**Study of lithiation mechanisms of high performance carbon-coated Si anodes by *in-situ*
microscopy**

Zheng-Long Xu,^a Ke Cao,^b Sara Abouali,^a Mohammad Akbari Garakani,^a Jiaqiang Huang,^a

Jian-Qiu Huang,^a Elham Kamali Heidari,^a Hongtao Wang^{b*} and Jang-Kyo Kim^{a*}

^a Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

^b Institute of Applied Mechanics, Zhejiang University, Hangzhou 310027, P.R. China

* Address correspondence to mejkkim@ust.hk (J. K. Kim), htw@zju.edu.cn (H. Wang).

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Abstract

Carbon coated Si (Si/C) composites with a high Si content of 81 wt.% are synthesized by one-pot carbonization of the mixture containing commercial Si particles and polyvinylidene fluoride (PVDF) at an optimized temperature. The Si/C electrodes deliver a high cyclic capacity of 2003 mAh g⁻¹ at 0.5 A g⁻¹ after 50 cycles and an enhanced rate capability of ~750 mAh g⁻¹ at 4 A g⁻¹ for over 200 cycles. The effect of ultrathin carbon coating on lithiation mechanisms of Si particles is evaluated using the *in-situ* transmission electron microscopy (TEM). It is revealed that the carbon-coated Si particles undergo an isotropic to anisotropic transition during the initial lithiation, whereas such transition is not observed for the uncoated Si particle. The lithiation rate of Si/C is 3 to 4.5 times faster than that of uncoated Si with the same diameter, a testament to high rate capacities of Si/C in real batteries. The flexible, amorphous carbon coating favorably alters the damage mode of Si particles from pulverization by multiple cracking to fracture by a single crack. The above findings offer fundamental understanding and practical guideline for designing carbon coatings of Si-based electrodes with much enhanced electrochemical performance.

Keywords: carbon coating; silicon particles; Li-ion batteries; *in-situ* TEM.

1. Introduction

Among many electrochemical energy storage devices, Li-ion batteries (LIBs) have gained widespread use in consumer electronics. To satisfy demanding applications like electric vehicles and smart-grids, however, next generation electrodes with higher energy/power densities, longer cycle life and lower manufacturing costs than what the current electrodes can offer should be developed [1-2]. Thanks to its many advantages, such as the high theoretic specific capacity of 3579 mAh g⁻¹ at room temperature, natural abundance, environmental benignity and low working potential (~370 mV), Si has been considered one of the most promising alternatives to the conventional graphite anode [3]. Nevertheless, the electrodes made from Si suffer from poor electrochemical reversibility and low rate capacities arising from the following unfavorable mechanisms [4-6], which hinder its widespread implementations. (i) The large volume expansion over 300 % occurring during the lithiation/delithiation cycles causes pulverization of the active

materials and delamination of the electrodes from the current collectors. (ii) The low electrical conductivity ($10^{-3} \text{ S cm}^{-1}$) and ion diffusivity ($10^{-12} \text{ cm}^2 \text{ s}^{-1}$) of Si limit the high-rate performance of the electrodes. (iii) The solid electrolyte interface (SEI) layer formed on Si electrodes becomes unstable due to repeated expansion and contraction of Si, causing low Coulombic efficiencies and fast capacity degradation.

Different forms of Si nanostructures [7-11] have been developed to address the volume expansion of Si, the first issue in the above, thus demonstrating significantly improved electrochemical performance. A carbon coating on Si has been considered the most effective and feasible strategy to address the last two issues by contributing to the following ameliorating effects [12-13]: (i) the carbon sheath improves the current transport, thus enhancing the reaction kinetics; (ii) the soft carbon coating functions as the buffer to contain the volume expansion of Si during lithiation; (iii) the carbon shell prevents the Si particles from direct contact with the electrolyte, effectively discouraging the formation of SEI layers [12]; and (iv) the carbon coating serves as physical barrier to prevent aggregation of active materials during cycles. Even after a myriad of reports on carbon-coated Si (Si/C) electrodes [14-21], several critical issues still remain to be resolved: namely, (i) simple and cost-efficient manufacturing techniques with low-cost and commercially available materials should be developed; (ii) the amount of Si used in electrodes has not been sufficient to take advantage of its extremely high capacity [17-20]; (iii) little attention has been paid to surface functionalization and dispersion of aggregated Si nanoparticles, which is an important factor influencing the cyclic stability of the electrodes [21-23]; and (iv) the electronically insulating PVDF is often employed as binder for casting electrode materials, which adds an extra weight to the overall electrodes and causes polarization [16].

