Nanoscale Silicon as Anode for Li-ion Batteries: The Fundamentals, Promises, and Challenges

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Abstract

Silicon (Si), associated with its natural abundance, low discharge voltage vs. Li/Li⁺, and extremely high theoretical capacity (~ 4200 mAhg⁻¹), has been extensively explored as anode for lithium ion battery. One of the key challenges for using Si as anode is the large volume change upon lithiation and delithiation, which causes a fast capacity fading. Over the last few years, dramatic progress has been made for addressing this issue. In this paper, we review the progress towards tailoring of Si as anode for lithium ion battery. The paper is organized such that it covers the fundamentals, the promises offered based on nanoscale designing, and the remaining challenges that need to be addressed to allow the using of Si based materials as high capacity anode for lithium ion batteries.

Key Words: Lithium ion battery; Si anode; Capacity fading; Nanoscale design; High capacity; Long cycle life

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1. Introduction

1.1 Advantages and disadvantages of Si-based anode

Li-ion batteries (LIB) appear to be tangible items of our daily life as they are indispensably used for portable electronics, electric transport, and grid energy storage[1]. In a conventional Li-ion battery, the anode is composed of graphite and the cathode is composed of LiCoO_2 . However, these conventional electrode materials suffer from low capacity, high cost and limited power output. In order to meet the increasing demand of higher energy density, cost effectiveness and long-term cycle life for Li-ion batteries, new electrode materials must be discovered and implanted for battery applications. Silicon is one of the most promising candidate materials as anode for lithium ion battery, potentially offering of high capacity for modern Li-ion batteries. Si possesses a capacity of 4200 mAhg^{-1} , which is about ten times of conventional graphite anode (372 mAhg^{-1}). Meanwhile, Si anode has a lithiation voltage plateau at 0.2-0.3 V vs. Li/Li^+ than the graphite anode ($< 0.1 \text{ V vs. Li/Li}^+$), which could avoid the undesired lithium plating and potential dendrite formation, alleviating the safety concern of the corresponding LIB system[2-14]. Therefore, Si appears to be a very promising anode material for the application in next generation electric vehicles (EVs) or hybrid electric vehicles (HEVs) which require to be powered by LIB with both higher gravimetric/volumetric energy density and less safety concern.

Silicon is abundant in earth and large-scale production of silicon based materials has been well realized for decades. However, translating the Si-based materials into industry scale usage as anode for lithium ion battery is not a straight forward process. A range of challenges needs to be tackled in the path for the industrial application of silicon-based materials as anode. The biggest challenge is the large volume change during lithiation of Si ($\sim 280\%$)[15-31]. Phenomenologically, such a large volume change will lead to a number of consequences, typically including cracking and fracturing of the Si anode, destruction and regeneration of solid electrolyte interphase (SEI) layer on the fractured surfaces, and degradation of electronic conductivity. These factors and their consequent effect on the electrochemical properties are now generally termed as a chemi-mechanical effect, which directly contributes to the fast capacity fading of the battery system.

To address the chemi-mechanical effect of Si based materials as anode for lithium ion battery, innovative nanostructure designing concepts have been emerged over the last few years. These nanostructural designing concepts set the foundation for optimized tailoring Si based material as high capacity anode for lithium ion battery. In addition, development of in-situ TEM over the last few years enables the direct visualization of the structural and chemical evolution of the nanostructured electrode materials under dynamic operating condition. The in-situ TEM technique has been widely applied to study the lithiation characteristics and failure/functional mechanisms of different Si based electrode materials, such as Si nanotube, Si nanowire, Si-carbon composite and porous Si anodes. The information captured using in-situ TEM experiments provides valuable insights for optimization of Si-based anodes with enhanced performances. This paper

summaries and reviews recent progress on the fundamental understanding of Si as anode for lithium ion battery, including the basic knowledge, the nanoscale designing concepts, and challenges that need to be addressed for Si based material as anode for lithium ion batteries. Considering the fast evolving nature of this field of research, we realized that what we have covered in this review does not necessarily mean we have captured every aspect of this extensive research topic.

1.2 Structure of crystalline Si

Silicon is the second most abundant element in earth, making up 28% of the earth's mass. The crystalline Si materials are diamond cubic close-packed crystal structure with lattice constants of 5.431 Å as shown by Figure 1. The Si crystal structure is similar to two identical face-centered cubic structure shifted along the bulk diagonal by one quarter of its length. Silicon metal has gray metallic color and is intrinsic semiconductor. Therefore, the conductivity of silicon increases with temperature. The outer shell of the silicon atoms has four valence electrons. In the natural environment, the prevalent formation of silicon compounds is SiO_2 , which is the major component of sand and rocks. To produce pure silicon crystal from quartz, a series of reduction reactions and purification processes are often used. Silicon-based materials have been widely used in electronics, semiconductor industry, silicone industry, automotive, health care, and cosmetics.

