The Development of Si Anode Materials by Nanotechnology for Lithium-ion Battery

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Abstract. Nowadays, lithium-ion batteries (LIBs) are applied in many fields for their high energy density, low cost, and long cycle life, highly appreciated in a commercial application. Anode materials, a vital factor contributing to high specific capacity, have caught great attention in next-generation LIBs development. Silicon (Si) has been generally considered one of the best substitutes for the commercial carbon-based anodes of lithium-ion batteries due to its extremely high theoretical capacity, excellent charge-discharge performance, and low cost compared with other anode materials. In this review, various silicon-based materials, including nanostructured silicon and silicon composite materials, are summarized, and both advantages and challenges are analyzed. The article emphasizes the remarkable electrochemical characteristics and significant improvement of battery performance by applying nanostructure and silicon composites conjugates. Besides, the challenges and outlook on the nanostructure design of Si and silicon composites are presented.

1 Introduction

Due to the growing traffic stress, more fuel vehicles are running on the street, leading to environmental degradation, manifested in both over-exploitation of fossil fuel and the greenhouse effect. Therefore, a rechargeable battery of lithium-ion batteries (LIB) offers characteristics of light weight, high power density, and high specific energies comparing with conventional batteries [1-3]. Besides, a higher energy density of LIBs is needed to satisfy the increasing requirement of electric vehicles. There are four parts involved in the LIB: cathode, anode, separator, and electrolyte, shown in Figure 1 [4]. Cathode materials involve commercial cathodes, including lithium iron phosphate ($LiFePO_4$) and lithium cobalt oxide ($LiCoO_2$), high-voltage cathode materials like $LiCoPO_4$, Li- and Mn-rich derivatives xLi_2MnO_2-$(1-x)LiMO_2$ of crystal structures of $LiMO_2$ (M = Ni, Mn, Co) [5], family of Li-rich layered oxides ($Li_{1+x}M_{1-x}O_2$ or xLi_2MnO_3-$(1-x)LiMO_2$, M=Mn, Ni, Co, etc.) as well as family of Ni-rich layered oxides ($LiNi_{1-x}M_xO_2$, M=Co, Mn and Al) [6,7], metal fluoride cathode materials (CuF_2, FeF_3, CoF_2, NiF_2) [8,9] and so on, shown in table 1, which summarize typical cathode materials [10]. Then, anode materials cover high-capacity anode materials like graphite and lithium titanate ($Li_4Ti_5O_{12}$, LTO) [11,12], which have been put into commercial applications. They also cover multiple high-capacity anode materials, which cover transition metal sulfides (NiS), oxides (Fe_2O_3) and fluorides (TiF_3) [13], and Silicon [14] shown in table 2. By comparing the specific capacity among different materials of cathodes and anodes, it is apparent that anode materials have more space to improve.
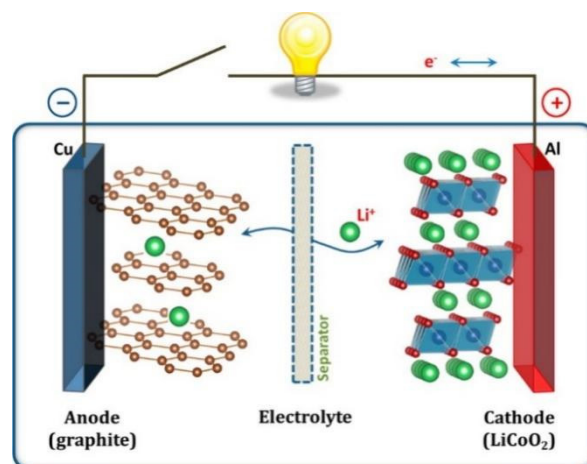

Figure 1. Schematic illustration of the first Li-ion battery ($LiCoO_2/Li^+$ electrolyte/graphite). Copyright 2013 J. Am. Chem. Soc.

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Table 1. Summary of selected cathode materials. Copyright 2020 Chem Soc Rev.

