Journal of Materials Chemistry A



View Article Online

View Journal | View Issue

PAPER



Cite this: J. Mater. Chem. A, 2014, 2, 13859

Received 5th May 2014 Accepted 13th June 2014 DOI: 10.1039/c4ta02246g www.rsc.org/MaterialsA

Introduction

There is currently a strong demand for developing lithium-ion batteries with high energy capacity, high power density as well as excellent cycling performance for next-generation electrical vehicles.^{1–3} Silicon is one of the most promising candidates as an anode material for advanced lithium-ion batteries owing to its abundance in nature, moderate Li-uptake potential, and the especially attractive highest theoretical capacity (4200 mA h g⁻¹, corresponding to Li₂₂Si₅) which is 10 times higher than that of commercial graphite. However, the practical application of silicon is hindered by its low intrinsic electric conductivity and large volume change (up to 400%) during Li⁺ ion insertion/

Synergistically reinforced lithium storage performance of *in situ* chemically grown silicon@silicon oxide core-shell nanowires on three-dimensional conductive graphitic scaffolds[†]

Chengxin Peng,^b Huixin Chen,^a Qiongyu Li,^c Weiwei Cai,^c Qin Yao,^b Qingsheng Wu,^b Jinhu Yang^{*b} and Yong Yang^{*a}

The silicon material is the most promising candidate for developing new-generation lithium-ion batteries with high energy and power output. However, there remains a significant challenge due to poor electrical conductivity and pulverization of the silicon based anode during cycles. Aiming to solve these problems, in this work we fabricate a novel 3D composite architecture made of a Si@SiO_x core-shell nanowire array grown on a 3D graphitic foam (Si CNW-3D GF) substrate by a well-designed multiple-step approach. The prepared Si CNW-3D GF composite shows the integrated advantages for high-performance lithium ion batteries, including its light weight, open macroporosity, high conductivity, high Si NW loading, excellent flexibility as well as SiO_x buffer layers. As a result, the Si CNW-3D GF composite exhibits excellent performance such as high reversible lithium storage capacity (3603 mA h g⁻¹ at a current density of 840 mA g⁻¹), excellent cycling performance (up to 100 cycles) and superior rate capability (2299 mA h g⁻¹ at 4200 mA g⁻¹ and 1206 mA h g⁻¹ at 8400 mA g⁻¹), which is 2 times that of the Si CNW electrode where Si CNWs were grown directly on a stainless steel current collector without the presence of 3D GF.

extraction, which causes poor charge transport and even the electrode pulverization and thus deteriorates the overall performance of the batteries.⁴

Many strategies have been pursued to circumvent the problems of silicon as a practical anode material. One main way is to reduce silicon materials down to nanoscale with rationally designed structures, in order to accommodate the volume change and stress relaxation. So far, a series of nanostructured silicon materials including nanoparticles,5 hollow spheres,67 nanowires (NWs),8-14 nanotubes,15,16 and three-dimensional porous particles17-19 have been reported with improved electrochemical performance over bulk silicon materials. Among these, 1D crystalline Si NWs grown directly on stainless steel current collectors have attracted special attention.8 Because each Si NW is electrically connected to the current collector, all the Si NWs can contribute to the capacity of the batteries. Moreover, Si NW arrays provide open space that allows rapid diffusion of Li ions and electrolytes and accommodates the volume change of the electrode, which may benefit the rate capability as well as cycling stability of the batteries. Another effective approach is to employ various types of carbonaceous materials as soft matrices²⁰⁻²⁷ or conductive coating layers²⁸⁻³³ for silicon to buffer the volume changes and simultaneously improve the electrical conductivity of the electrode. As a unique class, three dimensional (3D) nanostructured carbon materials

^aState Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Department of Chemistry, Xiamen University, Xiamen, Fujian 361005, PR China

^bDepartment of Chemistry, Institute for Biomedical Engineering & Nano Science, Tongji University, Shanghai 200092, PR China. E-mail: yangjinhu2010@gmail.com

^cDepartment of Physics, Fujian Key Laboratory of Semiconductor Materials and Application, Xiamen University, Xiamen 361005, PR China

