

Core-shell CNT-Ni-Si nanowires as high performance anode material in lithium ion battery

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Abstract

Core-shell carbon nanotube (CNT)-Si heterogeneous nanowires have been identified as one of the most promising candidates for future anode materials in lithium ion batteries. However, stress in these nanostructures, is the long-existing bottleneck, rendering severe fading of the capacities and even failure of the batteries. We prove that the interfaces between CNT cores and Si shells play a critical role in the stress engineering. With rationally engineered interfaces, our core-shell nanowires with CNT-Ni-Si structure are able to offer excellent capacity retention and rate performance. The improvement is attributed to the rough Ni interfacial layer which leads to much more effective strain relaxation, greatly enhanced adherence with the Si shell, and also significantly accelerated charge transport. This core-shell CNT-Ni-Si nanostructure provides a simple but effective pathway towards realization of long lifetime and high performance lithium ion batteries.

1. Introduction

In order to improve the performance of lithium ion batteries for next-generation portable electronics, advanced electrode materials have become the focus of research in this field. Among

a number of candidates, Si turns out to be the most promising anode material owing to its extraordinary high specific capacity of 4200 mAh/g, corresponding to the $\text{Li}_{4.4}\text{Si}$ phase. [1] Unfortunately, conventional bulk-form Si anodes face many preliminary problems, such as unstable solid electrolyte interface (SEI), significant volume change and poor electrical conductivity. Among them, the huge volume change up to 400% during insertion/extraction of lithium may be the most severe. It causes cracks in the material, pulverization of anode, and hence the failure of the battery. Moreover, poor conductivity of Si hinders efficient charge transport, and constrains its rate performance as an anode material. To overcome these drawbacks, nano-structuring is now considered as one of the most important strategies. [2-4] Si nanostructures have already demonstrated significant advantages over their bulk-form counterparts. Through engineering of the Si material into forms of nano films, nanoparticles and nanowires, the capacity retention of Si anodes can be improved without compromising their high capacities.

This strategy begins by direct coating thin Si film onto the flat metal current collectors. [5-7] However, the challenge is to realize high energy densities for practical battery applications. When the Si film is made thicker to enhance material loading, its performance deteriorates quickly as problems associated with bulk-form Si tend to emerge. [8] Nano-sized cores coated with Si shell structures can be considered as a solution for the scale-up of the thin flat film. Firstly, the critical advantage of nanostructured core materials, such as nanospheres, nanowires, nanotubes is their huge surface area/volume ratio. Due to significantly increased surface area, large quantities of Si material can be accommodated, even if the coating thickness on individual nanostructures is maintained at sub-micrometer. As such, the potential towards high energy density for practical application is provided. Furthermore, due to their advantages in electrical,

thermal or mechanical characteristics, core materials are possible to make positive impacts on the battery performance. In addition, core-shell structures rooted on the current collectors are able to provide direct charge transport pathways during charging and discharging. Apparently, the choice of the core materials, the control over their properties, and the interfaces between cores and shells will play decisive roles in the performance of the core-shell anodes. [9]

Among all the core materials under research, carbon nanotubes (CNTs) have been considered as one of the most promising choices, because of their superior electrical, thermal and mechanical properties. [4, 10-16] First of all, CNTs offer effective and efficient routines for electron transport because of their ballistic electrical transport characteristic. [17] Secondly, their exceptionally high thermal conductivity is able to promote thermal dissipating, which is beneficial for long term work safety. [18] Meanwhile, the stiffness and structural stability of CNTs can help to constrain volume change of Si shell during cycling. [19, 20] In addition, as a result of intensive research on the synthesis technologies of CNT since its discovery by Iijima in 1991, [21] parameters of CNT, such as length, diameter and density, are now controllable to meet the requirements of particular applications. For instance, ultra-thick CNTs have been successfully fabricated to anchor large quantities of Si material. [12]