Figure 1 The diamond cubic crystal structure of silicon metal

1.3 Si-Li phase diagram derived based on heat treatment

For application of Si as anode for lithiation battery, it is rather important to know the details of the phase diagram of Si-Li system. It should also be realized, the phase diagram derived based on thermal process does not necessarily can be reproduced during the electrochemical process. As shown by Figure 2, a series of Si-Li alloy phases can be formed through the heat treatment method. Those phases include crystalline forms of LiSi, $\text{Li}_{12}\text{Si}_7$, $\text{Li}_{13}\text{Si}_4$, and $\text{Li}_{22}\text{Si}_5$ [32]. These crystalline phases normally have lower Gibbs free energy than the amorphous counterparts as shown in the Figure3. However, during the real electrochemical lithiation process, these Li-Si crystalline phases do not form despite the lower Gibbs free energy. Driven by the electrochemical kinetics, the initial Li-Si reaction product is always amorphous Li_xSi (with $0 < x < 3.75$) alloys.. It has been found that when x reaches 3.75, there is amorphous to crystalline phase transition as discussed in a late section of this paper.

Figure 2 Phase diagram of Li-Si system. Redrawn based on the that published in Okamoto, et al. Reprinted with permission from Refs.[5] and[32].

Figure 3 Calculated formation energy of the Li_xSi in crystalline and amorphous forms. Reprinted with permission from Ref.[5].

2. Characteristics of the electrochemical Lithiation of crystalline Si anode

2.1 Solid state amorphization induced by electrochemical reaction

Electrochemical insertion of Li into crystalline Si will inevitably lead to the formation of amorphous Li_xSi , corresponding to the electrochemical reaction induced solid state amorphization. As shown by the TEM results in Figure 4a, the crystalline Si nanowire reacts with Li electrochemically[5]. At first, the surface layer of the Si nanowire reacted with Li and formed an amorphous Li_xSi shell as shown by the high resolution TEM image in Figure 4b. As shown by the STEM EELS elemental mapping, the reaction product at this early stage of lithiation is composed of a Li-rich shell and the Si crystalline core, as presented in Figure 4(c-f) [5].

Figure4 General microstructural features of the lithiated core-shell nanowire. (a) TEM image of Si core cladded with an a-Li_xSi shell. (b) Atomically resolved TEM image of the atomically abrupt and faceted a-Li_xSi/Si interface. (c) STEM image showing the Si core and a-Li_xSi shell. (d) Li distribution by EELS mapping. (e) Si distribution by EELS mapping. (f) Superposed Li and Si distribution. Reprinted with permission from Ref.[5].

2.2 The atomic model of crystalline silicon lithiation

On atomic level, lithiation of crystalline Si is featured by the atomic ledge peeling mechanism. Through lattice-scale in-situ TEM imaging of the reaction interfaces during the lithiation of Si anode, Liu et al.[33] revealed the dynamic process and ledge peeling of the Si (111) atomic facet by Li-ions, which produce amorphous Li_xSi alloy layer by layer as shown in Figure 5. This observation can also explain the orientation-dependence of anisotropic swelling of the Si anode during lithiation. As shown by the lattice resolution image in Figure 5 (a-b), the interface between the crystalline Si core and amorphous Li_xSi shell is very sharp with only about 1 nm thick interface. The atomic model vividly shows the insertion process of Li ions into the Si structure in Figure 5 (c-d). This result shed light on the atomic scale lithiation process of solid-state amorphization of Si[33].

Figure 5 Atomically resolved structure of the amorphous/crystalline interface (ACI). (a) High-resolution TEM image at the early stage of lithiation, showing the 112 ACI with a long smooth 111 facet in the middle and a series of short, inclined 111 atomic facets on the two sides; (b) The 112 ACI in the late stage of lithiation, with short 111 atomic facets surviving; (c) Relaxed atomic structure of a 112 ACI from molecular orbital theory calculations (see Methods), showing the high local concentration of lithium atoms (green) that invade the exposed 112 surface of the c-Si (red); (d) Proposed mechanism of solid-state amorphization based on TEM observations: silicon atoms break away from the c-Si by a mechanism with low energy barriers, in which several lithium atoms enclose a single silicon or a Si---Si pair located near the edge of 111 atomic facets, weaken the Si---Si covalent bonding, and cause the easy dissociation of c-Si. Reprinted with permission from Ref.[33].

2.3 Lithiation induced anisotropic volume swelling of crystalline silicon

Lithiation of both crystalline and amorphous Si will lead to a volume increase of 280%. In addition, the lithiation of crystalline Si is accompanied by a large anisotropic volume expansion, which is very revealed by both ex-situ and in-situ TEM and SEM studies and supported by theoretical consideration. Liu et al. [34] and Yang et al. [28] have studied the origin of the anisotropic volume expansion of crystalline silicon in detail and reported a consistent experiment and modeling work of the lithiation of Si, as shown in Figure 6(a-b). It has been found that the anisotropic swelling is controlled by the orientation-dependent mobility of the interface between the amorphous Li_xSi and crystalline Si core. In another word, the lithiation reaction rate at the phase boundaries is different for different crystal directions. The high reactivity of Li^+ at the 110 phase

boundaries results in the dominant Li^+ flux in the $\langle 110 \rangle$ directions as shown by the lithium flux profiles in Figure 6(c). The plastic flow behind the moving interface between the shell and Si core is important for the structural relaxation of the Si anode. The kinetics exhibited by the unique Si lithiation reaction is the driving forces of the amorphous Li_xSi phases and the geometry of the product after full lithiation[28, 34].

Figure 6 Comparison between experiment and modeling. Reprinted with permission from Refs.[13] and [34]. (a) and modeling. Reprinted with permission from Ref.[28]. (b) in terms of the cross-sectional morphologies of fully lithiated SiNWs with different axial orientations. (c) Lithium flux profiles at a representative lithiation snapshot ($t = 0.4$) for all the four SiNWs, showing that the dominant flux in the $\langle 110 \rangle$ directions, a direct consequence of high reactivity of Li at the 110 phase boundary. Reprinted with permission from Ref.[28].