[†] Electronic supplementary information (ESI) available: SEM images of Ni foam with/without a graphitic wall (Fig. S1), Si CNW arrays on the SS304 substrate (Fig. S3) and Si CNWs after 100 cycles (Fig. S6), EDX panel of Si CNW/3D GF (Fig. S2), cycling performance of the 3D GF electrode based lithium-ion battery (Fig. S4), schematics of the battery mechanism (Fig. S7) and impedance parameters (Tables S1 and S2). See DOI: 10.1039/c4ta02246g

such as reduced graphene oxide aerogel^{21,22} and carbon nanotube arrays^{25,26} have shown remarkable performance as anode materials of the silicon-based lithium ion battery. It is noteworthy that 3D graphitic foam (GF), as a newly emerging deformable porous network offering good conductivity and excellent mechanical properties, has been proven to be an efficient scaffold supporting metal oxides (NiO,³⁴ Co₃O₄,³⁵ MnO_2 ,^{36,37} Fe₃O₄,³⁸ SiO₂,^{39,40} RuO₂,⁴¹ *etc.*) for high-efficiency energy storage. Therefore, it is of great interest to integrate the Si NWs and 3D GF into one system with combined multifunction for advanced lithium ion batteries. However, under stringent synthetic conditions, the preparation of the Si NW array on a 3D GF matrix with controlled structure and composition, and especially high performance, remains a big challenge and has not been realized so far.

On the other hand, it is reported that a thin Si oxide layer coated on Si particles^{13,44} can balance the stress of the Si electrode resulting from the lithiation and delithiation, and is responsible for a stable and high reversible lithium storage capacity. Inspired by the points addressed above, in this paper we report a novel 3D composite structure of the Si@SiOx coreshell NW (Si CNW) array grown on 3D GF via a multiple-step approach and investigate its augmented lithium storage performance as an anode. As shown in Fig. 1A, thin graphitic wall coated Ni foam was first formed by a chemical vapor deposition (CVD) method using CH₄ as a carbon source. Then the Ni foam template was removed in a FeCl₃-HCl mixture solution to form the 3D GF with hollow skeletons. Subsequently, the 3D GF was served as a scaffold for the catalytic growth of Si CNWs via a vapor-liquid-solid (VLS) approach coupling with an in situ oxidization process, leading to a freestanding Si CNW-GF composite with a high Si mass load (50 wt%). It is noted that the complete removal of the Ni foam template is critical for the successful preparation of the Si NWs, otherwise only Ni-Si alloy nanowires are preferentially formed instead. The real samples of the Ni foam precursor and the freestanding 3D GF and Si CNW-3D GF composite are shown in Fig. 1B, respectively. The as-synthesized Si CNW-3D GF

composite combining the advantages of the 3D GF and Si CNWs is a promising anode material for lithium batteries in theory: (i) open interconnected macropores to facilitate Li⁺ ion diffusion, (ii) 3D electrode to shorten the Li⁺ ion diffusion length, (iii) high surface area with highly loaded active Si NWs to accommodate Li⁺ ion insertion, (iv) integrated conductive networks to promote charge transport, (v) higher compatibility of the Si-GF-M (M: metal current collector) contact than the Si-M contact, and especially, (vi) the flexible scaffold as well as the SiO_r layer to buffer the volumetric expansion/shrinkage of the Si NWs during lithium-ion insertion/extraction, all of which are beneficial for the battery with improved capacity, rate capability and cycling stability. As expected, the Si CNW-3D GF based batteries exhibit high lithium storage capacity (3603 mA h g^{-1} at a current density of 840 mA g^{-1}) and high rate capability (2299 mA h g^{-1} at 4200 mA g^{-1} and 1206 mA h g^{-1} at 8400 mA g^{-1}), which are almost twice as high as that of the Si CNW based batteries.

Experimental section

Pretreatment of the Ni foam precursor

The rough Ni foam samples (Changsha Lyrun New Material Co. Ltd., China, ~ 1800 g m⁻² foam density, ~ 5 mm thickness) were cut into circular pieces with a diameter of 10 mm, treated with acetone, 2 M hydrochloric acid solution and deionic water in turn to remove the grease and oxides on the surface, and finally dried in vacuum boxes for further use.

Preparation of 3D GF

3D GF was prepared by the CVD method with some modification using the pretreated Ni foam as the template and CH_4 as the carbon source. The Ni foam was firstly placed in the center of a quartz tube furnace. The tube was pumped down to vacuum, filled with a gas mixture of Ar (40 sccm, 99.999%) and H₂ (10 sccm, 99.999%), heated rapidly to 1050 °C and held for 30 min to completely reduce the oxide layer on the Ni foam. Subsequently, the Ni foam was exposed to the mixed gas flow of



Fig. 1 (A) Schematic illustration shows the development of Si CNW–3D GF electrodes. (B) Photographs show real samples of Ni foam (grey), 3D GF (black), and Si CNW–3D GF (blown).