Although core-shell CNT-Si structures have demonstrated outstanding results as anode materials, further improvements are required. Revealed by recent in-situ TEM experiments, [9, 22] small cracks are likely to occur on the Si shell after shrinkage and expansion, which may result in fracture of the shell eventually. In fact, this is a stress-oriented problem, commonly encountered in core-shell Si anodes.[3, 5, 10] Aforementioned, there are several key factors, especially core material and core/shell interface, determining the performance of these core-shell anodes. To

solve the stress problem, current work is more focused on the utilization of different kinds of CNTs as the cores, as well as engineering of the Si shells into various morphologies. However, the core/shell interfaces, which could play critical role in such core-shell nanowires, have rarely been investigated. In fact, the importance of engineering the interfaces has already been demonstrated in traditional thin film Si anodes. In this novel work, we show that the core/shell interface does have significant influence on the performance of core-shell CNT-Si nanowire anodes. Through engineering of the interface by introducing a rough Ni layer in between the CNT core and Si shell, core-shell CNT-Ni-Si anodes with stable capacity retention and excellent rate performance are realized.

2. Experimental

2.1 CNT growth

Round stainless steel (SS) foils with diameters of 1.5 cm were used as the substrates. After sequentially ultrasonic cleaned in acetone, isopropyl alcohol and de-ionized water, the foils were blow-dried by N₂ and baked in oven. The foils were then coated with TiN barrier layer in an Elite sputtering system, followed by electron beam deposition of thin Ni layer as catalyst in an Auto 306, HHV system. CNT growth was carried out in a Nano Instrument plasma enhanced chemical vapor deposition (PECVD) system. The process gases were 240 sccm NH₃ and 60 sccm C₂H₂. Chamber pressure was kept at 9.0 mbar. Temperature were ramped up and kept at 800 °C during growth. A radio frequency (RF) electric field was applied and biased at 700 V in the chamber with a power of 120 W.

2.2 Ni and Si coating

Ni deposition was fulfilled by magnetron sputtering. The deposition rate was calculated to be around 30 nm/minute on flat surface. Si coating was performed in a Cello PECVD system with 50 sccm SiH₄ mixed with 160 sccm N₂ as the precursor. The process temperature was 200°C and the deposition rate was around 60 nm/minute on flat surface. The Ni and Si mass loading were determined by weighing the samples before and immediately after the coating processes using an analytical balance (Mettler Toledo XP 26, 0.002 mg). The mass ratio of Ni and Si was around 1:1.

2.3 Electrochemical characterization

The obtained CNT-Ni-Si nanowires rooted on SS substrates were directly assembled into CR 2032 type half cells without any binders or conductive additives used while pure Li metals were used as the counter electrodes. The assembly was carried out in a glove box filled with pure Ar (Innovative Technology, Inc.). The electrolyte used was LiPF₆ (1.0 M) dissolved in ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume). Charge/discharge capacities were measured by galvanostatic cycling the half cells over the potential range of 0.01-1.2 V vs. Li/Li⁺ in a battery tester (NEWARE BTS-5 V, Neware Technology Co., Ltd.).

2.4 Structure characterization

SEM images were taken in a LEO 1550 Gemini field-emission scanning electron microscope (SEM). Transmission electron microscopy (TEM), high resolution TEM (HRTEM), scanning TEM (STEM) and energy-dispersive X-ray spectroscopy (EDX) mapping were carried out using a Tecnai X-TWIN TEM equipped with an EDAX Si (Li) detector. Raman spectrum was obtained using a WITec Raman system with a laser wavelength $\lambda=532$ nm.

3. Results and discussion

Fig. 1(a) is the SEM image of the obtained CNT array fabricated on a SS current collector using PECVD. Raman characterization shows a typical spectrum of multi-walled CNTs (see Fig. S1). The process parameters have been optimized to tailor the properties CNTs, such as density and inter-wire spacing, to be suitable for battery application. Most of the CNTs exhibit diameters of around 100 to 150 nm and have fairly large inter-wire spacing. Fig. 1(b) is the SEM image of the CNT-Ni-Si core-shell nanowires after magnetron sputtering of Ni and PECVD coating of Si onto the CNTs. Diameters of the nanowires are increased to 200 to 400 nm. Nevertheless, there is still much space kept between the nanowires, which not only helps to accommodate radial expansion of the Si shell, but also offers efficient access of electrolyte to the entire core-shell nanowire array.