Although there exist many studies on carbon coating as a means to improve the electrochemical performance, few efforts have been made to explore the roles of carbon coating during electrochemical reactions and the structural evolution of Si particles upon reaction. The *in-situ* transmission electron microscopy (TEM) has emerged as an indispensable tool to probe in real-time the lithiation/delithiation process of electrodes on an atomic scale [24-25]. Following the recent *in-situ* TEM characterization of nanostructured Si and Si composites, like Si nanoparticles (NPs) [26-27], alucone/Si NPs [28], graphene/Si NPs [29], carbon nanofiber (CNF)/Si NPs [30] and Si/C yolk/shell structure [31], this paper is dedicated to identifying the reaction mechanisms

and morphological changes in Si/C NP electrodes in real-time. To the best of our knowledge, this is the first report of studying the amorphous carbon-coated Si particles by *in-situ* TEM.

High capacity Si/C electrodes with enhanced cyclic stability were synthesized by coating PVDF on modified Si NPs which were directly carbonized. The *in-situ* TEM analysis revealed abnormal lithiation behaviors in both the uncoated Si and Si/C particle electrodes. The conductive carbon coating contributed significantly to the lithiation dynamics at initial stage and the enhancement of reaction kinetics by improving the electron/ion transport efficiencies. The cracking mechanisms in the electrodes were also established. These new findings can allow one to elucidate the capacity fading mechanisms and the limiting factors for better design of Si/C composite electrodes.

2. Experimental

2.1 Synthesis of Si/C electrodes

The agglomerated Si nanoparticles of average particle size 50-150 nm (Shanghai ST-Nano Science & Technology) were monodispersed in aqueous solution by amino-silane functionalization followed by F ion mediation, according to our previous work [22]. To prepare Si/C, 0.6 g of treated Si particles was mixed with 0.4 g PVDF as the carbon precursor and N-methyl-2-pyrrolidone (NMP) solvent using a magnetic stirrer overnight. The mixture was cast on a copper foil to form a composite film of ~20 μm in thickness, which was dried at 85 $^{\circ}\text{C}$ in a vacuum oven overnight. The films were cut into pellets of 1.2 cm in diameter and carbonized at different temperatures ranging 550-950 $^{\circ}\text{C}$ for 1 h with a N_2 gas flow in an electric tube furnace (Lindberg/Blue, 1700 $^{\circ}\text{C}$). The final products were designated as Si/C-550, Si/C-750 and Si/C-950 respectively, depending on the carbonization temperature. The average mass loading of active materials was $\sim 1.0 \text{ mg cm}^{-2}$, which is generally higher than those of previous reports on similar Si NPs-based electrodes [16,21].

2.2 Characterization and electrochemical tests

The absorption spectra were obtained by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum One). The functionalized Si/PVDF films or Si/C composites were scratched off

from the copper substrate and mixed with potassium bromide (KBr) by grinding and pressed into pellets. The morphologies of Si/C composites were examined by scanning electron microscopy (SEM, JEOL 6700) and transmission electron microscopy (TEM, JEOL 2010). The crystal structures were evaluated on an X-ray diffraction (XRD) analyzer (PW1830, Philips) for $2\theta = 10-80^\circ$. The N_2 adsorption and desorption isotherms were analyzed at 77 K on a Micromeritics ASAP 2020 analyzer and the Brunauer-Emmett-Teller (BET) method was used to determine the surface areas. To evaluate whether Si contained any impurity phases, the three Si/C electrodes were peeled off from the Cu foil using diluted acid and analyzed the bottom surfaces on an energy-dispersive X-ray spectroscope (EDS). The thermogravimetric analysis (TGA, Q 5000) was employed to study the compositions, and the X-ray photoelectron spectroscopy (XPS, PHI5600, Physical Electronic) was applied to evaluate the surface chemical states.