2.4 Congruent phase transformation process from amorphous to crystalline in the Li_xSi system

Lithiation of Si of both amorphous and crystalline in nature will unanimously induced the formation of amorphous Li_xSi alloy. It has been noticed that when x reaches to 3.75, the amorphous $\text{Li}_{3.75}\text{Si}$ crystallizes spontaneously to crystalline phase of $\text{Li}_{15}\text{Si}_4$. This spontaneous amorphous to crystalline transformation is featured by a congruent phase transformation and can only happen by electrochemical induced process. This feature is only uniquely revealed by the in-situ TEM as illustrated in Figure 7 based on the lithiation of Si nanowire. The lithiated layer increase in thickness and Si core reduce in diameter as shown by Figure 7. At the end of the Li insertion, the distribution of Li is

relatively uniform. As x increases and reaches 3.75, it suddenly crystallize to form the $\text{Li}_{15}\text{Si}_4$ phase as shown by the in-situ TEM results of Figure 7. During the crystallization process, no composition fluctuations are seen as indicated based on EELS map in Figure 7. In addition, during the crystallization from $\text{Li}_{3.75}\text{Si}$ amorphous phase to $\text{Li}_{15}\text{Si}_4$ crystalline phase, no significant volume changes are seen[5]. As confirmed from the Gibbs free energy calculation shown in Figure 3, the formation energy of crystalline $\text{Li}_{15}\text{Si}_4$ and $\text{Li}_{21}\text{Si}_5$ have significantly lower energy than the amorphous counterparts or other crystalline alloy phases[5]. As shown in Figure 8(a-b), the calculated density of states (DOS) of the crystalline and amorphous Li_xSi alloys, the splitting between the 3s and 3p states is larger with Li concentration increasing to 4.4 ($\text{Li}_{22}\text{Si}_5$). This is largely due to the disturbance of the Si-Si interactions and the weakening of the s-p hybridization. As x increase to the critical value of 3.75, the electronic structure of the amorphous $\text{Li}_{3.75}\text{Si}$ phase becomes very similar to the electronic structure of the crystalline $\text{Li}_{15}\text{Si}_4$ phase. Therefore, the phase transformation is possibly driven by the similarity of the electronic structures between the amorphous and crystalline phase at high lithium concentrations[5].

It has been confirmed by DFT calculations and in-situ TEM that the amorphous Li_xSi alloy transform to $\text{Li}_{15}\text{Si}_4$ through a spontaneous congruent phase transformation process without long-distance atomic diffusion as shown in Figure 8(b). This mechanism differs from the classic nucleation and growth process, which includes the process of atomic diffusion over long distance or phase separation depending on the formation kinetics[5]. It should be pointed out that the electrochemical induced congruent phase transformation observed for the Li-Si system has also been predicted for the Li-P electrochemical system based on computational simulations. It appears true that the electrochemical induced phase transformation characteristics will not necessarily happen by thermal induced equilibrium.

Figure 7 STEM annular dark-field image and EELS elemental distribution maps showing the congruent phase transition characteristics of the a- $\text{Li}_{3.75}\text{Si}$ to c- $\text{Li}_{15}\text{Si}_4$ (a-d) Progression of the lithiation from bottom to top. (e-h) As x approaches 3.75 in a- Li_xSi . (i-l) following the crystallization of a- Li_xSi to c- $\text{Li}_{15}\text{Si}_4$. Reprinted with permission from Ref.[5].

Figure 8(a) Density of states (DOS) projected on Si atoms in various crystalline and amorphous LiSi alloys with the Fermi energy level set to zero. (b) Schematic of the silicon nanowire lithiation process and the spontaneous congruent phase transition of

amorphous Li_xSi to $\text{c-Li}_{15}\text{Si}_4$ when x reaches the critical value of 3.75 in the amorphous phase. Reprinted with permission from Ref.[5].

3. Accommodation or effect of anisotropic volume swelling

3.1 Lithiation induced crack and fracture of crystalline silicon

Accompanying the lithiation induced large volume change of silicon is the generation of stress, which may lead to the fracture or pulverization of the particle, which shows dependence on the particle size. Liu and coworkers found that the silicon particle that is larger than $\sim 150\text{nm}$ in diameter may lead to the formation of surface cracks during the lithiation process as shown in Figure 9[35]. Upon lithiation, the particle that is large than the critical dimension will fracture and explode into pieces as shown in Figure 9(c). The crack formation is thought to be resulted from hoop tension on the surface of the particle. The fracture of Si anode inevitably results in fresh surfaces for regeneration of SEI, therefore consuming liquid electrolyte, leading to fast capacity loss, rapid impedance built-up, and deterioration of cycling stability. The result suggests that the use of smaller Si nanoparticles benefit the long-term cycling of Si-based anode in the Li-ion battery.

Figure 9 Fast fracture of a free-standing 620-nm SiNP during chemical lithiation in one minute. (a-c) Time sequence of crack initiation and growth. Reprinted with permission from Ref.[35].