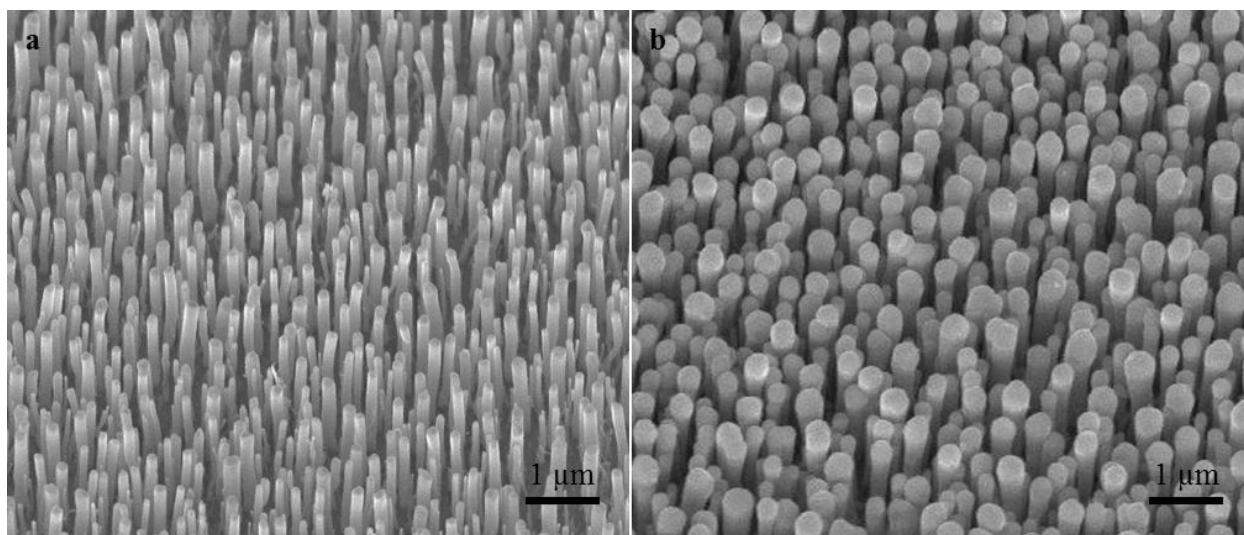


Fig. 1 Tilted angle SEM images of (a) the CNT array and (b) the CNT-Ni-Si nanowire array.

Fig. 2(a) is the TEM image of a randomly selected CNT-Ni-Si nanowire. The tri-layer structure in the nanowire is clearly displayed. The EDX mapping data in Fig. 2(b) affirms the structure

with a tri-layer element distribution of C-Ni-Si. In this PECVD process, CNTs follow a tip-growth mode with wedge-shape catalyst particles wrapped in their tips (Fig. 2(a)). As shown in Fig. S2, the sidewalls of the CNT are constituted by stacked cone-segment shaped graphene sheets which are nearly parallel to the bottom part profile of the catalyst particle.[23, 24] The brightest region in Fig. 2(a) is the Ni layer with a thickness of about 10 to 20 nm. HRTEM image in Fig. 2(c) shows that the Ni layer consists of small particles and its rough morphology is distinctly different from the smooth surface of the underneath CNT (see Fig. S2). The roughness could be caused by the small coating thickness. Moreover, edges of the graphene planes constituting the CNTs may serve as the nucleation centers for Ni atoms, promoting the formation of Ni particles. The outer Si layer is around 40 to 50 nm thick. Under HRTEM, no obvious crystalline structures can be found and the corresponding fast Fourier transform (FFT) pattern shows that the Si layer is amorphous. As the Si shell is coated on the rough Ni layer, it also exhibits a non-continuous morphology with micro valleys spreading all over its surface.