The as-prepared Si/C pellets were directly used as anodes without binders or conductive additives. The uncoated Si control electrodes were prepared by mixing the Si particles, super P and PVDF with a weight ratio of 7:2:1. 2032 coin cells were assembled in an Ar-filled glove box with Li foil as the counter electrode. A solution of 1 M $LiPF_6$ dissolved in ethyl carbonate (EC): dimethyl carbonate (DMC) mixture (1:1 v:v) was used as the electrolyte and the microporous polyethylene film (Celgard 2400) was employed as the separator. The electrochemical performance was measured on a LAND 2001 CT system between 0.02 and 1.0 V at different current densities.

2.3 *In-situ* TEM examination

The *in-situ* electrochemical experiments were carried out on a JEOL 2100F TEM equipped with a Nanofactory® scanning tunneling microscope (STM)/TEM holder [24]. The uncoated Si or Si/C particles were dispersed on a gold rod of 200 μm in diameter as one electrode while a tungsten wire covered with Li metal was used as the counter electrode. The holder with the electrode/counter electrode assembly was quickly transferred to the TEM column while protecting the assembly with Ar gas flow. During this process, a thin layer Li_2O was believed to form as solid electrolyte for the nano-cell configuration. Lithiation took place when the Au rod was driven to contact with the Li_2O/Li cathode while a negative bias was applied to the Si/C anode allowing Li ion transport through the solid electrolyte.

3. Results and discussion

3.1 Structure and morphology of Si/C composites

The as-supplied Si particles were severely agglomerated, requiring dispersion and surface functionalization before mixing with the polymer precursor [22]. The amino-silane groups (Figure S1) were shown to form covalent chemical bonds with Si particles, which helped ameliorate the particle dispersion and interactions with the polymer [32]. Figure 1a schematically illustrates the synthesis of Si/C electrodes. The carbonization of PVDF-coated Si particles in a N₂ atmosphere led to the formation of composite nanospheres consisting of a crystalline Si (c-Si) core and an amorphous carbon (a-C) shell. One of the main advantages of the current method compared to the previous multi-step preparation of carbon-coated Si particles [17-21] is the use of as-synthesized freestanding films as anode without further treatment or binders/additives, potentially reducing the manufacturing costs. The morphologies of the final Si/C composites are shown in Figures 1b-e and S2. The SEM image (Figure 1b) shows a Si/C-750 composite film of thickness ~23 μm attached to the Cu foil. The film was not a tightly-packed solid, but was an assembly of spherical Si/C nanoparticles with interconnected pores in between (Figure 1c). These macropores can allow easy permeation of the electrolyte while accommodating the volume expansion of Si/C particles during discharge [23, 33]. The individual Si spheres of diameters 50-100 nm were joined by the amorphous carbon coating with a thickness about 6 nm (Figures 1d and e). The carbon shell functioned not only as buffer to accommodate the volume expansion/contraction of Si particles, but also as conductive path to enhance the electronic/ionic transport [14-20]. The SAED pattern (inset of Figure 1d) indicates the crystalline nature of the Si core. Note that the degree of PVDF graphitization depended on the carbonization temperature, the PVDF coating carbonized at 550 and 750 °C presented mainly an amorphous structure, whereas a few graphitic layers were observed on the surface of Si/C-950 (Figure S2) [34]. It should be mentioned that the degree of graphitization of carbon on Si/C-950 was still very low with a high I_D/I_G intensity ratio of 2.51 according to the Raman spectra (Figure S4a), where the I_D/I_G ratio measures the disorder in carbon.

The representative XRD patterns of three different composites are shown in Figure 2a, where the dominant diffraction peaks are assigned to the crystalline Si (PDF: 27-1402) and Cu (PDF: 04-0836) substrate. It's interesting to note that as the carbonization temperature increased from 750 to 950 °C, the peak at ~43° significantly intensified as a result of thermal reactions taking place between Si and Cu at a high temperature to form copper silicide (Cu_{6.69}Si, PDF: 51-0915) [35].