Active materials	Specific capacity mA h g^{-1}/mA h cm^{-3}	Potential (V *vs.* Li$^+$/Li)	Advantages	Disadvantages
LiFePO$_4$	170/612	3.4	Low cost, long stable cycle, commercialization	Low electronic conductivity, low specific capacity, low energy density
LiCoO$_2$	140/714	3.8	Long cycle, mature technology, high voltage, high energy density	High cost, low thermal stability, irreversible phase change
High-voltage LiCoO$_2$	185/944	3.95		
LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$	200/930	3.8		
LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$	220/979	3.6		
LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO)	147/625	4.7	Super high voltage, high energy density	Low specific capacity, low thermal stability, irreversible phase change, electrolyte decomposition, poor cycle stability
LiNiPO$_4$ (LNP)	169/657	5.1		
LiCoPO$_4$ (LCP)	167/618	4.8		
CuF$_2$	528/2002	3.55	High specific capacity, low cost, high energy density	Large voltage hysteresis, poor cycle stability, low reversibility, poor rate capability, material dissolution, volume change
FeF$_3$	712/2196	2.74		
CoF$_2$	553/2038	2.80	High specific capacity, high energy density	
NiF$_2$	554/2040	2.96		
CuCl$_2$	399/1115	3.17	High specific capacity, low cost	Highly soluble in liquid
FeCl$_3$	496/1172	2.83		
S	1675/1937	2.28	Abundant, low toxicity, rather low cost, high specific capacity, high energy density	Dissolution and shuttle, low working potential, low electronic conductivity, large volume change
Li$_2$S	1166/1937	2.28		
O$_2$	1675/2698	2.96		Rather poor reaction kinetics
Li$_2$O$_2$	1168/2698	2.96		
Se	679/1659	2.07	High specific capacity, high electronic conductivity	High cost/high toxicity, dissolution and shuttle, low working potential
Li2Se	578/1659	2.07		

Table 2. Summary of selected anode materials. Copyright 2020 Chem Soc Rev.

Active materials	Specific capacity mA h g^{-1}/mA h cm^{-3}	Potential (V *vs.* Li$^+$/Li)	Advantages	Disadvantages
Graphite	372/735	0.17	Commercialization, long cycle stability	Low specific capacity, low energy density
Li	3861/2062	0	High specific capacity, low working potential, high energy density	Infinite volume change, Li dendrite formation, short circuit, high reactivity, consuming electrolytes
Si	3579/2190	0.4	High specific capacity, low working potential, high energy density, low cost	Large volume change, unstable interface, low first CE
P (red)	2596/2270	0.8	High specific capacity, high energy density, low cost	Large volume change, unstable interface, low first CE
Al	993/1386	0.38		
Sn	994/1991	0.38	High specific capacity, high energy density	Large volume change, unstable interface, low first CE, high cost
Ge	1384/2179	0.4		
Li$_4$Ti$_5$O$_{12}$, (LTO)	175/607	1.55	No volume change, long cycle stability, high rate capacity	Low specific capacity, low energy density, high working potential, high cost
Fe$_2$O$_3$	1007/2741	1.2	High specific capacity	High working potential, high cost, low first CE, large volume change
NiS	591/1571	1.3		
TiF$_3$	767/2002	1.4		

Silicon (Si), as one kind of anode material, is a promising alternative material to meet the demand for the higher energy density of LIBs. Since the theoretical capacity of Si is 3572 mA h g^{-1}, which is higher than that of a traditional graphite anode (372 mA h g^{-1}) by 10 times. Therefore, Si is regarded as a perfect substitute with carbon-base materials due to the higher theoretical capacity, low working voltage (~0.2 V vs. Li/Li$^+$), and higher abundant available from the earth. However, many obstacles block the practical commercial applications for Si anode, such as low electrical and ionic conductivity, huge volume expansion, and unstable solid electrolyte interface (SEI). The Li$^+$ intercalation-deintercalation progress of silicon will cause a larger volume change (>300%) than that of graphite materials during the charge-discharge processes, which will not only cause repeated

cracking and fragmentation of Si, but also the disintegration, fracture, and electrical isolation of Si. The continuous cracking progress will damage the SEI and the advanced interface, which will result in rapid consumption of Li^+, ending up an unstable and repeating-fragmented SEI film, which may contribute to low initial Coulombic efficiency (ICE) and the drastic decrease of capacity.

