aggregates into larger grains and still uniformly wraps on the surface of MCFs. Three dimensional Si/MCFs electrodes can therefore be fabricated with different Si loadings.

The differential capacities as a function of potential calculated using the initial two charge–discharge cycles of pure MCFs and Si/MCFs (R0.1) electrodes are shown in Fig. 3. It is clear that the MCFs are of very weak reactivity toward lithium in the given potential window, as no any obvious redox peaks are recorded. By zoning into the details (inserted plot), the MCF electrode shows a very broad reduction peak around 0.75–0.8 V in the first cycle, corresponding to the solid electrolyte interphase (SEI) formation of coke [15]. In the following cycle, the MCFs become completely inactive. It indicates the TCVD grown MCFs are of non-perfect graphite structure similar to coke, which is conductive but has very limiting capacity. Therefore, the MCFs only act as a three dimensional current collector without providing meaningful capacity.

For the Si/MCF electrode, the typical reactions of Si toward lithium are recorded with several sharp reduction peaks at 0.26 V and 0.16 V,

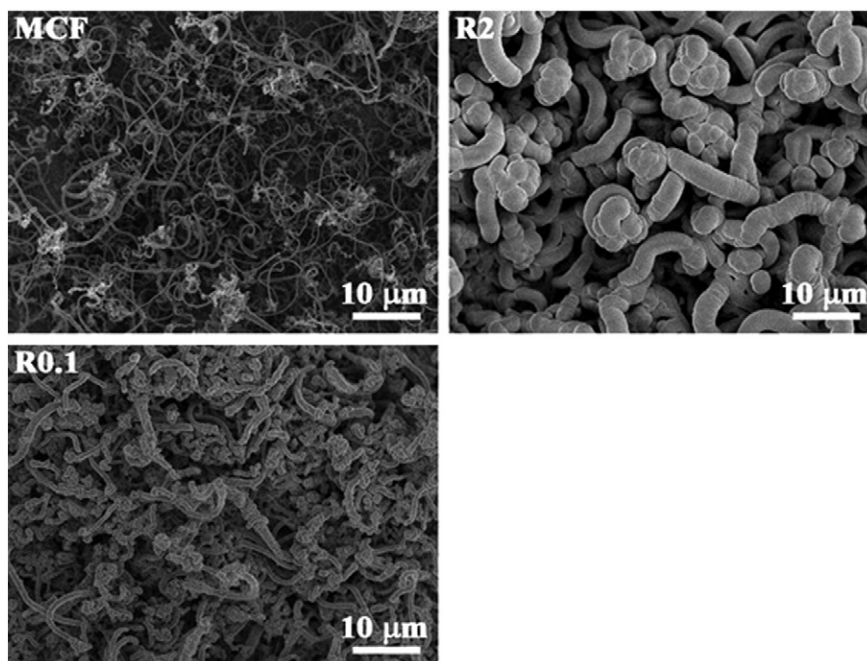


Fig. 2. SEM images of MCFs electrodes and Si/MCFs electrodes with R values.

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