High performance carbon nanotube–Si core–shell wires with a rationally structured core for lithium ion battery anodes†

Yu Fan, Qing Zhang,* Congxiang Lu, Qizhen Xiao, Xinghui Wang and Beng kang Tay

Core–shell Si nanowires are very promising anode materials. Here, we synthesize vertically aligned carbon nanotubes (CNTs) with relatively large diameters and large inter-wire spacing as core wires and demonstrate a CNT–Si core–shell wire composite as a lithium ion battery (LIB) anode. Owing to the rationally engineered core structure, the composite shows good capacity retention and rate performance. The excellent performance is superior to most core–shell nanowires previously reported.

To meet the energy demands of future portable electronics and hybrid electric vehicles (HEVs), advanced electrode materials with high capacities are desired to produce LIBs with not only high energy density but also high power capability.† Silicon is a very promising candidate for anodes because it exhibits an extremely high theoretical capacity of 4200 mA h g⁻¹ and some other advantages such as abundance and non-toxicity.†,‡ Unfortunately, traditional Si anodes based on bulk or micron-sized Si exhibit very poor capacity retention for several reasons such as huge volume change, unstable solid electrolyte interface (SEI) and poor conductivity. Among them, the significant volume change induced fracture and pulverization have been identified as the major cause of the poor cyclability. In recent years, nanostructuring has proved to be an effective approach to alleviate the volume change problem because nanostructures could more efficiently release the internal stress, in comparison with their bulk or micron-sized counterparts.

Among the various Si nanostuctures/composites such as nanotubes,⁴–⁶ nanospheres,⁷–¹⁰ and nanowires,¹¹ et al.,¹²–¹⁵ core–shell nanowires rooted on current collectors¹⁶–⁰⁰ have attracted much attention because their unique structure offers several distinct benefits such as enhanced energy density due to elimination of binders and effective charge transport owing to the robust core nanowires. Actually, the essential benefit of such a structure is that the core nanowires greatly increase the virtual surface area of the current collector such that a very thick Si film on a conventional flat current collector could be accommodated in such a structure with a very thin Si coating.

However, it should also be noted that a Si thin film deposited on conventional flat current collectors shows much better electrochemical performance than a core–shell composite with the same Si coating thickness. For example, Takamura et al. demonstrated a 50 nm Si thin film on a flat nickel foil current collector that exhibited a high capacity exceeding 2000 mA h g⁻¹ and superior cyclability of over 1000 cycles at a rate of 12 C.²¹ On the other hand, none of the core–shell nanowire composites demonstrated until now could achieve a comparable performance even if their Si coating thickness is smaller. Therefore, it is reasonable to conclude that structures of the core nanowires (alignment, inter-wire distance, wire diameter, etc.) also play very important roles in such core–shell composites. For instance, a Si thin film on a flat current collector is subjected to stresses in both in-plane and perpendicular-to-plane directions, owing to the expansion/contraction of the Si film in the two corresponding directions. In core–shell nanowires, the two stresses correspond to radial and axial stresses. At the same time, curvature of the core nanowires introduces another stress, hoop stress, which is confirmed by recent calculations and in situ transmission electron microscopy (TEM) investigations.¹⁹,²²–²³ Wang et al. even observed crack propagation in a Si shell driven by the hoop stress.²⁴ In this regard, core nanowires with large diameters would be advantageous because of their reduced curvature effect. Another structure parameter that definitely plays a role is the inter-wire spacing. A Si thin film has sufficient space above the surface to accommodate the volume change perpendicular to the plane and for access to the electrolyte. On the other hand, core–shell nanowires with random orientation would inevitably suffer from insufficient space at some locations such as the bottom. Therefore, we believe that vertically aligned core–shell nanowires with a relatively large inter-wire spacing would be advantageous in both volume change accommodation and electrolyte access.
Unfortunately, although many works on core–shell nanowire composites have been demonstrated, most were dedicated to synthesis of new core nanowire materials and very few focused on engineering core nanowire structures. This is not surprising because in most of the works, the core nanowires were fabricated through thermal chemical vapour deposition (CVD) processes that usually produce randomly aligned thin nanowires and have almost no control over nanowire structures other than the length.\textsuperscript{16–19} Here, for our proof of concept, we synthesize vertically aligned carbon nanotubes (CNTs) with large diameters and large inter-wire spacing as the core wires and investigate the electrochemical performance of the CNT–Si core–shell wire arrays as LIB anodes.