Scientists and engineers have developed various methodologies in pursuit of stable Si-anode LIBs. Nanotechnology was used to develop all kinds of nanostructures of Si in the past couple of years. Nano sized silicon particles (the critical value <150 nm) can withstand the high mechanical stresses due to volumetric change without fracture, which can tackle the problems caused by continuous lithiation /delithiation. Additionally, the larger surface area of nano-structured Si materials, including nanowires, nanotubes, and some newly developed nanostructures like nano-vault, is also beneficial to increase the electrode-electrolyte contact area. It contributes to a more rapid lithiation and delithiation and enhancing the electrode kinetics and electronic contact between the anode material, the current collector and the electrolyte, and improving the electrochemical performance (e.g., high reversible capacity of approximately 2000 mA h g^{-1} [15]). At the same time, Si-C nanocomposites material is also considered a good solution to the challenges raised by the conventional Si-anode LIBs. The carbon matrix can provide voids that allow the volume change of the nanoparticles and a stable solid-state interface between the electrode and the electrolyte. It makes the Si-C nanocomposites a compatible anode material with high electric conductivity and recyclability (the capacity reached as high as 1006 mA h g^{-1} after 500 cycles). However, a volumetric change of more than 300% during battery cycling causes repeated expansion and contraction in the anode structure, leading to particle cracking and active material isolation, ultimately resulting in a rapid, reversible capacity loss.

2 Nanostructured Si applied in Lithium-ion battery

The application of nanotechnology can relieve the volume expansion problems and has been proven beneficial in improving the reversible capacity of the silicon-based lithium-ion battery [16]. The nanostructured Si anode is resistant to high mechanical stress and making it be able to accommodate the significant strain caused by the electrochemical alloying without crack. In general, the main purpose of this topic is to illustrate and discuss the currently existed cases of the use of different nanostructure morphologies (nano-porous silicon, Si nano tube, nano wire, nano flake, nano sheet or the combination of these structures) in the improvement of silicon-based anode LIBs concerning their functionalities and limitations that need to be tackled in the further studies.

2.1 Nano-porous silicon (NP-Si)

Nano-porous silicon has been proven to be a promising material for the anode of LIBs for its outstanding cyclability. Dr. Cho has delicately prepared a 3D nano porous Si by depositing Si particles on SiO2 nano porous templates through a meticulous and complicated procedure, in which carbon is necessary to be applied to prevent the formation of SiO_x on the Si particles [17]. Hence this nano geometry can accommodate the continuous volume change caused by lithiation and delithiation, which has a little negative impact on the coulombic efficiencies of the electrodes during electrochemical alloying after plenty of cycles. Thus, there is not a considerable degradation in the capacity of the 3D-porous Si (up to 100% remaining, approximately over the range of 2400 to 2800 mAhg−1 depending on the rate of cycling). Meanwhile, there present no perceptible morphological variations even after 100 cycles shown in Figure 2.
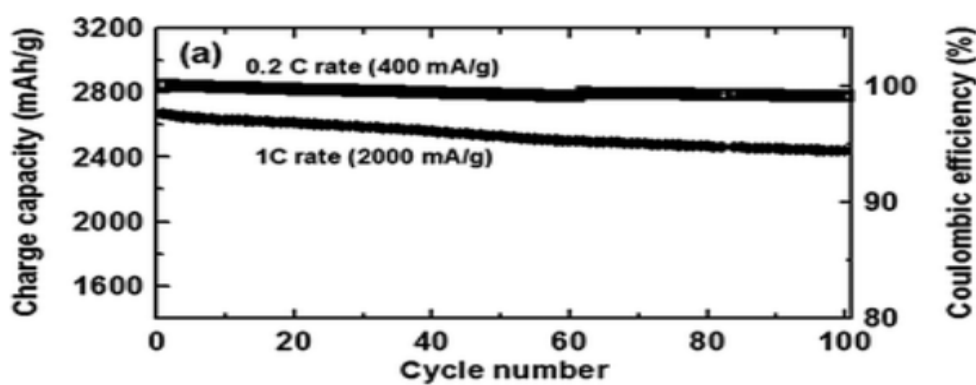