Ar (40 sccm, 99.999%), H_2 (5 sccm, 99.999%) and CH_4 (5 sccm, 99.999%) for 60 min and cooled down to room temperature at a rate of 10 °C min⁻¹. Then, the as-synthesized graphitic wall coated Ni foam was immersed into 1 M FeCl₃–1 M HCl aqueous solution at 80 °C for 24 h to remove the Ni foam template. The produced GF was washed with water, rinsed with isopropanol and dried at 50 °C under ambient conditions for 12 h. Before use, the 3D GF was heated at 600 °C with a protective Ar gas for 6 h to remove the residual moisture.

Preparation of the Si CNW-3D GF composite

The fabrication of the silicon@silicon oxide nanowire-3D graphitic foam composite was realized using a two-step process involving Au catalyzed VLS growth of Si NWs coupling with in situ oxidization. In brief, the 3D GF was firstly sputtered with a Au catalyst for 20 min and positioned into a tube furnace. Then 20 sccm of H₂ was introduced for 60 min at 600 °C for the gold catalyst activation. Subsequently, the Au catalyst-deposited 3D GF was used as a scaffold for catalytic growth of Si NWs at 540 °C via a VLS approach using SiH₄ as the silicon source. After 20 min growth, the sample was cooled down in a H₂ atmosphere. Finally, the composite sample with fresh Si NWs was in situ oxidized under O₂ flow (5 sccm, 99.999%) for 24 h at room temperature. The final mass ratio of Si is about 50% in the composite. The growth of Si CNWs on the SS304 substrate is almost the same as that of the Si CNW-GF composite, except that SS304 was used instead of the 3D GF. The loading densities of Si CNWs for the Si CNW-3D GF composite and the Si CNW electrodes are about 0.55 mg cm⁻² and 0.28 mg cm⁻², respectively.

Material characterization

The morphology was characterized by scanning electron spectroscopy (S-4800, Hitachi) and transmission electron spectroscopy (FEI Tecnai F30, Philips). The XRD patterns were collected using a Rigaku D/MAX-RC diffractometer that was equipped with Cu-K α radiation by step scanning (0.05° s⁻¹) in the 2 θ range of 10–90°. For measurements with excitation at 532 nm, an XploRA confocal Raman microscope (Horiba Jobin Yvon, France) was used.

Electrochemical measurements

Electrochemical performance was evaluated in a CR2025-type coin cell configuration with free-standing Si CNW-3D GF as the working electrode, a metallic lithium foil as the counter electrode, and a Whatman GF/A borosilicate glass-fiber as the separator. The electrolyte was a commercial solution composed of 1 mol L^{-1} LiPF₆ in an ethylene carbonate–diethyl carbonate mixture (1 : 1 in volume, battery grade, from Dongguan Shanshan Battery Materials Co., Ltd, China), with 10 wt% vinylene carbonate (VC, 99% purity, from Aladdin Reagents Co., Ltd, Shanghai) as an additive. The cells were assembled inside an Arfilled glovebox (M. Braun Inert Gas Systems Co. Ltd, Shanghai) with water and oxygen contents both less than 0.1 ppm. No binders or conductive carbon were used during the electrode preparation processes. The specific capacity of the flexible Si

CNW-3D GF was calculated based on the loaded mass of Si NWs, which was determined by subtracting the weight of the 3D GF from the overall weight of the Si CNW-3D GF composite. A high mass ratio of 50 : 50 (Si-C) of the two materials was obtained in the composite. All the weight values were determined using a high-precision analytic balance (METTLER TOLEDO Excellence XS Precision Balance). Galvanostatic charge–discharge measurements were carried out on an LAND CT2001A cell test system to evaluate the cycling performance and rate capability in the voltage range from 0.005 to 2.0 V vs. Li/ Li⁺ at ambient temperature. Electrochemical impedance spectroscopy (EIS) measurements were conducted on two-electrode coin cells by applying an AC voltage of 50 mV amplitude and DC open circuit voltage (OCP) in the frequency range of 1 MHz to 0.01 Hz at room temperature.

Results and discussion

A SEM image in Fig. 2A presents the typical 3D flexible network of the GF comprising interconnected macropores with sizes ranging from 100 to 500 μ m, which completely replicates the structure of the precursor of Ni foam (Fig. S1†). Fig. 2B reveals that the skeleton of the 3D GF has a hollow interior and a smooth graphitic wall. Owing to the unique structure, the 3D GF



Fig. 2 SEM images of 3D GF (A and B) and Si CNW–3D GF composite (C–F). The inset of A is the real sample of the 3D GF with excellent mechanical strength and flexibility. The inset of F shows several individual Si CNWs with a uniform diameter of 50 nm.