3.2 Self limiting lithiation due to internal stress

Experimentally, it has been observed for crystalline Si of both nanoparticle or nanowire, the lithiation speed of the Si nanostructures is not constant[36]. Quite often the lithiation is fast in the initial state, and slows down afterwards. The gradual decreasing of lithiation speed is related to the internal stress caused by the lithiation induced volume expansion[18, 37]. As shown by Figure 10, the thickness of the Li_xSi shell increase very fast in the first 3600s, but the reaction speed dropped sharply after enough stress formed in the reaction interface. Even after 14380s, the thickness of the Li_xSi only increased by

about 25nm compared to the 30nm in the first 3600s. The stress induced lithiation kinetics has been well recognized experimentally and interpreted based on theoretical derivations[7, 18, 37, 38] .

Figure 10. Growth kinetics of amorphous LiSi alloy on SiNWs. (a-e) Morphological evolution of SiNW in 4 h. (f) Plots of etch depth and diameter of SiNW and thickness of the a-Li_xSi shell versus time. The growth of a-Li_xSi slowed down in the SiNW during the long lithiation process. Reprinted with permission from Ref.[36].

3.3 Coalescence of the lithiated particles

Another consequence of lithiation induced volume expansion of Si is the filling of the empty space for conglomerated particle system, which may lead to packing up or densifying of several particles. As reported by Gu et al, the volume expansion of the Si nanoparticles can result in the coalescence of the Si particles anchored on the carbon fiber matrix[3]. As shown in Figure 11, the particles p1-3 were contacted with each other. During the electrochemical lithiation process, the volume of all Si particles grew and the two particles began to merge into one big particle after final lithiation, as shown by the images at 25 min and after 2nd discharge. This interesting growth behavior is very similar to the sintering of two nanoparticles through neck growth at high temperature. The contact flattening of silicon particles is driven by the deformation through viscous flow. However, this coalescence behavior is only exhibited by the particles confined by the surroundings. The silicon particles in contact but not confined spatially do not show this coalescence

behavior. This finding is instrumental in explaining the rate and capacity decay of silicon anode materials. In most Li-ion batteries, the electrode materials are confined to a very limited space in the package. Therefore, the swelling of the Si anode during lithiation invariably leads to the merge and coalescence of Si anode particles. The coalescence of the Si nanoparticles significantly reduces the surface to volume ratio of the Si anodes, lowering the rate performance of the Li-ion batteries.

Figure 11. TEM image showing microstructural evolution of the surface-attached nanoparticles at 0 min, 7 min, 25 min, and 2nd discharge. Reprinted with permission from Ref.[3].

4 Characteristic of the electrochemical lithiation of amorphous Si anode

Lithiation of amorphous Si share most of the lithiation characteristics of crystalline Si as described previous, typically such as two phase lithiation characteristics, volume expansion, and dependence of phase transformation on the lithium concentration. However, due to the amorphous nature of the Si, it indeed shows some different characteristics upon lithiation as compared with that of crystalline Si. As shown in Figure 12, the lithiation of amorphous Si ball shows no anisotropic signature during the lithiation reaction[15]. The volume swelling is isotropic and the amount of volume expansion is similar to the crystalline Si. During the first lithiation of amorphous Si, it seems to form an amorphous Li_xSi shell and the boundary between the Li_xSi and amorphous Si core are discernable based on the in-situ TEM images as shown in Figure 12. In addition, the lithiation rate proceeds approximately in a linear fashion with time, which is in great contrast with the significant retardation during the later stage of the lithiation of the crystalline Si. Due to the symmetrical and isotropic lithiation characteristics, the amorphous Si balls do not show fracture with a size up to 870nm, which is much bigger than the critical fracture limit of the crystalline Si $\sim 150\text{nm}$. The difference of lithiation behavior between crystalline and amorphous Si suggests that amorphous Si may be favorable for use in high performance Li-ion batteries[15].

Figure 12(top) Time series of the lithiation of a single a-Si sphere.(bottom) Summary of the first lithiation and subsequent cycling of a-Si and c-Si. This figure is color-coded by Li content with blue as pure Si and red as the fully lithiated phase. The first lithiation for both materials is characterized by a two-phase reaction, but there are important differences. The c-Si particle undergoes anisotropic lithiation and volume expansion, leading to a faceted Si core; in addition, the lithiated phase is very nearly fully lithiated. The a-Si particle is lithiated isotropically, and the concentration of Li in the lithiated phase is probably lower than the crystalline case and may vary with position. Reprinted with permission from Ref.[15].

5 Key factors that affect the lithiation kinetics of silicon

5.1 The electronic conductivity on lithiation rate

The lithiation rate of the Si anode determines critically the rate performance of the Li-ion batteries. A number of factors have been found to have great influence on the lithiation performance of Si anode, such as carbon coating, composite with conductive polymer, and elemental doping. Among all, the lithiation rate changes dramatically following the phosphor doping of Si NW as shown in Figure 13[39]. The reaction speeds increased several orders of magnitude after the P-doping, which is largely due to the enhanced electrical conductivity of the Si nanowire. In addition, intrinsic Si nanowire often leaves an un-reacted Si core during lithiation due to stress generated at the interface between the reacted Li_xSi shell and un-reacted Si core. In contrast, the highly-doped Si nanowire exhibited ultrafast lithiation and seems to be able to avoid the formation of the unavailable Si core during lithiation. Therefore, in order to reach the optimum loading efficiency and fully utilize the active Si, efficient doping to increase the conductivity of the Si anode is very important.

