A Well-Defined Silicon Nanocone–Carbon Structure for Demonstrating Exclusive Influences of Carbon Coating on Silicon Anode of Lithium-Ion Batteries

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ABSTRACT: Nanotechnology and carbon coating have been applied to silicon anodes to achieve excellent lithium-ion batteries, but the exclusive influence of carbon coating on solid–electrolyte interphase (SEI) formation is difficult to exhibit distinctly because of the impurity and morphological irregularity of most nanostructured anodes. Here, we design a silicon nanocone–carbon (SNC-C) composite structure as a model anode to demonstrate the significant influences of carbon coating on SEI formation and electrochemical performance, unaffectedly as a result of pure electrode



component and distinctly due to regular nanocone morphology. As demonstrated by morphological and elemental analysis, compared to the SNC electrode, the SNC-C electrode maintains a thinner SEI layer (\sim 10 nm) and more stable structure during cycling as well as longer cycle life (>725 cycles), higher Coulombic efficiency (>99%), and lower electrode polarization. This well-defined structure clearly shows the interface stability attributed to carbon coating and is promising in fundamental research of the silicon anode.

KEYWORDS: lithium-ion batteries, silicon nanocone, carbon coating, solid-electrolyte interphase, electrochemical performance

INTRODUCTION

The lithium-ion battery has now been widely used in potable electronics, electrical vehicles, and the aerospace field due to its high safety and high energy density. To satisfy the requirement of higher energy density for further applications, many electrode materials such as Si, Sn, Ge, and Ga have been developed,¹⁻⁴ in which the silicon is the most attractive choice as anode material in lithium-ion batteries to gradually replace graphite. Silicon has a theoretical capacity of 3580 mAh g⁻¹ for forming Li₁₅Si₄ at room temperature, which is 10 times higher than 350–365 mAh g⁻¹ of commercial graphitic anode material.⁵⁻⁸ Furthermore, silicon is environmentally friendly and abundant in the earth's crust, and the well-developed semiconductor manufacturing technology also provides the convenience for utilizing silicon material.⁹

Despite the many advantages of silicon, conventional silicon anodes also have two major shortcomings. One is that the volume expansion can reach to 320% after lithiation,¹⁰ and this tremendous volume variation could lead to structural pulverization and the loss of electronic contact in the electrode.^{11–13} The other obstacle is that the solid–electrolyte interphase (SEI) layer would form continuously on the surface of silicon anode, which results in irreversible consumption of electrolyte and lithium source from the cathode,^{14–16} thus further leading to low Coulombic efficiency and poor cycle life.

In recent years, nanostructured silicon has been developed to solve the above-mentioned problems, such as nanoparticles,¹⁷ nanotubes, 21,22 and nanowires, $^{23-25}$ in which free space is offered to accommodate the volume variation of silicon. Many coating materials have been reported to improve electrochemical performance of Si-based anodes, such as metal, metal oxides, coordination complex, and carbon, $^{10,26-28}$ in which carbon coating is considered as a common technique due to its unique physical and chemical properties. Carbon coating can protect the electrode from contacting the electrolyte directly, improve the surface electrochemical property,²⁹ and increase the electrical conductivity of the electrode.³⁰ Liu et al. reported a silicon/ carbon yolk-shell structure for a stable Si anode;⁹ Yoo et al. utilized carbon coating to compensate for the low electric conductivity of silicon nanotubes;³¹ Yin et al. synthesized silicon/carbon nanoporous microspheres by the electrospray method.³² Nanotechnology and carbon coating have been applied to silicon anode to maintain a stable and thin SEI layer and excellent electrochemical performance.³³ However, direct experiments have rarely been reported to distinctly prove the exclusive effect of the carbon coating on SEI formation due to the

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Figure 1. Schematic diagram of fabrication process and structure of the SNC-C electrode.

irregular morphology of most nanostructured silicon-based anodes and the inevitable influences of binders, additives, and current collectors.