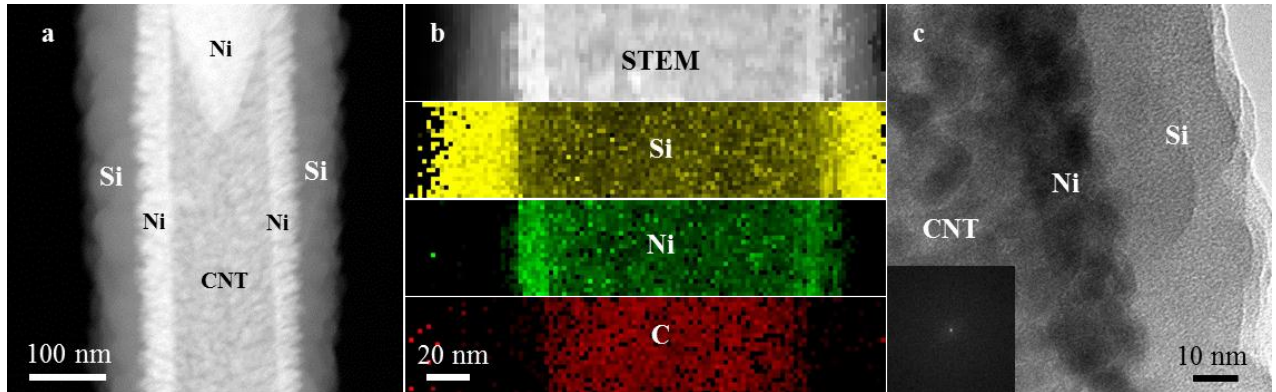


Fig. 2 (a) TEM image of a CNT-Ni-Si core-shell nanowire; (b) STEM image of a portion of the nanowire and the corresponding EDX mapping data of Si, Ni, C, respectively; (c) HRTEM image of the CNT-Ni-Si interface, inset is the corresponding FFT pattern of the Si layer.

To evaluate the electrochemical performance, button-type half cells are assembled with core-shell nanostructures on SS as the working electrodes and lithium foils as the counter electrodes. The capacity retention performance is presented in Fig. 3(a). The testing is carried out over the potential range of 0.01-1.2 V at 0.2 C (1 C equals to 4200 mA/g). Here, all the current rates and capacities are calculated based on the mass of Si. Although CNTs could react with lithium ions, they are covered by electrochemically inactive Ni layers and therefore inaccessible to lithium ions. During galvanostatic cycling, the de-lithiation capacity exhibits an initial value of 2527 mAh/g and then increases slightly at the second cycle, after which the capacity remains quite stable. The initial capacity suppression may be caused by activation of the surface against electrochemical reaction. After 110 cycles, there is still a capacity of 1960 mAh/g, which is 78% of the initial capacity, corresponding to a fading rate of only 0.2% per cycle. Columbic efficiency of the CNT-Ni-Si nanowires during cycling is also presented in Fig. 3(a). After surface activation in the first several cycles, the efficiency maintains at almost 100%, demonstrating good structural stability of the electrodes against lithiation and de-lithiation. Fig. 3(b) is a typical voltage profile in a complete charge/discharge cycle. The voltage profile is consistent with previous studies on Si anodes, showing a sloping charge/discharge behavior. [2] Another important performance of battery is rate output, as shown in Fig. 3(c). Firstly, a charge/discharge current of 0.2 C is applied for 10 cycles to activate the Si material. At the 10th cycle, a de-lithiation capacity of 2508 mAh/g is obtained, consistent with the value in Fig. 3(a). The current is then raised to 0.5, 1, 2, 4, 8 and 12 C and the corresponding de-lithiation capacities are 2115, 1885, 1569, 1308, 1046 and 585 mAh/g, respectively. Eventually, when the current is set back to 0.2 C, the de-lithiation capacity recovers to 2246 mAh/g. The excellent rate performance

suggests that the CNT-Ni-Si tri-layer structure enables fast charge transport and also structural stability even at very high rates.