Figure 13 Ultrafast charging of carbon-coated and phosphorus-doped silicon nanowires. (a-i) Morphology evolution in 72 s after the bias was applied. The spiral shape was observed only at very high lithiation rates (reaction front marked by red arrows). The average speed for the reaction front was 213 nm/s. Reprinted with permission from Ref.[39].

5.2. Native oxide layer

Figure 14 Captured in situ TEM images showing the lithiation behavior of the native oxide-coated Si nanoparticle: (a-c) pristine, mid-lithiation, and lithiated morphology. Insets are corresponding EDPs, HRTEM, and dark-field image. (d) Delithiated particles far away from the lithium source. Scale bars are 50 nm. Reprinted with permission from Ref.[8].

Pristine silicon nanoparticles normally have amorphous SiO_x layers on the surface. This layer is insulating in nature and may block the electron conduction that is necessary for lithiation. He et al have recently carefully studied the effect of the native SiO_x layer on the lithiation behavior of Si nanoparticle [8]. As shown in the Figure 14, the silicon particles began to grow in size upon the start of the lithiation process[8]. The surface oxide SiO_x layers transformed to Li_2O and Li_xSi at low biasing voltage. The dark field TEM images in Figure 14c shows that the insulating Li_2O crystalline islands after lithiation. The openings between the Li_2O islands still provide routes for electron conductivity. The volume expansion and electron diffraction of the particles indicate that the lithiation of the particles is far less than the fully lithiated $\text{Li}_{3.75}\text{Si}$ phase. These lithiation characteristics are likely associated with the increased impedance of the system due to the formation of the Li_2O . Despite of the fact that the in situ open-cell tests used lower biasing voltage than real battery, the low conductivity as a result of the oxide layers likely results in the same behavior. After delithiation, the particles also exhibited porous structure, which is consistent with the previous studies[8].

5.3 Artificial coating layers

5.3.1 Alucone coating

He et al also used the lattice-resolution in-situ TEM to probe the functional mechanism of Aluconecoated silicon particles upon electrochemical cycling[8]. It is found that the Aluconecoating process chemically etched the thin SiO_x layer and replacing it with a mechanically flexible metal-carbon-oxygen network. Upon lithiation, the Alucone coating becomes more conductive. The Aluconecoated silicon particles show “balloon-like”, fast and highly reversible lithiation behaviors due to fast Li⁺/e⁻ conductivity and mechanical resilience of alucone coating. In contrast to the insufficient delithiation in SiO_x coated Si particles, the Aluconecoated Si particles show no pore formation and sufficient delithiation to irregular shaped amorphous Si (Figure 15). The electrical and mechanical benefits provided by the Alucone coating improve the cyclic performance and Coulombic efficiency of the battery. [8].

Figure 15 Schematics of surface reactions and cycle behavior of silicon nanoparticles with different coating conditions. Reprinted with permission from Ref.[8].

5.3.2 Metallic coating

Figure 16 In-situ Lithiation/delithiation process for a silicon NW with a ~20 nm copper layer evaporated onto one side. (a) TEM images and schematic of a pristine single-crystalline NW with copper (dark contrast) on the left sidewall. (b) TEM image and SAED pattern of a similar fully lithiated NW. (c) TEM image and SAED pattern of a delithiated NW. The top of the NW is immersed in ionic liquid electrolyte. The NW is bent with the copper layer on the outer edge because the silicon undergoes axial contraction during delithiation. (d) A low-magnification view of the same delithiated NW showing bending along the entire length. All unlabeled scale bars in this figure are 100 nm. Reprinted with permission from Ref. [19].

Metallic coating is another way to increase the electronic conduction of nanostructured Si. The metallic coating species should not react with Li and electrolyte, but still need to transport Li ions. This appears to be hard to choose such a metallic species. One way to do that is coating the nanostructure partially instead of a conformal coating layer. McDowell et al. [19] reported that Cu metallic coatings applied on the Si NWs can improve rate performance and cycle life. In-situ TEM observation as shown in Figure 16 demonstrates that the Cu coatings can help suppress the volume expansion during lithiation. The Cu coating is only deposited on one side of the nanowire to avoid

the enclosure of Li^+ in/out exit. During lithiation, the length and width of the Si nanowire expand, while the Cu support remains intact. Due to the dimensional mismatch between the Cu and lithiated phase, the Cu-coated Si NW bends without breakage. The diffraction pattern shows that the Cu never lithiated with Li throughout the whole process. The Cu coating not only maintains the structural integrity, but also maintains a high electrical conductivity in the composite wire [19].

5.3.3 Conductive polymer coating layer

Figure 17 Schematics of the technical approaches to address volume change issue in battery materials. (a) Traditional approaches use acetylene black (AB) as the conductive additive and PVDF polymer as mechanical binder. (b) Conductive polymer with dual functionality, as a conductor and binder, could keep both electrical and mechanical integrity of the electrode during the battery cycles. (c) The molecular structure of the PF-type conductive polymers, with two key function groups in PFFOMB, carbonyl and methylbenzoic ester, for tailoring the conduction band and for improving the mechanical binding force, respectively. Reprinted with permission from Ref. [40].

Fabricating Si-carbon composite is one important path for solving the bad electrical conductivity of Si and increasing the power output of Si-based anodes. Traditionally, people use a mixture of carbon materials and Si nanoparticles bonded by non-conductive polymer glue. As shown by Gu et al. [6], this design suffers from insufficient electrical conductivity that only the Si materials connected by the carbon is efficient in battery cycling, the ones away from the carbon network do not react with Li

ion at all. Not all Si nanoparticles actually react with Li^+ during electrochemical cycling. In comparison, the traditional design involves the possible scenario of Si particles being deactivated by pushing away the adjacent carbon particles during volume expansion as shown by Figure 17a [40]. As a result, the Si particles become inert and result in capacity decay of the batteries.