Here, a silicon nanocone-carbon (SNC-C) composite structure is designed to distinctly and directly demonstrate the significant and exclusive influence of carbon coating on SEI formation by taking advantage of its regular structure and pure component. The silicon nanocones (SNCs) are obtained by an ICP etching method. This ICP etching method has several advantages for silicon anodes. First, the ICP-etched SNCs are vertically aligned with controllable sufficient space for volume variation and subsequent carbon coating. Second, the SNCs are achieved by direct etching on the silicon wafer, so the SNCs and the substrate are an organic whole without the substrate adhesion problem and the influences of binders, conductive additives, and current collectors. Third, the ICP-etched silicon has ordered cone structure rather than disordered agglutinating nanoparticles, and this regular morphology provides a great advantage for observing SEI formation. Along with the carbon coating by a controllable CVD method, the SNC-C composite structure can avoid excessive SEI growth, keep regular cone shape, and achieve significant improvement in cycling performance. By comparing the electrochemical performance and postcycling morphology of the SNC electrode and the SNC-C electrode, the significant and exclusive influence of carbon coating on silicon anode is demonstrated distinctly in this study. The fabrication process for the SNC-C electrode is illustrated in Figure 1.

METHODS

Materials Preparation. The SNCs were fabricated by inductively coupled plasma (ICP, Oxford Plasmalab System100) reactive ion etching system using sulfur hexafluoride and oxygen as the etching gas. The aspect ratio and density of the SNCs were modulated by changing the etching parameters such as gas flow ratio (SF_6/O_2), gas pressure, etching power, and temperature. The as-fabricated SNCs were used as the substrates to deposit amorphous carbon by tube furnace using a CVD method, in which methylbenzene was used as the precursor gas and the temperature was set at 900 °C. The thickness of the deposited carbon was determined by gas flow ratio and growth time.

Electrochemical Test. The SNC-C composite electrodes were assembled into Swagelok-type batteries with lithium foils as the counter electrodes in an argon-filled glovebox. The electrolyte used in the batteries was 1 mol L⁻¹ lithium hexafluorophosphate (LiPF₆) solution with ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1 by volume) as the bicomponent solvent. The assembled batteries were all discharged to a limited capacity (100 μ Ah cm⁻²) and charged to 2.0 V vs Li⁺/Li at room temperature by galvanostatic cycling through a battery tester (Land BA2100A, Wuhan LAND Electronics Co., Ltd.). The rates of the cycling were set at 0.5 and 5 C separately, to which the corresponding current densities are 50 and 500 μ A cm⁻², respectively. The cyclic voltammogram test and electrochemical impedance spectroscopy were obtained by a multichannel potentiostat system (BioLogic VSP-300).

Physical Characterization. The characterizations of the samples were obtained by a scanning electron microscope (SEM, Hitachi S-4800) with energy-dispersive X-ray spectroscopy (EDX) and a transmission electron microscope (TEM, JEOL 2010F) with selected area electron diffraction (SAED). Raman spectra were obtained by a Raman spectrometer (JY-T64000) with 532 nm wavelength incident laser light. The electrical conductivities of the SNC electrode and the SNC-electrode were measured by the Hall effect measurement system (Ecopia HMS-3000) using the four-point probe method.

Research Article

RESULTS AND DISCUSSION

Scanning electron microscope (SEM) studies show the morphological and structural information on the SNC electrode and the SNC-C electrode. Figures 2a, 2c, and 2e present tilted



Figure 2. Tilted angle SEM images of (a) the SNC arrays (b) and the SNC-C arrays; top view SEM images of (c) the SNC arrays (d) and the SNC-C arrays; cross section SEM images of (e) the SNC arrays (f) and the SNC-C arrays.

angle, top view, and cross section SEM images of the SNC arrays. The density and the aspect ratio of the SNCs can be controlled by changing the etching parameters; therefore, the intercone space could be modulated to an appropriate value. The average height of the SNCs chosen for this study is approximately 1.5 μ m while the half-width of each SNC is about 100 nm. Thus, the diameter of SNC is less than the critical size (300 nm) for silicon nanowires, below which the strain can be relaxed without cracking.³⁴ In addition, these high-aspect ratio SNCs are vertically aligned with relatively even and sufficient intercone space to accommodate their tremendous volume variation