The small peak at 36° is attributed to $\text{Cu}_{0.83}\text{Si}_{0.17}$ (PDF: 23-0223) [16]. The minor copper silicide is thought to be beneficial because they can improve the contact and prevent delamination between the Si/C particles and the Cu current collector during cycling, but the reaction products have to be kept minimum to avoid the over consumption of active materials. The EDS analyses shown in Figure S3 indicate that the Si/C-550 electrodes were not doped by Cu during the thermal treatment, while Cu-containing impurities were formed at the bottom surfaces of the Si/C-750 and Si/C-950 electrodes, in agreement with the XRD results. No prominent peaks were observed for a-C, probably due to its low content and amorphous nature [36]. The lattice parameters of Si calculated using the Bragg's law with an estimated error of $4 \times 10^{-4} \text{ \AA}$ [33] were 5.4314, 5.4313, 5.4321 and 5.4323 $\text{\AA}$ for pristine Si, Si/C-550, Si/C-750 and Si/C-950, respectively. The slightly increased lattice parameters for Si/C-750 and Si/C-950 may have been caused by the stresses generated during the thermal treatment due to the difference in coefficient of thermal expansion between the native oxide, C layer ($1.3\text{-}7.0 \times 10^{-6} \text{ K}^{-1}$) [37] and Si core ($2.59 \times 10^{-6} \text{ K}^{-1}$) [38], in consistent with previous reports [16, 39]. The comparison of pore size distribution curves between the uncoated Si and Si/C (Figure 2b) clearly indicates that the carbon shell was mainly mesoporous with a dominant pore size of $\sim 3 \text{ nm}$. Both the BET surface area and the pore volume of Si/C-750, $122.7 \text{ m}^2 \text{ g}^{-1}$ and 0.285 , were a few times larger than those of the uncoated Si, $37.3 \text{ m}^2 \text{ g}^{-1}$ and $0.095 \text{ cm}^3 \text{ g}^{-1}$ (Table S1) [36, 40]. The surface chemistries were probed by XPS, as shown in Figures 2c-d, and the corresponding elemental compositions are summarized in Table S1. The strong F1s peak at 686.7 eV for Si/PVDF almost totally disappeared after carbonization (Figure 2c), indicating that the fluorine present in PVDF polymer outgassed during carbonization to create mesopores in the carbon shell. Note that the residual amount of F was dependent on carbonization temperature so that it continuously decreased with an increase in carbonization temperature (Table S1). The deconvoluted C1s spectra show that the $-\text{CF}_2$ (290.5 eV) and $-\text{CH}_2$ (286.1 eV) peaks of PVDF disappeared and an amorphous carbon C-C (284.2 eV) peak emerged after the thermal treatment [41]. These observations are in agreement with the formation of D- (disorder) and G- (graphitic) bands in Raman spectra while they were absent in Si/PVDF precursor composites (Figure S4a). The thermal characteristics of Si/C-750 composites were studied by TGA (Figure S4b): the gradual weight reduction below $\sim 300^\circ \text{C}$ is attributed to the release of adsorbed gasses and moisture in porous carbon [42] while the sudden weight drop between 520 and 650°C refers to the oxidization of carbon. In fact, the uncoated Si particles may not be oxidized below 650°C according to the

previous report [43]. Thus, it can be said that the weight content of Si in the composite was about 81 %.

3.2 Electrochemical performance of Si/C composite electrodes

Figure 3a shows the galvanostatic charge/discharge profiles of the uncoated Si and Si/C-750 electrodes measured between 0.02 and 1.0 V. The uncoated Si delivered a high initial discharge capacity of 3020 mAh g⁻¹ with a long plateau at 0.05 V owing to Li-Si alloying at 0.2 A g⁻¹. The discharge capacity is lower than the theoretical capacity of 3579 mAh g⁻¹ similar to many previous reports [14-16], which can be explained by a few reasons, including the formation of amorphous Li_xSi instead of crystalline Li₁₅Si₄ during discharge [28, 31], oxidization of Si NPs [16] and partial utilization of active materials. Its initial reversible capacity was 2144 mAh g⁻¹ with a low Coulombic efficiency of 70.9 %. The large irreversible capacity loss can be explained by several possible reasons, such as the formation of thick SEI layers, the disconnection of some Si particles from the conductive additives and the trapping of Li ions within the active particles during delithiation [3-6]. The profile of the Si/C-750 electrode in the first cycle at 0.2 A g⁻¹ showed lithiation/delithiation behavior similar to the uncoated Si electrode. It delivered an initial reversible capacity of 2707 mAh g⁻¹ with a higher Coulombic efficiency of 88 %. After 5 cycles, the reversible capacity of the uncoated Si electrode was almost negligible, 80.8 mAh g⁻¹. In contrast, the charge/discharge profiles of the Si/C-750 electrode at 0.5 A g⁻¹ in the following cycles were very stable with excellent reversible capacities of 2382 and 2057 mAh g⁻¹ at the 3rd and 40th cycle, respectively. It should be noted that both the uncoated Si and Si/C electrodes were subjected to two cycles at 0.2 A g⁻¹ before cycling at 0.5 A g⁻¹.