The CNTs are synthesized through a plasma enhanced CVD (PECVD) process with a Ni thin film deposited on stainless steel (SS) current collectors as the catalyst. In this process, diameter and inter-wire spacing of the synthesized CNTs could be controlled through the thickness of the Ni catalyst film. The produced CNTs are also straight and vertically aligned due to the existence of a strong electric field. Fig. 1(a) shows a tilted angle scanning electron microscopy (SEM) image of the fabricated CNT core array. It can be seen that the CNTs are vertically aligned with a relatively large inter-wire spacing. Although some CNTs with small diameters can be observed, most CNTs exhibit diameters of \( \sim 150 \text{ nm} \), larger than that of most core nanowires previously reported.\textsuperscript{16–19} The structure of the CNT array presented here is thus distinctly different from that of previously reported core nanowires. Finally, a smooth Si shell is coated on the CNT core wires in a PECVD system to realize a CNT–Si core–shell wire array. Fig. 1(b) shows a top view SEM image of the CNT–Si wire array. After Si coating, the inter-wire spacing is still quite large, which is beneficial for volume change accommodation as well as efficient access of the electrolyte to the bottom of the structure. Fig. 1(c) displays a TEM image of a randomly selected CNT–Si wire, showing a rather smooth Si coating of \( \sim 60 \text{ nm} \) thick. From the TEM image, the diameter ratio of the CNT–Si wire to the CNT core is \( \sim 2 : 1 \). The mass ratio of Si to CNT is calculated to be \( \sim 2 : 1 \) (Si : CNT) (refer to the ESI\textsuperscript{†}). Raman characterization (Fig. S1\textsuperscript{†}) of the composite confirms that the Si coating is mainly amorphous.

To evaluate the electrochemical performance of the CNT–Si composite, button type half-cells are assembled with the CNT–Si wire array directly rooted on SS as the working electrode and lithium foil as the counter electrode. Fig. 2(a) presents the capacity retention performance of the composite over the potential range of 0.01–1.2 V at 0.2 C \( (1 \text{ C} = 4200 \text{ mA g}^{-1}) \). In this demonstration, only the mass of Si is considered to reveal quality of the structure. Although the CNTs are also active against Li\textsuperscript{+}, their contribution is rather small, as demonstrated in the ESI (Fig. S2\textsuperscript{†}). Fig. 2(a) shows that in the first several cycles, charge–discharge capacities of the anode gradually increase. The phenomenon can be attributed to an activation process involving reconstruction and activation of Si and electrode/electrolyte interface, as supported by the cyclic voltammogram (CV) curves shown in Fig. S3.\textsuperscript{†} In the 7\textsuperscript{th} cycle, the anode achieves the maximum de-lithiation capacity of 2755 mA h g\textsuperscript{−1}, after which the capacity remains quite stable. Fig. 2(b)}
shown in Fig. 1(c), the Si shell appears brighter as thick CNTs are robust enough to be free of damage caused by anode shows quite a good cycling performance. Because of this, the composite that the Si shell remains adhered to the CNT core strongly, during the previous lithiation process. However, it is apparent lithiation/de-lithiation.

metallic backbone is found to get bent or distorted during the previous lithiation process. For addition, the Si shell surface is covered by a very rough indicating an increased porosity, which is as expected. In Fig. S4† shows TEM image of a single CNT–Si wire after cycling. Compared to the pristine wire shown in Fig. 1(c), the Si shell appears brighter after cycling, indicating an increased porosity, which is as expected. In addition, the Si shell surface is covered by a very rough film, which is most likely the SEI. It is well known that the SEI formed during the pristine Si surface is not stable and de-lithiation induced significant volume contraction would break the SEI formed during the previous lithiation process. However, it is apparent that the Si shell remains adhered to the CNT core strongly, without noticeable pulverization. Because of this, the composite anode shows quite a good cycling performance.