Figure 3. (a) Upper left: a low-magnification TEM image of a single SNC. Lower left: the corresponding SAED pattern. Right half: a high-resolution TEM image at the edge of the SNC. (b) Upper left: a low-magnification TEM image of a single SNC-C. Lower left: the corresponding SAED pattern. Right half: a high-magnification TEM image at the top of the SNC-C. (c) Raman spectra of the SNC electrode and the SNC-C electrode. (d) EDX element weight ratios of the SNC electrode and the SNC-C electrode.

during the lithiation process compared to randomly aligned silicon nanowires.³⁵ The sufficient space also allows for subsequent deposition of the amorphous carbon with enough space left. The SNCs and the silicon substrate are an organic whole without the substrate adhesion problem and the need of binders, conductive additives, and current collectors.

Figures 2b, 2d, and 2f present tilted angle, top view, and cross section SEM images of the SNCs coated with carbon. It can be seen that the deposition is homogeneous with every SNC coated by carbon. The thickness of the carbon coating is controlled to make sure that the carbon coating completely covers each SNC and that the left intercone space is enough to accommodate the volume variation of the SNCs. The carbon coating could also accommodate the strain of volume variation due to its elasticity³ and outer free space. The carbon coating layer can protect the SNCs from contacting with electrolyte directly and enhance the conductivity of the SNC electrode, resulting in excellent performance of the batteries. The four-point probe measurement indicates that the conductivity of the SNC electrode gets enhanced from 4.75 to 4.55×10^4 S m⁻¹ after carbon coating, which is ascribed to the well-connected conductive network of the amorphous carbon.

To further characterize the SNC electrode and the SNC-C electrode, transmission electron microscopy (TEM) with selected area electron diffraction (SAED), Raman spectra, and energy-dispersive X-ray spectroscopy (EDX) analysis were carried out. Figures 3a and 3b show the TEM images and the SAED patterns of the SNC and SNC-C electrodes. The upper left of Figure 3a shows a single SNC with high aspect ratio, and the SAED pattern (lower left of Figure 3a) with a series of spots

shows the crystalline nature of the SNC, which is also evident from the high-resolution TEM image (right half of Figure 3a) of the SNC. In addition, a thin amorphous layer (about 2 nm) at the edge of the SNC can also be observed in the high-resolution TEM image, which is the native surface oxide layer. The upper left of Figure 3b shows a single SNC-C, and the corresponding high-magnification TEM image of the SNC-C composite structure is shown in the right half of Figure 3b. The carbon coating layer completely covers the SNC with an average thickness of 50 nm. The SAED pattern (lower left of Figure 3b) with diffraction rings indicates the amorphous nature of the carbon coating layer.

Figure 3c shows the Raman spectra of the SNC electrode and the SNC-C electrode. The peaks at 520 cm⁻¹ in both spectra indicate the crystalline nature of the SNCs.³⁷ It can be observed that the peak of SNC for crystalline silicon is the same with SNC-C, and the peaks of D and G in the Raman spectrum of the SNC-C electrode are corresponding to the amorphous carbon coating.³⁸ Figure 3d shows the EDX analysis of the SNC electrode and the SNC-C composite electrode. Silicon and oxygen are detected from the SNC electrode, and the corresponding weight ratios are 98.65% and 1.35%, respectively. Silicon, carbon, and oxygen are detected from the SNC-C electrode, and the corresponding weight ratios are 60.87%, 35.25%, and 3.88%, respectively. The small amount of oxygen is caused by the natural oxidation of the silicon surface, and it has been reported that the surface SiO_r is ion-permeable and can serve as a mechanical constraining layer during the volume expansion of silicon.³⁹ It is also notable that this native surface oxide layer cannot maintain a continuously significant clamping



Figure 4. Charge/discharge capacity versus cycle number plots of (a) the SNC electrode and (b) the SNC-C electrode at 0.5 C. The voltage versus capacity plots of (c) the SNC electrode and (d) the SNC-C electrode at 0.5 C for the 1st, 10th, 25th, and 50th cycles.

effect since it is very thin for the SNCs; therefore, the carbon coating plays the major role in accommodating the volume variation of the silicon as well as protecting the silicon from contacting the electrolyte directly.