To better understand the stability of Si/C particles over uncoated Si, their *ex-situ* SEM and TEM images were taken after 5 cycles, as shown in Figure S5. In the case of uncoated Si, Si particles were covered with thick SEI layer and cracks were formed through the electrode thickness (Figure S5a), suggesting pulverization and mechanical damage to the whole electrode during cycles (Figure S5c) [3]. The typical TEM image revealed large voids within the Si particles (Figure S5e), possibly a consequence of the coalescence of vacancies generated by the extraction of Li ions. The isolated, conductive super P particles are also seen among the Si particles, signifying disrupted electron/ion transfer between them during the lithiation/delithiation process [44], leading to electrical isolation of Si particles. Note that SEI was washed off by diluted acid before TEM

analysis [14]. In contrast, the connected Si/C-750 particles with an intact spherical structure are clearly seen from the SEM and TEM images (Figures S5b, d and f), indicating that the carbon shell effectively helped to prevent the pulverization of Si nanoparticles [14]. The structural durability of the electrode was confirmed by the undamaged Si particles due to the protection by the carbon coating (Figure S5f), leading to enhanced electrochemical stability of the electrode [13-16].

The influence of carbonization temperature was studied on cyclic performance of the three different Si/C composite electrodes, as shown in Figure 3b. For the activation of the electrodes, two initial charge/discharge cycles were carried out at a low current density of 0.2 A g^{-1} . The lower capacities delivered by Si/C-950 at 0.2 A g^{-1} may result from the formation of electrochemically inert copper silicide, as discussed above. When cycled at 0.5 A g^{-1} , the three electrodes exhibited very similar, high reversible capacities of 2309, 2382 and 2330 mAh g^{-1} for the Si/C-550, Si/C-750 and Si/C-950 electrodes, respectively. The overall performance was the best for the Si/C-750 electrode which delivered a notable reversible capacity of 2003 mAh g^{-1} with capacity retention of 84 % after 50 cycles and a high average Coulombic efficiency of 98.4 % [21-23]. The residual volumetric capacity (VC) of the Si/C-750 electrode was $\sim 871 \text{ mAh cm}^{-3}$, corresponding to the specific capacity of 2003 mAh g^{-1} , for an average mass loading of $\sim 1.0 \text{ mg cm}^{-2}$ and a thickness of $\sim 23 \text{ }\mu\text{m}$ (Figure 1b). The VC value obtained here is much higher than those of other Si-based electrodes [14-15, 45-46] or that of graphite anodes, 550 mAh cm^{-3} [47].

The rate performance and high rate capacities of the Si/C-750 electrode are shown in Figure 3c. When the current density was increased 40-folds from 0.1 to 4.0 A g^{-1} , the ensuing capacity was reduced to 775 mAh g^{-1} at the 30th cycle. The charge/discharge profiles of the electrode obtained at different current densities (inset Figure 3c) show characteristics of amorphous Si-Li alloying/dealloying processes. When the current density was recovered to 0.2 A g^{-1} after 30 cycles, the electrode sustained a remarkable reversible capacity of 2383 mAh g^{-1} at 35th cycle. To demonstrate its high-rate stability, the electrode was subjected to another 200 cycles at 4.0 A g^{-1} following the step-wise rate tests. It is worth noting that there was almost no capacity degradation for 200 cycles. The exceptional high-rate capacities and cyclic stability of the Si/C-750 electrode (Figures 3b-c) are attributed to the synergy arising from the high capacity Si core and conductive carbon shell, such as the fast electron/ion transport through the carbon networks, the formation of

stable SEI layers during the pre-rate cycles [42], as well as the mechanical flexibility of the electrode offered by the moderate carbonization temperature [12].