Recently, Liu et al. [40] showed that using conductive polymer binder to encapsulate the Si anode materials is a more efficient way to increase efficient Si loading and therefore the cycling stability and capacity in Figure 17(b-c). The conductive polymer is resilient during the cycling of Si anode and efficiently provides the conductive pathway to all the Si particles. In addition, this approach does not need conductive carbon additives, which allows the enhanced efficient loading of Si materials to increase the energy density of the Li-ion batteries.

Gu et al. [6] used in-situ TEM to probe the mesoscale origin of the functional mechanism of the conductive polymer binder in Li ion batteries. The dynamical changes of the Si-conductive polymer approach are vividly shown by the following in-situ TEM micrographs in Figure 18. The enhanced cycling stability of the conductive polymer allows the maintenance of very good electrical contact between all Si nanoparticles during electrochemical cycling. In addition, the conductive polymer-Si anodes show reversible lithiation-delithiation cycles. The volume of the conductive polymer-Si anode increases during lithiation, while it returns to the same volume compared to the pristine state after delithiation as shown in Figure 18. The function of the conductive polymer is to maintain a structural integrity and electrical contact of all the Si nanoparticles. In addition, Gu et al. [6] found that the overall volume changes of the Si-conductive polymer can be represented by the mesoscale functional units (a few Si nanoparticles bonded by conductive polymer) and measured to be only 80% rather than the ~280% as shown by single Si nanoparticle. Therefore, the conductive polymer solves the critical conductivity issue and relieves the volume expansion problems of Si anode [6].

Figure 18(a) Schematic drawing showing the volume expansion of the Si anode on Si NW during lithium insertion and extraction; (b) Captured video frames of the in-situ TEM imaging during the lithium insertion and extraction processes in the SCP anode at different time; first row: 1st lithium insertion; second row: 1st lithium extraction; third row: 2nd lithium insertion. Reprinted with permission from Ref.[6].

6 Strategies to mitigate the chemi-mechanical effect associated with volume expansion of Si during lithiation process

6.1 Si nanoparticle and carbon fiber composite

Figure 19 Comparison of the lithiation characteristics of the particles attached to and embedded in the CNF. The lithiation of the embedded particles is delayed as compared with the particles attached to the carbon surface. Lithiation of the embedded particles leads to the cracking of the carbon fibers. Reprinted with permission from Ref.[3].

Carbon appears to be an indispensable component of anode for lithium ion battery. To make Si nanoparticle as a practical anode, silicon and carbon based composite would be the ideal route. To increase the electrical conductivity and accommodate the volume expansion, researchers have come up with a Si-carbon composite with Si nanoparticles embedded inside a carbon fiber matrix. Gu et al. [3] used in-situ TEM to observe the lithiation characteristics of such Si-carbon fiber composite. However, it is found that the carbon matrix is not able to sustain the stress that is generated by the volume expansion of the Si particles upon lithiation. It is shown in Figure 19 that the lithiation of the embedded Si particles inside the carbon fiber inevitably cause the crack of the carbon fibers. The breakage of the carbon fiber invariably leads to the new surfaces, which will consume electrolyte for the generation of the SEI layers on the freshly fracture surface. In addition, the crack formation and breakage of the carbon matrix lead to electrical contact failure of the anode materials. This failure mechanism encourages us to find new routes to limit the volume expansion of Si-C composites. Further, embedding of the Si nanoparticle in a thick carbon matrix will lead to the delayed lithiation as Li has to transport through the carbon materials. Therefore, selection of coating layer thickness will be a key parameters. It points to the direction that a good Si-anode design needs to leave some free room/space for the Si nanoparticles to freely expand during lithiation.

6.2 Yolk-shell silicon-carbon anode

Figure 20(a) A magnified schematic of an individual Si@void@C particle showing that the SiNP expands without breaking the carbon coating or disrupting the SEI layer on the outer surface. (b) In situ TEM lithiation of the Si@void@C yolk-shell structure, the Si expansion is seen during electrochemical lithiation. (c) Electrochemical cycling results for Si@void@C electrodes. (A) Delithiation capacity and CE of the first 1000 galvanostatic cycles between 0.01–1 V (alginate binder). The rate was C/10 for one cycle, then C/3 for 10 cycles, and 1C for the subsequent cycles. Reprinted with permission from Ref.[28].

An ingenious approach to tackle the volume expansion of Si upon lithiation, while still manage the SEI layer consistently is the design of the yolk-shell Si-C composite[27, 28,41]. The yolk is the silicon nanoparticle, while the shell is composed of a thin layer of carbon. Most importantly, there is enough room between the Si yolk and carbon shell, which allows the Si yolk to expand freely without fracture or pulverization. As shown by Figure 20, the void between the Si yolk and C-shell is filled during the lithiation of the Si yolk. The carbon shell maintains the structural stability and integrity with minimum volume changes during lithiation. In the meantime, the electrical conductivity of the Si-yolk is always maintained by the contact with the carbon shell, which forms the conductive network of the electrode. Due to the carbon shell is in the contact with the liquid electrolyte, the SEI layer formed on the carbon shell will not fracture upon cycling. This smart design leads to long-term cycling without noticeable capacity fading. This composite anode structure can retain 100% of the capacity in the first 300 cycles, and the capacity retention values after 1000 cycles are 74% [28].