The carbon coating exhibits remarkable improvements in cycling performance and electrode polarization of the batteries in the electrochemical test. Figures 4a and 4b show the charge/ discharge capacity versus cycle number plots of the SNC electrode and the SNC-C electrode. The current density is 50 μ A cm^{-2} , and the discharge capacity is limited to 100 μ Ah cm^{-2} (corresponding to a gravimetric capacity of 2100 mAh g^{-1} through estimation), which means the Coulombic efficiency is numerically equal to the charge capacity. To make sure that only the silicon nanocones are lithiated without the influence of lithiated silicon substrate that would crack and cause continuous formation of SEI, the batteries are discharged to a limited capacity instead of a certain voltage. The first charge capacity of the SNC-C electrode at 0.5 C reaches to 76.8 μ Ah cm⁻², which is higher than 74.8 μ Ah cm⁻² of the SNC electrode. The charge capacities of both electrodes increase gradually during the first several cycles, indicating the activation process for each electrode.⁴⁰⁻⁴² The initial Coulombic efficiency of SNC electrode is 74.8%, and it is maintained about 96% at the 12th cycle and drops below 90% at the 85th cycle. The initial Coulombic efficiency of SNC-C electrode is 76.8%, and it is maintained about 99% at the 12th cycle and stays above 99% for 169 cycles.

It can be clearly observed that the SNC-C electrode has higher Coulombic efficiency and better cycling performance than the SNC electrode, which can be attributed to the efficient carbon coating. First, carbon coating layer acts as a kind of passivation layer that prevents the silicon from contacting with the carbonate electrolyte directly; thus, the continuous side reactions are avoided.^{43,44} Since the side reactions are irreversible, less side reactions means higher Coulombic efficiency. Second, the carbon coating could maintain a stable and thin SEI on its surface, while the exposed silicon in electrolyte would cause an unstable and thick SEI films which consume electrolyte continuously.¹⁵ Excessive SEI leads to the exhaustion of the electrolyte and further speeds up the dry-out of the battery eventually, which in turn indicates the important role of the carbon coating layer also helps to accommodate the volume variation of the silicon and maintain the integrity of the SNCs.^{25,45} Such relatively stable electrode structure has a prominent improvement on the cycle life of the batteries.

Figures 4c and 4d show the voltage versus capacity plots of the SNC electrode and the SNC-C electrode at 0.5 C for the 1st, 10th, 25th, and 50th cycles. The discharge voltage of the SNC electrode drops below 0 V (about -0.1 V) after discharging to the limited capacity, and the charge voltage is close to 0.4 V at the beginning of the charge process, while the difference value of charge/discharge plateau is about 0.61 V. The lithiation voltage drops below 0 V, and the initial delithiation voltage after lithiation process is high above 0 V, indicating that the polarization of the SNC electrode is high,^{40,46} which can be improved by carbon coating. In contrast, the discharge voltage of the SNC-C electrode stays above 0 V during the whole discharge process (ends at about 0.1 V), and the charge voltage begins at about 0.2 V, while the difference value of charge/discharge plateau is about 0.25 V. These differences indicate that the polarization of the SNC electrode is higher than the SNC-C electrode. In this study, since the amount of silicon substrate is much larger than the amount of silicon nanocones, the total lithium storage capacity is much higher than that of the silicon nanocones, and the silicon is sufficient for alloying with lithium.