The aforementioned cyclic stability and rate capacities of the Si/C-750 electrode are among the best when the electrochemical properties are compared between the various Si/C composite electrodes reported in the literature, as shown in Table S2 and Figure S6. The electrodes made from the Si/C yolk/shell structure [18], C scaffold/Si [36] and the Si/rGO/Ni composite foam [48] delivered marginally higher capacities at current densities above 2 A g^{-1} than the present Si/C-750 electrode. Nevertheless, their complicated and costly synthesis procedures may not be as appealing nor favorable for real-world applications as the one-pot carbonization process employed in the current study. Although large improvements in cyclic stability and Coulombic efficiency have been achieved by carbon coating of Si in this work, further studies are still needed for better optimization of the Si/C electrodes with long-term cyclic performance.

3.3 *In-situ* TEM examination

Although the carbon coating has been demonstrated to significantly improve the electrochemical performance of Si electrodes in this work and previously [12-21], the underlying mechanisms are still elusive. It is vital to understand how the carbon coating affects the structural evolution, reaction kinetics and degradation mechanisms of Si particles during lithiation. Here, we employed an *in-situ* TEM device to reveal in real-time the electrochemical lithiation of uncoated Si and Si/C particles. The Si/C-750 electrode was selected and designated as Si/C for the *in-situ* experiments. The electrode was configured as schematically illustrated in Figure S7, and a negative potential of -2 V basing *versus* Li^+/Li was applied to the working electrode to allow lithiation.

Figures 4a-d and Movie S1 depict the lithiation process of an individual uncoated Si particle designated as #1 which had a spherical shape with $\sim 122 \text{ nm}$ in diameter prior to lithiation. After 25 s of lithiation, an amorphous Li_xSi (a- Li_xSi) shell with a bumpy surface was formed around the irregularly-shaped crystalline Si (c-Si) core as a result of anisotropic lithiation (Figure 4b). After lithiation for 65 s, the c-Si core became facet-shape (Figure 4c), another evidence of anisotropic reactions between the c-Si and Li ions [26-27]. After a crack was initiated from the surface of lithiated region, more cracks were formed at different locations of the particle, as indicated by red arrows (Figure 4c). As the lithiation was continued inwards, the multiple cracks further grew, eventually leading to pulverization of the particles into several pieces (Figure 4d). The SAED

pattern shown in Figure S8 confirmed that the fully lithiated product was $\text{Li}_{15}\text{Si}_4$. The above observations are in good agreement with the previous reports on lithiation of neat Si particles [25-27].

The initial lithiation process of the Si/C particles was examined under the same condition and illustrated by a series of time-resolved TEM images in Figures 4e-h captured from Movie S2. Two Si/C particles designated as #2 and #3 with Si core diameters of ~128 and ~40 nm, respectively, coated with a uniform a-C layer of ~6 nm were selected for examination (Figure 4e). After 10 s of lithiation in #2 particle, a thin layer of a- Li_xSi phase was formed between the dark c-Si core and light a-C shell (Figure 4f). The morphologies of both a- Li_xSi and c-Si remained spherical, suggesting an isotropic lithiation process so far [29]. Upon lithiation and expansion of Si NPs, a compressive stress was generated in the radial direction of carbon coating [29, 49]. Further lithiation resulted in the expansion of the carbon shell with an enlarged diameter, as seen in Figure 4f. Moreover, the thickness of carbon coating slightly increased from ~6 nm to ~8 nm, possibly due to the lithiation of a-C and the expansion of Si core [49]. The lithiation resulted in inward migration of the two phase interface between c-Si and a- Li_xSi , and after 30 s, the spherical a- Li_xSi layer became substantially thick on the surface of c-Si core. The c-Si core started displaying a few facets, as highlighted by a white arrow (Figure 4g), as a consequence of anisotropic lithiation similar to the uncoated Si. At the same time, a prominent crack was initiated on the carbon shell at the junction with another large particle, see the red arrow, indicating that the stress arising from Si expansion exceeded the fracture strength of the amorphous carbon coating [30]. The crack kept growing as lithiation continued, eventually leading to the fracture of the particles. Unlike the aforementioned pulverization of uncoated Si, the Si/C composite showed the formation of a crack only one side while the other side was intact (Figure 4h). This can be potentially beneficial in real batteries for limiting the formation of SEI layers while maintaining uninterrupted electrical conduction for Si. It is interesting to note that the diameter (~128 nm) of the cracked Si/C particle was below the critical particle size of 150 nm reported previously [26]. The abnormal failure of the Si/C particle can be ascribed to the carbon coating which triggered the crack to initiate and propagate into the Li_xSi core during lithiation. The crack initiation in carbon coating effectively released the accumulated stress and provided preferential lithiation paths to amplify the degradation of Si particle [27]. Similarly, the structural failure of Si nanowires below the critical diameter was also induced by the surface coating [50, 51]. The #2 particle reached full lithiation