6.3 Double walled Si nanotube design

Controlling the SEI layer growth is the key to maintain the high capacity over long cycle life for Li-ion batteries. As shown by Yi Cui's group in Figure 21, the performance of the double walled Si nanotube anode so far beats all other designs of Si anode[25]. The authors believe that the Li^+ -permeable silicon oxide layer on the outer shell of the tube will give the confinement effect that can effectively prevent the outward expansion of the silicon tube, instead it will lead to the inward expansion of the

tube. Due to the fact that the inner wall of the Si nanotube is not exposed to the liquid electrolyte, a stable solid-electrolyte interphase layer is formed at the outside of the tube. The battery cell assembled with such a designed material has been demonstrated to result in a capacity of approximately eight times of that of the conventional graphite anode and can retain 85% of the capacity after as many as 6,000 cycles. In addition, due to the high surface area of the silicon nanotube, the charging rates of this Si nanotube battery can reach as high as 20C. This design concept vividly demonstrates the mitigation of chemi-mechanical effect associated with the volume expansion of Si upon lithiation.

Figure 21(a) TEM image of DWSiNTs, showing the uniform hollow structure with smooth tube walls; (b) Designing a mechanical constraining layer on the hollow silicon nanotubes can prevent silicon from expanding outside towards the electrolyte during lithiation. As a result, a thin and stable SEI can be built. (c) Lithiation/delithiation capacity and CE of DWSiNTs cycled at 12C for 6,000 cycles. There is no significant capacity fading after 6,000 cycles. Reprinted with permission from Ref.[25].

6.4 Self-healing polymer approach

Another smart design for using silicon as anode is the wrapping of silicon particle by using self-healing polymers[22]. Wang et. al. [22] showed that self-healing of polymers can be spontaneously repaired by the randomly branched hydrogen bonds in itself. The mechanical and electrical self-healing behavior is driven by the dynamic re-association of hydrogen bonds at room temperature. As pointed out, due to the large volume expansion of Si upon lithiation, traditional silicon-polymer composite anodes often suffer from cracks and fracture if the Si nanoparticle is larger than the critical dimension of ~ 150 nm. These mechanical fractures often limit the cycle-life of Li-ion batteries due to the breakage of the conductivity network and formation of unstable SEI layers. However, it has been observed that silicon particle of several micrometer enclosed by the self-healing polymer can lead to amazingly longer cycle life. The dramatically increased cycle life of the battery using this type of large silicon particles based anode is attributed to the contain effect of the self-healing polymer. Again, what has been demonstrated by this design is another example as how to smartly mitigate the chemi-mechanical effect caused by the volume expansion of Si upon lithiation.

Figure 23 Design and structure of the self-healing electrode. Scheme 1: schematic illustration of the design and behavior of a conventional silicon electrode that shows failure of the electrode because of cracking in particles and polymer binder, which results in loss of electrical contact. Scheme 2: schematic illustration of the design and behaviour of our stretchable self-healing electrode that shows the maintaining of electrical contact between the broken particles and no cracks in the polymer binder because of the stretchability and incorporation of self-healing chemistry. Reprinted with permission from Ref.[22].

6.5 The delicate effect of deformable coating layer on lithiation and delithiation of Si

Applying a thin layer of coating on Si nanoparticle appears to be effective for enhancing the capacity retention or cyclability of the electrode as summarized in previous sections. However, fundamental understandings of how these surface coatings alter the lithiation/delithiation behavior and kinetics of Si nanostructures are largely unknown. Based on in-situ TEM studies, Luo et al have noticed that the coating layer can dramatically affect the lithiation rate of the Si as the Li ions have to transport through the coating layer. Generally speaking, the coating layer on the Li ion transport can be evaluated from the following two aspects: (1) The intrinsic Li ion transport characteristics of the coating layer, for which a slow Li ion transport in the coating layer may become a lithiation rate limiting step [38]. (2) The stress effect due to the confinement of the coating layer [18]. As summarized in previous section, the lithiation of both crystalline and amorphous Si follow a two-phase process. The lithiation rate is critically affected by the internal stress due to the volume expansion. With the forming of a conformal coating layer, the internal stress is even hard to be relieved, therefore leading to retardation of lithiation. The internal stress associated with the conformal coating layer depends on the deformation characteristic and thickness of the coating layer. It would be expected that a coating layer with a plastic deformation characteristic would lead to the less degree of lithiation retardation than a stiff coating layer. It has been observed that a constraint of a

deformable coating layer can cause Li ion diffuse out from the lithiated shell, corresponding to the stress induced “self-delithiation” or “self-discharging” effect. Furthermore, associated with the confinement of the coating layer, the critical dimension for fracture of Si nanoparticle is increased. Luo et al have observed that for the deformable polymer coated nanoparticle has a critical size of ~ 380 nm, which is significantly larger than the previously reported size of ~ 150 nm for bare Si nanoparticle [35]. Li transport rate is directly related to the charge and discharge rate of the battery. Therefore, collecting all these together, it can be clearly seen that the coating of Si nanoparticle will lead multiple roles both positive and delirious in terms of battery performance.