Figure 5. Charge/discharge capacity versus cycle number plots of (a) the SNC electrode and (b) the SNC-C electrode at 5 C. The voltage versus capacity plots of (c) the SNC electrode and (d) the SNC-C electrode at 5 C for the 1st, 10th, 25th, and 50th cycles.



Figure 6. Cyclic voltammogram curves of (a) the SNC electrode and (b) the SNC-C electrode at a scan rate of 0.1 mV s⁻¹. (c) Charge capacities of the SNC electrode and the SNC-C electrode at various rates. (d) Electrochemical impedance spectroscopy of the SNC electrode and the SNC-C electrode after 30 cycles.

With the cutoff condition of a preset discharge capacity, the lithiation still proceeds even though it is kinetically difficult with the voltage below 0 V,⁴⁷ in which the voltage is highly polarized and nonequilibrium. The improvement of polarization by carbon coating is observable from the comparison of the whole processes

of charge and discharge. This enhancement is attributed to the higher electrical conductivity of the SNC-C electrode compared to the SNC electrode.³³

To evaluate the electrochemical performance of the SNC electrode and the SNC-C electrode at higher rate, a cycling rate

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Figure 7. Tilted angle SEM images of SNC electrode after (a) 10 cycles, (d) 25 cycles, and (g) 50 cycles; tilted angle SEM images of SNC-C electrode after (b) 10 cycles, (e) 25 cycles, and (h) 50 cycles. Element weight ratios detected by EDX of the corresponding SNC and SNC-C electrodes after (c) 10 cycles, (f) 25 cycles, and (i) 50 cycles.

of 5 C was tested in the same condition with 0.5 C. Figures 5a and 5b show the charge/discharge capacity versus cycle number plots of the SNC electrode and the SNC-C electrode at 5 C, the current density is 500 μ A cm⁻², and the discharge capacity is limited to 100 μ Ah cm⁻². The initial Coulombic efficiency of SNC electrode is 69.2%, and it is maintained about 96% at the 5th cycle and stays above 96% for 85 cycles. The initial Coulombic efficiency of SNC-C electrode is 79.8%, and it is maintained about 99% at the 5th cycle and stays above 97% for 725 cycles. It is clearly that the SNC-C electrode has higher Coulombic efficiency and outstandingly longer cycle life than the SNC electrode at 5 C, indicating the improvements of SEI formation and structural stability caused by carbon coating.⁴⁸ This result is consistent with the situation at 0.5 C.

Figures 5c and 5d show the voltage versus capacity plots of the SNC electrode and the SNC-C electrode at 5 C. The discharge voltage of the SNC electrode drops below -0.4 V at the first cycle and even drops close to -0.8 V after 50 cycles, while the difference value of charge/discharge plateau changes from 1.27 to 1.89 V. The discharge voltage of the SNC-C electrode drops close to -0.2 V at the first cycle and keeps above 0 V at the 50th cycle, while the difference value of charge/discharge plateau is about 0.38 V. It is clearly that the carbon coating can decrease electrode polarization more effectively at higher rate. As

previously described, the carbon coated on the surface of silicon increases the conductivity of the electrode from 4.75 to 4.55 \times 10⁴ S m⁻¹, and the higher conductivity of SNC-C electrode can decrease electrode polarization at high rate.⁴² In addition, the similarity between the charge/discharge curves at different cycles in Figure 5d indicates the electrochemical and structural stability of the SNC-C electrode in comparison to SNC electrode.