after ~70 s, as shown in SAED pattern (Figure S8). At that point, the #3 particle expanded from 40 to ~64 nm in diameter with volume expansion of ~300 %, indicating full lithiation (Figure 4h). However, it did not fracture, due to the relatively high tolerance to mechanical stress by the smaller Si particles [26].

The transition from isotropic to anisotropic lithiation in the Si/C particle upon initial discharge warrants further discussion. Indeed, similar transition was also observed for Ni-encapsulated Si nanowires [50]. A model was proposed to explain the transition phenomenon based on the concurrent reaction and plasticity [52]:

$$\Delta G = \Delta G_r - e\phi + 1/x (\sigma_m^{\text{Si}} \Omega^{\text{Si}} - \sigma_m^{\text{Li}_x\text{Si}} \Omega^{\text{Li}_x\text{Si}}) \quad (1)$$

where ΔG_r is the neat free energy change of Li-Si alloying reaction and $-e\phi$ is the driving force due to the applied voltage. The last term in the bracket refers to the driving force arising from the mechanical stresses at the reaction front: σ_m^{Si} and $\sigma_m^{\text{Li}_x\text{Si}}$ are the mean stresses induced by Si core and lithiated Si, respectively, while Ω^{Si} and $\Omega^{\text{Li}_x\text{Si}}$ are the corresponding volumes per Si atom and unit Li_xSi , respectively. It was argued that at the early stage of lithiation the external force, $-e\phi$, was uniformly applied to the Si core through the conductive carbon shell and played a dominant role for isotropic lithiation, resulting in the formation of a spherical Li_xSi shell and Si core. Once lithiation continued deep into the anode, the driving force brought by the external voltage significantly diminished due to the high transfer resistance by the thick Li_xSi shell. The reaction would then be controlled by the intrinsic free energy change, ΔG_r , so that the reaction rates became different at different crystal planes [27]. This in turn resulted in the formation of facets with projected hexagonal symmetry. It is also argued that the isotropic expansion was partly attributed to the lithiation-induced stress from the carbon coating, which in turn helped to reduce the anisotropic expansion by increasing the hydrostatic pressure at the reaction front and slowing down the anisotropic lithiation kinetics [50]. The transition signifies that highly conductive carbon coating played an important role in initial lithiation dynamics of Si particles.

It is worth noting that the #2 Si/C particle was fully lithiated much quicker than the #1 uncoated Si particle (70 s vs 130 s) (Figure 4), although their sizes were pretty much similar (~122 nm vs ~128 nm), suggesting an enhanced lithiation rate by carbon coating. To eliminate the effect of carbon coating on lithiation kinetics, we took another *in-situ* TEM observation of the two kind