Several factors could account for the good stability. First, the thick CNTs are robust enough to be free of damage caused by the stress at the CNT–Si interface. In contrast, a very thin metallic backbone is found to get bent or distorted during lithiation/de-lithiation.\(^{19-24}\) Second, the large CNT diameter reduces the hoop stress in the Si shell, resulting in less stress accumulation. Third, the relatively large inter-wire spacing in the vertically aligned CNT–Si array can efficiently accommodate the lithiation/de-lithiation induced volume changes. For comparison, we also fabricated CNTs with smaller diameters and smaller inter-wire spacing as the core by using a thinner Ni catalyst film. Fig. S5a and b† present a SEM image of the fabricated CNT array and a TEM image of a single CNT–Si wire, respectively. The diameter ratio of the CNT–Si wire to the CNT core for this control sample is also ~2 : 1. Fig. S6† shows cycling performance of the thin CNT–Si. After 50 cycles, ~91% of the maximum de-lithiation capacity is retained. On the other hand, the retention rate of the thick CNT–Si is 96.4%, clearly evidencing the superiority of employing core wires with large diameters and large inter-wire spacing. In addition, in situ TEM investigation on lithiation/de-lithiation of a single carbon fiber–Si core–shell wire showed that the adhesion between coated Si and carbon core is very strong.\(^{22}\) Therefore, the Si coating could strongly adhere to the CNT core even if cracks have developed in the Si coating. We notice that previously vertically aligned Cu rods with a relatively large diameter have been fabricated through electro-deposition with anodic alumina membranes (AAO) as the template and investigated as core wires,\(^{16}\) but capacity retention of such Cu–Si core–shell composites is not so good as our CNT–Si composite. The inferior adhesion between Cu and Si, compared with that of carbon and Si, is probably an important reason.

Actually, the cycling performance of our CNT–Si composite could be further improved through either lithiation voltage control or surface passivating coating. It has been demonstrated in many works that by setting a relatively high lithiation voltage of above 50 mV to limit the amount of Li\(^{+}\) intercalated and therefore, suppress the volume changes, significantly improved cycling performance could be achieved.\(^{19,20}\) But in that case, the capacity of Si would be compromised a lot. Another effective approach is to apply a surface coating such as carbon to passivate the unstable SEI on the Si surface.\(^{17,25,26}\) The method has been intensively investigated and therefore is not demonstrated here. Even though, owing to the good core structure, the CNT–Si composite in this work still shows a very good cycling performance that is better than most of core–shell composites including those with surface coatings demonstrated before.

Fig. 2 (a) Variation of charge–discharge capacities of the CNT–Si anode versus cycle number and (b) typical charge–discharge voltage profiles of the CNT–Si anode.

Fig. 3 SEM image of the CNT–Si anode in the de-lithiated state after 50 galvanostatic cycles at 0.2 C.
Another output parameter that is of significance, especially for future LIBs in HEV applications, is rate performance. Fig. 4 presents the rate performance of the CNT–Si wire composite. In the first 10 cycles, a relatively low charge–discharge rate of 0.2 C is applied to activate the materials. At the 10th cycle, a de-lithiation capacity of ~2670 mA h g⁻¹ is retained, consistent with the value in Fig. 2(a). After that, the rate is gradually increased to 0.5, 1, 2, 4, 8 and 12 C, and the de-lithiation capacities at the corresponding rates are ~2280, 2010, 1730, 1480, 1170 and 985 mA h g⁻¹, respectively. Finally, when the current is reverted to 0.2 C, the de-lithiation capacity recovers to over 2500 mA h g⁻¹. The remarkable rate performance suggests that the CNT–Si composite is able to facilitate fast charge transport and maintain structural stability at very high rates.

The rate performance demonstrated here is superior to most core–shell nanowires previously reported. We believe that the superiority could be attributed to the relatively large inter-wire spacing in our core–shell structure. Consequently, the whole Si coating including that at the bottom of the array can gain sufficient access to the electrolyte, effectively alleviating the concentration polarization problem at high charge–discharge rates. In addition, the previous in situ TEM investigation showed that due to the fast diffusion of Li⁺ in carbonaceous materials, lithiation in such carbon–Si core–shell nanowires occurs from both the Si shell surface and the carbon–Si interface, which eventually depletes the Si in the middle of the shell. In other words, the carbon–Si interface could serve as a fast Li⁺ transport channel and could be another reason of the good rate performance of our CNT–Si anode. This feature indicates that a carbonaceous core is perhaps more advantageous in fast charge transport than electrochemically inert core materials such as Cu.

In conclusion, we have demonstrated a CNT–Si core–shell wire composite that employs vertically aligned CNTs with a large diameter and large inter-wire spacing as the core to alleviate the shortcomings of previously reported core–shell nanowires. Owing to the rationally engineered core structure, the CNT–Si wire demonstrates good capacity retention and rate performance, much superior to most core–shell nanowires in previous reports, strongly verifying the important role the core structure plays in such core–shell composites.

Acknowledgements

This work is supported by MOE AcRF Tier2 Funding, Singapore (MOE2011-T2-1-137).

Notes and references