To further demonstrate the advantages of silicon nanoconecarbon structure, cyclic voltammogram (CV), rate capability, and electrochemical impedance spectroscopy (EIS) were tested for both the SNC electrode and the SNC-C electrode. Figures 6a and 6b show the CV curves of the SNC electrode and the SNC-C electrode at a scan rate of 0.1 mV s⁻¹. A cathodic peak at around 0.6 V is observed in the first discharge process of both electrodes, which can be ascribed to the formation of SEI layer.⁴⁹ This peak disappears in the subsequent cycles for SNC-C electrode. The cathodic peaks at around 0.19 V can be associated with the formation of a sequence of Li_xSi alloys.⁵⁰ Two characteristic anodic peaks at around 0.34 and 0.55 V in the charge process indicate that the phase transition between a-Li_xSi and a-silicon occurs to both the SNC electrode and the SNC-C electrode.³⁰ The current of the anodic peaks increases with cycling due to the activation process of both electrodes, and the peak current of the SNC-C electrode is several times larger than the peak current of Figure 6c shows the rate capabilities of the SNC electrode and the SNC-C electrode. The discharge capacity is limited to 100 μ Ah cm⁻², and the charge current density changes from 50 to 500 μ A cm⁻² (0.5, 1, 2, and 5 C). The rate capability of the SNC-C electrode is distinctly better than the SNC electrode. The reversible charge capacities of the SNC-C electrode are always higher and more stable than those of the SNC electrode, and the capacity gap becomes larger as the rate gets higher. The superior rate capability of the SNC-C electrode is due to the higher electrical conductivity enhanced by carbon coating and a stable and thin SEI layer,⁹ which can also be demonstrated by EIS test shown in Figure 6d. After 30 cycles, the charge transfer resistance of the SNC-C electrode (900 Ω) is much smaller than that of the SNC electrode (1400 Ω).

The regular cone shape of the electrode provides a great advantage for observing SEI formation. The morphology and the elemental analysis of the SNC electrode and the SNC-C electrode after different cycles have been distinctly observed by SEM and EDX, which demonstrates the previous explanation about how the carbon coating improves the Coulombic efficiency and the cycling performance of the battery. The cycling rate is set at 0.5 C, the current density is 50 μ A cm⁻², and the discharge capacity is limited to 100 μ Ah cm⁻². As shown in Figures 7a and 7b, some granular SEI particles are formed on the SNCs while the SEI growth on the SNC-C electrode is not obvious after 10 cycles. After 25 cycles, the SEI particles increase observably on the SNCs and the structure of the SNCs changes to a disordered state (Figure 7d), yet the SNC-C composite structure still keeps its shape (Figure 7e). After 50 cycles, the SEI layer almost covers the cavities between the SNCs (Figure 7g), while the SNC-C electrode is nearly the same with the previous cycles (Figure 7h).

Figures 7c, 7f, and 7i show the element weight ratios of the corresponding SNC and SNC-C electrodes after 10, 25, and 50 cycles, respectively, in which the element concentrations of Si, C, O, F, and P are displayed. C cannot represent SEI because the carbon coating is only on the SNC-C electrode. The weight ratios of O, F, and P represent the amount of SEI since their increments are caused by the formation of SEI layer.⁵¹ The difference value of O, F, and P between the cycled electrode and the original electrode increases as the cycling going on. After 10 cycles, the weight ratios of O and F of the SNC electrode are 13.57% and 2.12%, respectively; P is not detected due to low SEI content. The weight ratio of O of the SNC-C electrode is 4.26%; F and P are not detected. After 25 cycles, the weight ratios of O, F, and P of the SNC electrode increase to 20.93%, 3.77%, and 1.24%, respectively. The weight ratios of O and F of the SNC-C electrode are 4.28% and 1.41%, respectively; P is not detected. After 50 cycles, the weight ratios of O, F, and P of the SNC electrode increase to 24.20%, 4.33%, and 1.51%, respectively. The weight ratios of O and F of the SNC-C electrode are 10.3% and 2.71%, respectively; P is not detected. It can be seen that with the cycle number increases, the weight ratios of O, F, and P increase for both SNC electrode and SNC-C electrode. Meanwhile, the weight ratios of O, F, and P of SNC-C electrode are always lower than that of SNC electrode, which means that the SEI of SNC-C electrode is less and more stable than the SEI of SNC electrode. This result is consistent with the illustration of the SEM images about SEI growth.