is endowed with excellent mechanical strength and flexibility and thus can be bent/folded (inset of Fig. 2A). Fig. 2C gives an overview image of the 3D GF after Si CNW growth. It can be seen that compared with the pristine 3D GF, the Si CNW-3D GF composite shows a different yellow color in appearance (Fig. 1B) and becomes hairy on its surface (Fig. 2C and D). At high magnification, Si CNWs grown densely on the skeletons of GF are observed (Fig. 2E and F). The nanowires exhibit a streamline shape with a uniform diameter of about 50 nm and a length of over 50 µm (Fig. 1F). The XRD and Raman characterizations of the Si CNW-3D GF composite, the 3D GF and the Si CNW array on the SS304 substrate are shown in Fig. 3. The XRD patterns in Fig. 3A display typical signals resulting from cubic structured Si (JCPDS card no. 27-1402) and graphitized carbon (JCPDS card no. 25-0284) in addition to those from SS304, confirming the exact element compositions of the three samples, respectively. The composition information is also well reflected by their corresponding Raman spectra (Fig. 3B). Both results demonstrate that the Si CNW-3D GF composite is made of Si and C elements. In addition, the high G/D intensity ratios in the



Fig. 3 XRD patterns (A) and Raman spectra (B) of the Si CNW–3D GF, the 3D GF and the Si CNW arrays on the SS304 substrate. In the Raman spectrum of 3D GF, there exists two weak peaks (1366.9 and 2452.7 cm⁻¹) and two strong peaks (1581.3 and 2706.7 cm⁻¹) corresponding to D bands and G bands, respectively, giving high G/D intensity ratios, which imply that the 3D GF has few defects and their walls are comprised of few layers of graphene sheets. For the Si CNWs/SS304 and the Si CNW–GF cases, only the typical peaks of Si in the range of 516.4–502.2 cm⁻¹ (F_{2g} mode) and of 937.3–926.8 cm⁻¹ (2TO mode) are observed, without the signals from the substrates of GF and SS304 due possibly to the dense coverage of Si CNW materials.

Raman spectrum of the 3D GF indicate that 3D GF is made of few layer graphene sheets and of high quality with few defects.

Further structural and composition analyses for the Si CNW-3D GF composite were characterized by TEM (Fig. 4) and EDX (Fig. S2[†]). As shown in Fig. 4A, a field containing a thin GF wall and Si CNWs of the composite was selected for closer observation. A high-resolution TEM image of the GF wall shows clear crystal lattice fringes, indicating that the 3D GF is highly graphitized (Fig. 4B), in good agreement with the results from XRD and Raman characterizations. Fig. 4C presents an individual Si CNW with a diameter of about 50 nm for element mapping observation. The Si and O maps (insets of Fig. 4C) show that both elements are uniformly distributed throughout the nanowire. The coexistence of Si and O elements is also confirmed by EDX measurement (Fig. S2[†]), where there are a high percentage of 61.67% (atomic ratio) for the Si element and a small percentage of 4.87% for the O element, respectively, in addition to 32.44% for the C element originated from the GF scaffold and negligible 1.01% for Fe from the stainless steel substrate. The insufficient O relative to Si indicates an incomplete oxidization of Si on the surface of the nanowire and the formation of SiO_x.¹³ In Fig. 4D, the Si CNW was found to have a 2 nm thick amorphous SiO_x shell and a well-crystallized Si core. Moreover, from the crystal lattice and electronic diffraction (ED) analysis, it can be concluded that the Si NW is a single crystal and grows along the [200] direction (Fig. 4E). All the above results evidence that the novel composite consisting of the Si@SiO_r core-shell NW array grown on the 3D GF scaffold has been obtained.

The electrochemical performance of the typical Si CNW-3D GF composite was measured and is shown in Fig. 5. For comparison, the Si CNW array grown directly on the stainless steel 304 (SS304) substrate was also prepared (Fig. S3[†]) and investigated together. The coin cells (CR2025-type) were assembled in a sandwich-like configuration by employing the Si CNW-GF composite electrode as the working electrode, Whatman GF/A borosilicate glass-fiber as the separator and metallic lithium foil as the counter electrode, respectively (Fig. 5A). It is pointed out that, in the composite electrodes, 3D GF instead of a normal metal substrate works as the current collector and no auxiliary additives such as binders are used. The binder-free electrodes can reduce the weight of batteries, increase the ratio of active materials and boost the entire performance of the battery.45 Fig. 5B and C display differential capacity profiles of the Si CNW-3D GF and the Si CNW electrodes in the 2nd, 5th, 10th, 20th and 30th cycles between 2 and 0.01 V at a current density of 840 mA g^{-1} (0.2 C) (1 C = 4200 mA g^{-1}). For the Si CNW-3D GF composite, two reduction peaks at 0.25 and 0.09 V and two oxidation peaks at 0.26 and 0.46 V are observed (Fig. 5B), respectively, corresponding to the lithiation $(Li^+ ion$ insertion) and delithiation (Li⁺ ion extraction) of the Si NWs $(Li_{3.17}Si \rightleftharpoons Li_{2.33}Si \rightleftharpoons LiSi)$.⁴² The third oxidation peak of 0.16 V is caused by the extraction of Li⁺ ions from thin layers of the 3D GF. Although the 3D GF is electrochemically active for lithium storage, it provides only a small contribution to the total capacity of the electrode (a small reversible capacity of 72 mA h g^{-1} at a low rate of 444 mA g^{-1} , Fig. S4[†]). For the Si CNW