Figure 2. The change of charge capacity of the 3-dimensional nano-porous silicon with respect to the number of cycles under different cycling rates (0.2C & 1C).
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However, the expense and highly inefficient fabrication procedure hinder it for practical application and commercial scale-up. This approach utilizes the network structure of the Si nano ligaments (or nanowires) surrounding the interconnected nanopores shown in

Figure 3 [18]. It is efficient and applicable, since bulk 3D nano porous Si can resist the volume change associated with lithium-ion insertion and extraction as the nanopores provide sufficient spaces for the Li ions, giving rise to the excellent ability of capacity retention. At the same time,

manufacture of this material only requires the basic and simple metallurgical top-down process – dealloying with

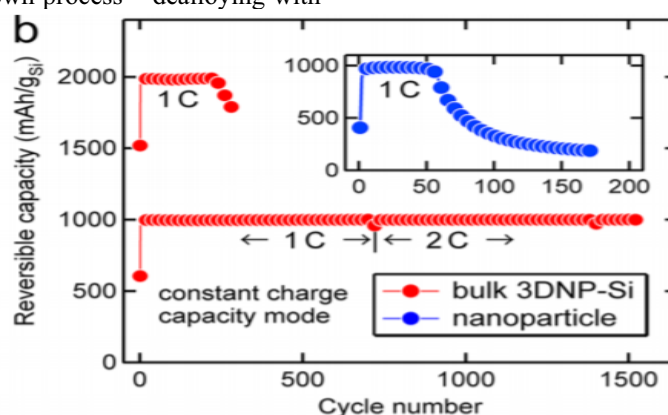metals with different alloy miscibility in a metallic melt.

Figure 3. The comparison between the 'capacity vs. cycle number' curves of bulk 3D nano porous silicon and commercially utilized nanoparticles under the constant charge capacity of 1000 and 2000 mAhg-1. Copyright 2010 Journal of Materials Chemistry.

2.2 Silicon nanosheet.

Although the 0D or 1D nanostructures of silicon nanomaterials have successfully provided the high specific capacity to the lithium-ion batteries, there are still some problems of pulverization and loss of relatively electrical connection between separated nanostructure after cycling of battery [19]. Silicon nanosheets, a kind of 2D nanostructures, have a leaf-like sheet morphology ranging from several ten to several hundred nano meters shown in Figure 4 [20], which Tritsaris develop in 2013 [21]. The developed silicon nanosheets offer excellent cycling stability while providing high specific capacity because of high lithium storage capacity, fast lithium diffusion rates, low discharging potential, and low diffusion energy barrier of lithium ion. 2D porous silicon nanosheets anode material developed by Tang under the template of graphene oxide nanosheets, aggregating silicon nanocrystals (~10 nm) reaches a reversible capacity of 800 mAh/g after 900 cycles at a rate as 8400 mA/g [22]. Ni-Si nanosheet network developed by Wang, shown in Figure 5, combines Si film with an interconnected Ni nanosheet network, achieving a high specific capacity of 2038 mAh/g at 840 mA/g after 100 cycles and excellent cycling stability of 655 mAh/g at 8400 mA/g over 1000 cycles [23].
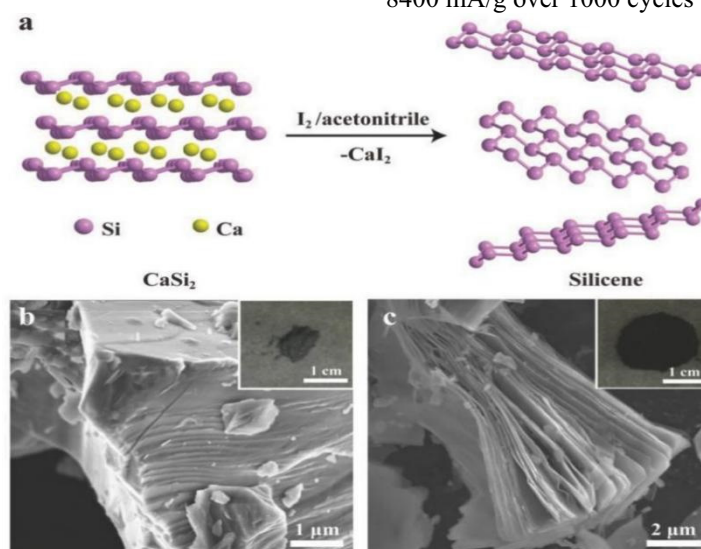