Both morphology and element analysis indicate that the carbon coating can not only maintain a stable and thin SEI but also keep the SNCs as their original structure, thus improving the Coulombic efficiency and cycling performance of the battery. Furthermore, the remarkable electrical conductivity of carbon coating can also lower down the polarization of the electrode.

Figures 8a, 8b, and 8c show the cross section SEM images of the SNC electrode and the SNC-C electrode after 10, 25, and 50



Figure 8. Cross section SEM images of the SNC electrode (upper half) and the SNC-C electrode (lower half) after (a) 10 cycles, (b) 25 cycles, and (c) 50 cycles. (d) TEM image of a single SNC-C after 50 cycles. Inset: the corresponding SAED pattern.

cycles, respectively, which are corresponding to the tilted angle SEM images shown in Figure 7. It can be clearly observed that the SEI layer on the SNCs accumulates gradually, and the structure is damaged finally as the cycle number increases, while no obvious SEI growth occurs to SNC-C electrode and the nanocone structure is still perfectly in order. Figure 8d shows the TEM image of a single SNC-C after 50 cycles, which has similar morphology with the original SNC-C before cycling shown in Figure 3b. The thickness of the coating shell is about 60 nm, which indicates that the SEI layer formed on the SNC-C is only about 10 nm thick. The SNC coated by carbon and SEI layer also keeps its integrity as a cone. The SAED pattern with diffraction rings and spots (inset of Figure 8d) indicates that part of the SNC-C still remains crystalline nature apart from the amorphous silicon, carbon, and SEI layer,⁷ which is due to the restraining discharge capacity.

The significant and exclusive influence of carbon coating on silicon anode is demonstrated distinctly by taking advantage of pure electrode component and regular nanocone morphology. The unique physical and chemical properties of carbon coating play a significant role in SNC-C composite structure. First, the elasticity of carbon coating along with the outer free space helps to accommodate the strain of volume variation of the silicon.²⁷ Second, the carbon coating can protect the SNCs from contacting with electrolyte directly as a passivation layer and form a thin and stable SEI layer on its surface as a result of remarkable electrochemical stability.⁴⁸ Third, the carbon coating can enhance the conductivity of the SNC electrode due to its excellent electrical conductivity.

Figure 9 shows a schematic diagram of SEI formation on the SNC electrode and the SNC-C electrode. As for the SNC





Figure 9. Schematic diagram of SEI formation on the SNC electrode and the SNC-C electrode.

electrode, the SNCs expand during lithiation while a thin and porous SEI layer forms on the surface. And then the SNCs shrink during delithiation with the porous SEI wrinkling; thus, the electrolyte permeates though the porous SEI and contacts the surface of the SNCs, leading to the continuous growth of SEI and forming a very thick SEI layer on the SNCs at last. In contrast, the carbon coating of the SNC-C electrode helps to accommodate the volume variation during lithiation and delithiation, and a thin and dense SEI layer forms on its surface. The conformal carbon coating layer also protects the SNCs from contacting with the electrolyte; thus, the further formation of SEI is terminated, and the thin SEI layer keeps stable during cycling.

CONCLUSIONS

In conclusion, we have designed a SNC-C composite structure as a model anode to distinctly and directly demonstrate the significant and exclusive influences of carbon coating on SEI formation and electrochemical performance of lithium-ion batteries. The nanocone structure is vertically aligned with sufficient space for volume variation and is part of the silicon substrate without adhesion problem and the influences of binders, additives, and current collectors. The regular cone shape of the SNC-C structure provides a great advantage for observing SEI formation. As demonstrated by SEM, TEM, and EDX analysis, the SEI layer covers the cavities between the SNCs after 50 cycles, while the SNC-C structure maintains a thinner SEI layer and more stable structure after cycling. The SNC-C electrode also shows better electrochemical performance with higher Coulombic efficiency (>99%), longer cycle life (>725 cycles), and lower electrode polarization. This well-defined structure clearly shows the interface stability attributed to carbon coating and is promising in fundamental research of silicon anode for lithium-ion batteries.

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Notes

The authors declare no competing financial interest.

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