Fig. 4 TEM images of the Si CNW–3D GF composite (A–E). (B) Graphitic wall region. (C–E) Single Si CNW of the composite. Insets in (C) are the element mappings of Si and O.

electrode, similar profile and peak potentials during chargedischarge are obtained, except the delithiation peak (0.16 V) of the 3D GF (Fig. 5C). Compared with the Si CNW electrode, the Si CNW-3D GF composite delivers almost a doubled differential capacity. AC impedance spectroscopy was further performed to understand the improved reaction kinetics of Li⁺ ions with the electrodes. As shown in Fig. 5D, the contact resistance (R_s) and charge-transfer resistance (R_{ct}) are fitted by ZView software according to an equivalent circuit in Fig. 5E. The values of R_s and $R_{\rm ct}$ for the Si CNW–3D GF electrode are 1.68 and 64.8 Ω (Table S1[†]), respectively. Both of them are much lower than those of the Si NW electrode (2.96 and 317 Ω). Notably, the R_{ct} of the Si CNW-3D GF electrode is only 20% of the Si CNW electrode, which represents a 400% exchange current (i_0) improvement of the composite electrode (Table S1^{\dagger}). The lower R_s and $R_{\rm ct}$ of the composite electrode are considered to arise from the improved conductivity and better electrode-electrolyte compatible interfacial contact due to the employing of the 3D GF, which can in turn accelerate the Li⁺ ion diffusing and inserting/extracting kinetics to obtain the higher capacity and rate capability. In addition, the second EIS fitting on the basis of a different equivalent circuit model including the resistance of SEI and contact was also conducted (Fig. S5[†]) according to the reported method,43 and the result was basically consistent with that obtained in Fig. 5D and E and Table S2.†

The voltage profiles of the two electrodes are shown in Fig. 6A. To investigate the lithium storage efficiency of Si CNWs on different substrates, *i.e.*, 3D GF or SS304, the specific capacities were calculated according to the loading mass of Si NWs in the electrodes. It is observed that the Si CNW-3D GF

electrode can uptake a reversible capacity of 3531 mA h g^{-1} in the second cycle at a current density of 840 mA g^{-1} (0.2 C), which is much higher than 1858 mA h g^{-1} of the Si CNW electrode. In addition, the hysteresis between the charge and discharge curves of the Si CNW-3D GF electrode is relatively narrower compared to the Si CNW electrode. This result suggests that the lower overpotential and improved electrochemical reaction kinetics were produced when using 3D GF as the supporting matrix for Si nanowires. Fig. 6B presents voltage profiles of the Si CNW-3D GF electrode at different current densities. The charge capacities display an upward trend with current densities decreasing, *i.e.*, from 1205 mA h g⁻¹ at 8400 mA g^{-1} (2 C) to 3765 mA h g^{-1} at 210 mA g^{-1} (0.5 C). Fig. 6C shows the cycling performance of the two electrodes at 0.2 C. In the first cycle, the Si CNW-3D GF electrode demonstrates a high reversible capacity of 3603 mA h g^{-1} , approaching the theoretical limit of lithium storage for silicon materials and far surpassing the capacity of 1917 mA h g⁻¹ for the Si CNW electrode. Meanwhile, a higher Coulombic efficiency of 88.1% is achieved in the initial cycle compared with the Si CNW electrode (83.4%). Then the Coulombic efficiency of the composite electrode increases to 99% in the second cycle and remains constant in the subsequent cycles. This high Coulombic efficiency is due to the employment of vinylene carbonate (VC), since VC was found to be able to promote and rebuild the SEI film formation for better cycling performance of batteries, as reported previously.44 The reversible capacity of the composite electrode decreases slightly in first 60 cycles and becomes relatively stable afterwards, giving a better overall cycling performance. Normally, an electrode of higher surface area may