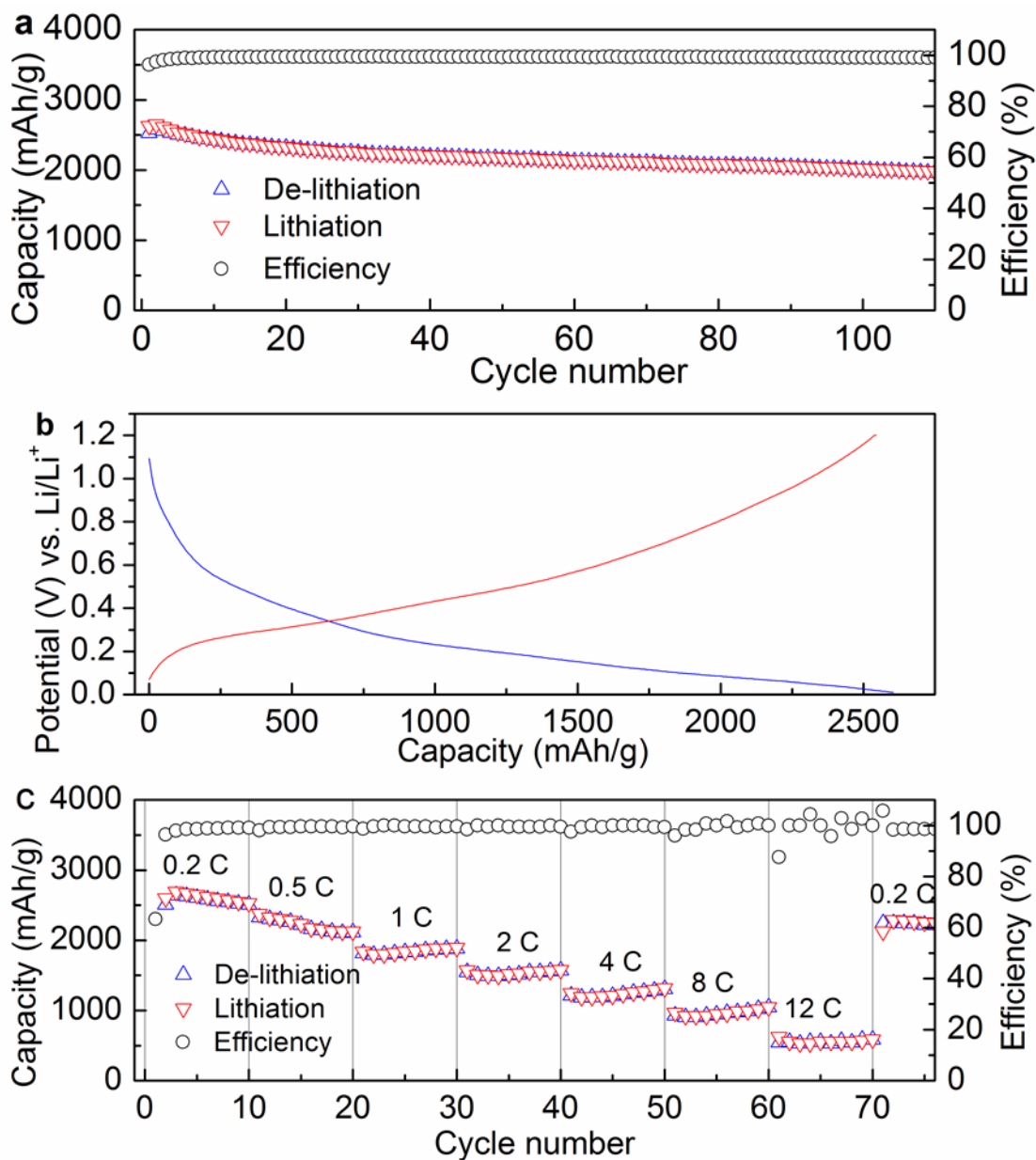


Fig. 3 (a) Specific charge/discharge capacities and Coulombic efficiency of the CNT-Ni-Si core-shell nanowire anode versus cycle number; (b) A typical voltage profile in a full galvanostatic

charge and discharge cycle at the 0.2 C rate; (c) Charge/discharge capacities for different current rates.