6.6 Mesoporous Si sponge design for high capacity and long cycle life

Figure 22 Structure of the mesoporous silicon sponge (MSS) (a and b) SEM images of the MSS at different magnifications. (c) TEM image of the MSS. The scale bar in a, b and c is 20 mm, 100 nm and 100 nm, respectively. Reprinted with permission from Ref. [14].

Another remarkable design relevant to mitigation of the chemi-mechanical effect is to use mesoporous Si sponge as anode for Li-ion batteries as illustrated in Figure 22 [14]. The pore size is ~ 50 nm in size and the Si wall thickness is ~ 10 nm. Due to the porous structure, the apparent volume expansion of Si sponge is greatly reduced, typically to 30% estimated by theoretical calculation, which is also consistently supported by that measured based on in-situ TEM observation. During lithiation, the wall of the silicon sponge increases while the tunnels or voids inside the sponge shrink. The total volume expansion therefore is efficiently reduced by the filling of the room in the anode. The capacity of the mesoporous Si sponge can reach ~ 750 mAhg⁻¹ and more than 80% of its

capacity can be retained after over 1,000 cycles. Above all, the smart nanostructured design concepts for mitigating the volume expansion effect include the incorporation of free spaces in the materials, and in the meantime, to confine the silicon particles that will lead to minimized apparent volume expansion. The effectiveness of these designs in improving cycle performance proves the significance of controlling volume expansion for using Si as an anode in lithium ion batteries.

7. Challenges for transferring the smart nanoscale designing concept from laboratory to real world industrial usage of silicon as anode

As always being the case, moving from the research laboratory to the industry manufacturing and utilization of Si-based anode materials in real world still face great challenges in terms of both technical matrix and economical competence. Great effort needs to be made on how to produce these nanostructured materials in large scale with marketable price and environmental benign. Along this line of thinking, Favors et al. have developed a process for scalable production of porous silicon, which is essentially converting sand into porous silicon[42]. This process is started by millingsand and granularsto nanoscale particle and with further purification. Subsequently, the key reaction follows by the reduction of SiO_2 into Si by using Mg metal. NaCl is added into the reaction to absorb the heat produced in the reaction, promoting the interconnected 3D nano-network. The as-formed MgO and Mg_2Si were then etched away by HCl, resulting in the formation of a 3D porous network of Si. Most importantly, this process is relatively simple and can be easily scaled up for industry applications. The final product-porous Si shows excellent performance over 1000 cycles. Apparently, a direct transferring of the nanoscale smart desining concepts appears not to be straightforward. However, these smart nanoscale designing concepts form the base to inspire concept for optimized tailoring of silicon based materials for practical usage as high capacity anode for lithium ion battery.

Figure 24 Schematic of the heat scavenger-assisted Mg reduction process of sand. Reprinted with permission from Ref.[42].

8. Concluding remarks

In this paper, we reviewed advantages and challenges for potential use of Si as anode for Li-ion batteries. Both ex-situ and in-situ TEM observations, in combination with theoretical calculations, have helped us to gain detailed information on the lithiation and delithiation characteristics of both crystalline and amorphous silicon, typically such as the lithiation kinetics, atomic scale lithiation process, the phase transformation characteristics of Si-Li system, the large and anisotropic volume expansion of crystalline silicon upon lithiation. The fundamental knowledge with respect to the lithiation characteristics of silicon forms the basis for attacking the barriers for using silicon as high capacity anode for lithium ion batteries.

Among all the obstacles of utilizing Si as practical anode, the ~280% volume change upon lithiation/delithiation and the corresponding chemi-mechanical effect are the most critical issue. The internal stress generated as a consequence of the volume expansion during the lithiation plays a major role on the modification of the lithiation kinetics. Broadly, three mechanisms can be identified to account for the failure of using Si as anode. (1) The mechanical instability: such as cracking and pulverization of the Si particle. This problem can be addressed in some way by using particles size that is smaller than the critical size of ~ 150 nm. Further, the critical size can be modified by surface modification or coating or using amorphous silicon. (2) Electrical instability: typically such as the loss of electrical contact among the particles and substrate. Addressing this problem can be mostly relied on the usage of stable conductive additive and coating of conductive polymer on the particle. (3) Electrochemical instability: this is related to the breakdown of SEI layer and reformation of new SEI layer that will consume the electrolyte. Resolving of this problem will be relied on the tailoring of surface chemistry of the Si particle and electrolyte to lead to the formation of a stable or even flexible SEI layer.

Focusing on resolving the above mentioned failure mechanisms of the silicon related anode materials, a range of smart nanostructural designing concepts have been emerged, typically such as Si-C composite, Si-C yolk-shell structure and its variations, oxide wall confinement, polymer coating, and porous structure. Electrode using silicon that was fabricated based on these smart designing concepts has been indeed demonstrated to lead to dramatic electrochemical performance. The key challenge is still the extension of the laboratory research scale to industrial manufacturing.

It appears to be rather ambitious to say that nanoscale design and the materials thereafter to be fabricated will be the route towards commercialization of Si as anode for lithium ion battery. However, it is rather certain that it is just these nanoscale designing concepts that provide key insights that are inspiring and leading to the evolving strategy for tackling the critical issues associated with the large volume change of Si as anode for lithium ion battery. We anticipate that the fundamental knowledge, the nanostructural designing concept summarized in this review will provide valuable clues for rational design of Si-based anode materials with high capacity and significantly enhanced cycle life that can meet the demands of high-energy density lithium ion batteries.

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