particles with exactly the same Si diameter of ~145 nm [51]. Typical lithiation processes as well as the measured thicknesses of the lithiated regions as a function of time are summarized in Figure 5. The lithiation behaviors of these particles are similar to those described in Figure 4. Figure 5g clearly shows that the thickness of lithiated Si layer increased much faster in Si/C than uncoated Si, in other words, the lithiation process was faster in the Si/C particles to reach full lithiation than the uncoated Si particle, i.e. ~80 s vs 370 s, in agreement with the results shown in Figure 4. This is the first report comparing the lithiation thicknesses between the Si/C and uncoated Si electrodes although the measurement for neat Si particles has been reported previously [27]. The faster lithiation is partly attributed to the higher diffusion coefficient of Li ions in a-C than Si, i.e. $\sim 10^{-7}$ [53] vs $\sim 10^{-12}$ cm² s⁻¹ [5, 29] and good electrical contact between Si core and carbon shell [49]. These findings are the testament to the much higher rate capabilities of Si/C particles than neat Si [14-23]. Another interesting observation is that the thickness of lithiation product increased rapidly in the Si/C particle after the crack initiation on its surface (Figure 5e), owing possibly to the penetration of Li ion through the cracks [27], which needs further investigation in the future. To mitigate the mechanical failure of the carbon-coated Si particles, several strategies can be devised, such as Si/C composites with small Si crystals below 15 nm [14], porous Si/C particles [17] and Si/C yolk-shell structure with an empty space around the Si particle [18, 31].

The above discussion signifies the importance of carbon coating on lithiation mechanisms of Si particles and offers direct evidence to the enhanced electrochemical performance of the Si/C composite electrodes. It should be pointed out, however, that the electrode/electrolyte interface in real batteries is different from that of the nano-cell used in *in situ* TEM [51]. In real batteries, the Si/C particles are surrounded by liquid electrolyte and SEI layers are formed during the lithiation process, thus the early and aggressive fracture of Si/C particles seldom takes place. Even so, the *in-situ* TEM experiments of the open-cell configuration offer an invaluable insight into how the carbon coating on Si electrodes enhances the lithiation kinetics with faster diffusion of Li ions and how it modifies the lithiation dynamics of isotropic to anisotropic transition along with associated fracture of Si particles in real batteries.

4. Conclusions

In summary, high capacity Si/C composites with enhanced cyclic stability and rate capability were synthesized in this work by one-pot carbonization of the mixture containing commercially-available Si particles and PVDF. *In-situ* TEM experiments were carried out to disclose the roles of the carbon coating on Si particles during lithiation. It is revealed that the carbon-coated Si particles undergo a transition from isotropic to anisotropic at the initial lithiation stage. The carbon coating fully encapsulated the Si particles significantly promotes the lithiation process of Si electrodes. The lithiation rate was 3-4.5 times faster for the Si/C electrodes than the uncoated Si counterpart, depending on the thickness of lithiation product. The flexible, amorphous carbon coating also modified the damage mode of Si particles from multiple-crack pulverization to single-crack fracture. The above findings for the first time elucidated the effects of carbon coating on Si particles, which in turn provide a practical guideline for the designs of carbon coatings for enhanced electrochemical performance of Si-based electrodes.

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Figure 1 (a) Schematic illustration of the synthesis of Si core/C shell composites; (b-c) SEM images of Si/C composite; (d) TEM and (e) HRTEM images of Si/C particles, inset (d) is the SAED pattern of Si/C particles.

Figure 2 (a) XRD patterns of Si/C composites; (b) N_2 adsorption/desorption isothermal curves and pore size distributions of uncoated Si and Si/C; (c) general XPS spectra of Si/PVDF precursor and Si/C composite; (d) deconvoluted C1s XPS spectra of Si/PVDF and Si/C.

Figure 3 (a) Charge/discharge voltage profiles of uncoated Si and Si/C-750 electrodes between 0.02 and 1.0 V; (b) cyclic performance of Si/C electrodes measured at 0.5 A g⁻¹; (c) rate capacities of Si/C-750 measured at current densities ranging 0.1-4.0 A g⁻¹ along with cyclic stability for another 200 cycles at 4.0 A g⁻¹, and galvanostatic charge/discharge voltage profiles at different current densities in inset.

Figure 4 Time-resolved TEM images of uncoated Si (a-d) and Si/C (e-h) particles during lithiation. The uncoated Si in (a) and Si/C particles in (e) are designated as #1, #2 and #3, respectively. The white arrows in (b) and (g) refer to bump-shaped Li_xSi and faceted Si, and the red arrows in (c-d) and (g-h) correspond to cracks.

Figure 5 Time-resolved TEM images of (a-c) uncoated Si and (d-f) Si/C particles with the same initial diameter of ~145 nm and the growth of their diameters upon lithiation; (g) plots of thickness of lithiation product vs time for the uncoated Si and Si/C particles, the red arrows indicate the crack initiation.

TOC