Fig. 5 (A) Schematic illustration shows a binder-free sandwich-like configuration of the coin cell based on the Si CNW–3D GF composite. (B and C) Plots of differential capacity of the Si CNW–3D GF and the Si CNW electrode, respectively after 2, 5, 10, 20 and 30 cycles at a rate of 840 mA g^{-1} (0.2 C) between 2 and 0.01 V in coin-type half cells at room temperature. (D) Impedance spectrum and (E) equivalent circuit of the Si CNW–3D GF electrode. R_s : contact resistance; R_{ct} : charge transfer resistance; CPE: constant phase element (space double-layer capacitance); Z_w : Warburg impedance.

give rise to increased solid electrolyte interface (SEI) films,^{15,44} leading to a higher kinetic barrier for Li⁺ ion transport and capacity loss with cycles. Therefore, the decay in the lithium storage capacity of the composite electrode is probably caused by the growth of the SEI film formed at the electrode–electrolyte interfaces due to the higher surface area of the 3D composite electrode. Even so, the specific capacity of the Si CNW–3D GF electrode can still remain as 2400 mA h g⁻¹ after 100 cycles, which is 2.2 times that of the Si CNW electrode and 7 times the practical capacity of the commercial graphite anode. The higher capacity retention (66%) for the composite electrode (57%), indicating an improved cycling performance in the presence of GF. It should be noted that although the Si CNWs have swollen up to ~400% in volume after 100 cycles of the lithiation/

delithiation, they still basically keep their integrated wire shape from being fractured (Fig. S6†), due to the effective protection of the SiO_x buffering layers.

Moreover, the Si CNW-3D GF electrode also exhibits superior rate capability compared to the Si CNW electrode. As shown in Fig. 6D, the composite electrode displays high charge areal capacities of 3574 mA h g⁻¹, 3189 mA h g⁻¹, 2299 mA h g⁻¹ and 1205 mA h g⁻¹ at the rates of 840 mA g⁻¹ (0.2 C), 2100 mA g⁻¹ (0.5 C), 4200 mA g⁻¹ (1 C), and even 8400 mA g⁻¹ (2 C), respectively. Relatively, the corresponding capacities of the Si CNW electrode, for instance, 2405 mA h g⁻¹, 1720 mA h g⁻¹, 1164 mA h g⁻¹ and 369 mA h g⁻¹ obtained under the same conditions are 33–69% lower than the composite electrode at 1 C and 2 C are 64.3% and 33.7%, while these are only 48.4% and



Fig. 6 (A) Voltage profiles of the Si CNW–3D GF composite and the Si CNWs for the second cycle at a rate of 840 mA g^{-1} (0.2 C). (B) Voltage profiles of the Si CNW–3D GF composite at rates between 840 and 8400 mA g^{-1} (0.2 C to 2 C). (C) Cycling performance of the Si CNW–3D GF composite at a current density of 840 mA g^{-1} (0.2 C). (D) Rate capability of the Si CNW–3D GF composite and the Si CNW at a current density between 840 and 8400 mA g^{-1} (0.2 C to 2 C).

15.3% for the Si CNW electrode. Moreover, when the rate returns from 8400 mA g^{-1} (2 C) to the initial 840 mA g^{-1} (0.2 C) after 50 cycles, the composite electrode still gives a high capacity retention of 77%.

All things considered, we suppose the excellent performance such as high reversible capacity and remarkable rate capability of the Si CNW-3D GF composite is attributed to the unique 3D architecture of the Si CNW-3D GF composite. As illustrated in Fig. S7,† firstly, 3D GF with interconnected macropores supplies open channels and shortened diffusion length for fast Li^+ ion diffusion, which facilitates the Li^+ ion diffusion kinetics and allows an excellent rate capability. Secondly, the composite provides high surface area and more loaded Si NWs that are fully available for Li^+ ion insertion and extraction, ensuring a low contact resistance and a high lithium storage capacity. Thirdly, the continuous skeletons provide 3D conductive networks as direct pathways for charge transport, contributing to both lithium storage capacity and rate performance. Finally, the excellent mechanical strength and flexibility of the 3D GF as well as the SiO_x buffer layer of the Si CNWs play a decisive role in protecting the electrode from being pulverized, responsible for the stable and high reversible capacity. In fact, there are more controlling factors related to reaction kinetics and thermodynamics of Li⁺ ions, including but not limited to those we discussed, have synergistic influence on the entire performance of the batteries. However, there is no doubt that excellent electrical conduction of the electrodes and stabilization of electrode structures are two most important factors we must consider.

Conclusion

In conclusion, a novel Si–C composite with a Si $@SiO_x$ core–shell NW array grown on a 3D GF scaffold has been synthesized *via* a well-controlled multiple-step procedure. The Si CNW–3D GF

demonstrates significantly improved electrochemical performance such as higher lithium storage capacity and superior rate capability when used as an anode of lithium batteries, compared to the Si CNW electrode. The remarkable improvement arises from the unique structure of the Si CNW–3D GF composite with integrated advantages, such as light weight, open macroporosity, high conductivity, high Si NW loading, excellent flexibility and a silicon oxide buffer layer, all of which account for the high performance of this novel electrode material.