It is noted that the CNTs and Si shells used here may not be identical with previous reports. In order to ascertain the influence of the interface, a control experiment has been carried out. In our control samples, CNT-Si nanowires are fabricated and tested, without introduction of the Ni layer, as shown in Fig. S3. In sharp contrast to the CNT-Ni-Si anode which shows excellent capacity retention, the CNT-Si anode only performs stable cycling for 70 cycles, after which the capacity drops very fast, as shown in Fig. S4. As stress can be alleviated by the buffering effect of a rough surface, increasing the surface roughness has proved to be an effective method for prolonged life-time of traditional thin film Si anodes. [8, 25] Similarly, the buffering effect is also introduced by the rough Ni layer in this work. The rough surface of the Ni layer provides more contact area, which is beneficial for anchoring the deposited Si material firmly. Moreover, as Si follows the rough morphology of the underneath Ni layer, valleys are created in the shell, providing space for Si to relieve stress during huge volume change. In core-shell structures, the types of stress include the radial, axial and hoop stress. The axial and radial stress corresponds to in-plane and out-of-plane stress in flat Si films, respectively, while the hoop stress is caused by the curvature of the shell. [10] For a core-shell Si nanowire, the radial stress is less detrimental due to the relatively small shell thickness and sufficient space around the nanowire to accommodate the radial expansion. The axial and hoop stress are mainly responsible for the structural damage of core-shell nanowires. [9, 22] In our CNT-Ni-Si nanowire anode, the hoop stress is possible to be effectively alleviated by the large-diameter CNT cores. [13] With the anchoring effect of the rough Ni layer, and also micro valleys created in the Si shell, both axial

and hoop stress are expected to be further alleviated. As a consequence, this CNT-Ni-Si nanowire anode becomes much more durable against stress.

In addition, benefits of engineering the interface may not be limited in the structural sense. Charge transfer from Si to Ni is probably more efficient, as compared to that from Si directly to CNTs. For interfaces between Si and graphenic carbon materials, such as CNTs and carbon nanowalls, the bonding is usually built through either amorphous carbon [4] or Si carbide, [26] as evidenced by previous reports. Normally, the electrical conductivity of amorphous carbon is relatively low [27, 28] and Si carbide is commonly known as a semiconductor. Therefore, neither of the two could surpass the electrical performance of the Ni-Si interface theoretically. In fact, Ni and Si alloy exhibits the lowest resistivity over all metal-Si alloys. [29, 30] The Ni-Si interface is likely to exhibit a much smaller contact resistance over amorphous carbon or Si carbide and is therefore more beneficial for effective charge transfer during charging and discharging of the battery.

4. Conclusion

We have developed a novel core-shell CNT-Ni-Si nanostructure as a high performance anode material. With the introduction of a Ni layer, the interface between CNT core and Si shell can be effectively improved for minimized stress and enhanced charge transport. Using the CNT-Ni-Si anode, we have demonstrated a high capacity over 2500 mAh/g and a low fading rate of merely 0.2% per cycle over 110 cycles. This work clearly proves the significant role of interface in such core-shell CNT-Si structures. The architecture presented here offers a new idea to optimize the performance of current core-shell CNT-Si anodes under intense research towards high capacity

as well as prolonged life-time lithium ion battery applications. Moreover, this method is not only limited to CNT-Si, but also applicable to other core-shell Si anodes.

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