Acknowledgements

This work was financially supported by National Natural Science Foundation (21001082, 21273161 and 21101117), the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning (no: 2013-13), Shanghai Innovation program (13ZZ026), Scientific Research Foundation for the Returned Overseas Chinese Scholars of SEM, Visiting scholar fund of the Key Laboratory for Ultrafine Materials of Ministry of Education, East China University of Science and Technology and the Fundamental Research Funds for the Central Universities.

References

- 1 J. M. Tarascon and M. Armand, Nature, 2001, 414, 359.
- 2 M. Armand and J. M. Tarascon, Nature, 2008, 451, 652.
- 3 M. S. Whittingham, Chem. Rev., 2004, 104, 4271.
- 4 M. Winter, J. O. Besenhard, M. E. Spahr and P. Novak, *Adv. Mater.*, 1998, **10**, 725.
- 5 H. Kim, M. Seo, M.-H. Park and J. Cho, *Angew. Chem., Int. Ed.*, 2010, **49**, 2146.
- 6 Y. Yao, M. T. McDowell, I. Ryu, H. Wu, N. Liu, L. B. Hu, W. D. Nix and Y. Cui, *Nano Lett.*, 2011, **11**, 2949.
- 7 H. Ma, F. Y. Cheng, J. Chen, J. Z. Zhao, C. S. Li, Z. L. Tao and J. Liang, *Adv. Mater.*, 2007, **19**, 4067.
- 8 C. K. Chan, H. L. Peng, G. Liu, K. Mcilwrath, X. F. Zhang, R. A. Huggins and Y. Cui, *Nat. Nanotechnol.*, 2008, **3**, 31.
- 9 H. T. Nguyen, F. Yao, M. R. Zamfir, C. Biswas, K. P. So, Y. H. Lee, S. M. Kim, S. N. Cha, J. M. Kim and D. Pribat, *Adv. Energy Mater.*, 2011, 1, 1154.
- 10 A. M. Chockla, J. T. Harris, V. A. Akhavan, T. D. Bogart,
 V. C. Holmberg, C. Steinhagen, C. B. Mullins,
 K. J. Stevenson and B. A. Korgel, *J. Am. Chem. Soc.*, 2011,
 133, 20914.
- 11 B. Wang, X. L. Li, X. F. Zhang, B. Luo, Y. B. Zhang and L. J. Zhi, *Adv. Mater.*, 2013, 25, 3560.
- 12 X. L. Li, J.-H. Cho, N. Li, Y. Y. Zhang, D. Williams, S. A. Dayeh and S. T. Picraux, *Adv. Energy Mater.*, 2011, 2, 87.
- 13 H. Yoo, J.-I. Lee, H. Kim, J.-P. Lee, J. Cho and S. Park, *Nano Lett.*, 2011, **11**, 4324.
- 14 H. T. Chen, J. Xu, P.-C. Chen, X. Fang, J. Qiu, Y. Fu and C. W. Zhou, *ACS Nano*, 2011, **5**, 8383.
- 15 H. Wu, G. Chan, J. W. Choi, I. Ryu, Y. Yao, M. T. McDowell1, S. W. Lee, A. Jackson, Y. Yang, L. B. Hu and Y. Cui, *Nat. Nanotechnol.*, 2012, 7, 309.

- 16 J.-K. Yoo, J. S. Kim, Y. S. Jung and K. Kang, *Adv. Mater.*, 2012, 24, 5452.
- 17 H. Kim, B. Han, J. Choo and J. Cho, Angew. Chem., Int. Ed., 2008, 47, 10151.
- 18 J.-I. Lee, K. T. Lee, J. Cho, J. Kim, N.-S. Choi and S. Park, Angew. Chem., Int. Ed., 2012, 51, 2767.
- 19 H. P. Jia, P. F. Gao, J. Yang, J. L. Wang, Y. N. Nuli and Z. Yang, *Adv. Energy Mater.*, 2011, **1**, 1036.
- 20 C. Martin, M. Alias, F. Christien, O. Crosnier, D. Bélanger and T. Brousse, Adv. Mater., 2009, 21, 4735.
- 21 X. S. Zhou, Y. X. Yin, L. J. Wan and Y. G. Guo, *Adv. Energy Mater.*, 2012, **2**, 1068.
- 22 K. Evanoff, A. Magasinski, J. B. Yang and G. Yushin, *Adv. Energy Mater.*, 2011, 1, 495.
- 23 C. Martin, O. Crosnier, R. Retoux, D. Bélanger,
 D. M. Schleich and T. Brousse, *Adv. Funct. Mater.*, 2011, 21, 3524.
- 24 K. Evanoff, J. Benson, M. Schauer, I. Kovalenko, D. Lashmore, W. J. Ready and G. Yushin, *ACS Nano*, 2012, 6, 9837.
- 25 J. P. Rong, C. Masarapu, J. Ni, Z. J. Zhang and B. Q. Wei, *ACS Nano*, 2010, **4**, 4683.
- 26 W. Wang and P. N. Kumta, ACS Nano, 2010, 4, 2233.
- 27 X. L. Chen, K. Gerasopoulos, J. C. Guo, A. Brown, C. S. Wang, R. Ghodssi and J. N. Culver, *ACS Nano*, 2010, 4, 5366.
- 28 D. M. Piper, T. A. Yersak, S.-B. Son, S. C. Kim, C. S. Kang, K. H. Oh, C. M. Ban, A. C. Dillon and S.-H. Lee, *Adv. Energy Mater.*, 2013, 3, 697.
- 29 R. Yi, F. Dai, M. L. Gordin, S. R. Chen and D. H. Wang, *Adv. Energy Mater.*, 2013, **3**, 295.
- 30 T. H. Hwang, Y. M. Lee, B.-S. Kong, J.-S. Seo and J. W. Choi, *Nano Lett.*, 2012, **12**, 802.
- 31 J. W. Deng, H. X. Ji, C. L. Yan, J. X. Zhang, W. P. Si, S. Baunack, S. Oswald, Y. F. Mei and O. G. Schmidt, *Angew. Chem., Int. Ed.*, 2013, **52**, 2326.
- 32 C. J. Yu, X. Li, T. Ma, J. P. Rong, R. J. Zhang, J. Shaffer, Y. H. An, Q. Liu, B. Q. Wei and H. Q. Jiang, *Adv. Energy Mater.*, 2012, 2, 68.
- 33 X. L. Chen, X. L. Li, F. Ding, W. Xu, J. Xiao, Y. L. Cao, P. Meduri, J. Liu, G. L. Graff and J.-G. Zhang, *Nano Lett.*, 2012, **12**, 4124.
- 34 X. H. Cao, Y. M. Shi, W. H. Shi, G. Lu, X. Huang, Q. Y. Yan,Q. C. Zhang and H. Zhang, *Small*, 2011, 7, 3163.
- 35 X. C. Dong, H. Xu, X. W. Wang, Y. X. Huang, M. B. Chan-Park, H. Zhang, L. H. Wang, W. Huang and P. Chen, *ACS Nano*, 2012, **6**, 3206.
- 36 Y. M. He, W. J. Chen, X. D. Li, Z. X. Zhang, J. C. Fu, C. H. Zhao and E. Q. Xie, ACS Nano, 2013, 7, 174.
- 37 W. Wang, S. R. Guo, K. N. Bozhilov, D. Yan, M. Ozkan and C. S. Ozkan, *Small*, 2013, 9, 3714.
- 38 J. S. Luo, J. L. Liu, Z. Y. Zeng, C. F. Ng, L. J. Ma, H. Zhang, J. Y. Lin, Z. X. Shen and H. J. Fan, *Nano Lett.*, 2013, **13**, 6136.
- 39 N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu and Q. W. Chen, *Sci. Rep.*, 2013, 3, 1568, DOI: 10.1038/srep01568.
- 40 Z. Favors, W. Wang, H. H. Bay, A. George, M. Ozkan and C. S. Ozkan, *Sci. Rep.*, 2014, 4, 4605, DOI: 10.1038/srep04605.

Paper

- 41 W. Wang, S. Guo, I. Lee, K. Ahmed, J. B. Zhong, Z. Favors,
 F. Zaera, M. Ozkan and C. S. Ozkan, *Sci. Rep.*, 2014, 4, 4452, DOI: 10.1038/srep04452.
- 42 B. A. Boukamp, G. C. Lesh and R. A. Huggins, *J. Electrochem. Soc.*, 1981, **128**, 725.
- 43 W. Wang, I. Ruiz, K. Ahmed, H. H. Bay, A. S. George, J. Wang,
 J. Butler, M. Ozkan and C. S. Ozkan, *Small*, 2014, DOI: 10.1002/smll.201400088.
- 44 S. Sim, P. Oh, S. Park and J. Cho, Adv. Mater., 2013, 25, 4498.
- 45 N. Li, Z. P. Chen, W. C. Ren, F. Li and H. M. Cheng, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 17360.