Figure 4. a) Schematic illustration for the synthesis of Silicone from CaSi₂via liquid oxidation and exfoliation. b,c) SEM images of pristine bulk CaSi₂ (b) and the as‑reacted product (c) with the insets showing their photographs.
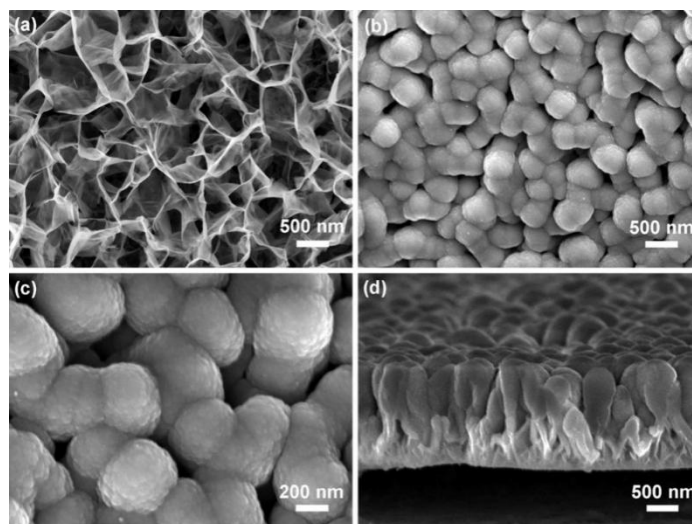. Copyright 2018 Adv. Mater.

Figure 5. The top view SEM image of (a) $Ni_3(NO_3)_2(OH)_4$ nanosheet networks; he (b) low and (c) high magnification SEM images of Ni–Si nanosheet networks; (d) side view SEM image of Ni–Si nanosheet networks.
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However, fabricating nano sheets of silicon still has challenges on the toxic precursors and cost. At present, three methods have been put forward to overcome these challenges, including etching and exfoliation, chemical vapor deposition (CVD), and template-directed synthesis (TDS) [24]. Thus, developing the large-scale and low-cost technique of silicon nanosheet fabrication or looking for the alternative nano structure of Si is highly demanded now.

2.3 Si nanowires

Silicon nanowires (NWs) have been widely investigated and attracted great attention due to the following reasons: (1) a high surface-to-volume ratio; (2) accommodate larger volume variation; (3) void space constructed by adjacent Si NWs; (4) provide rapid pathways for electronic and ionic transportations [25]. The vapor-liquid-solid synthesis (VLS) method based on chemical vapor deposition (CVD) is one of the most used approaches to prepare Si NWs. Chan et al. [26] reported a Si anode design conception adopted NW electrodes which were grown directly onto current stainless collectors. These Si NWs can accommodate large strain produced during the Li^+ insertion-extraction progress, shorten the Li^+ diffusion distance and keep good electronic contact with the current collector, as shown in Figure 6. Nguyen et al. [27] produced highly interconnected Si NWs with a specially designed structure that could avoid the separation of Si NWs from substrates under excessive tension and improved the cycling performance of the anode material. The initial specific capacity is 3500 mAh/g, and after 40 first cycles, the discharge rate of 2.1 A/g and capacity retention is almost 100% (3100 mAh/g). The capacity retention slightly decreased to 94.5% after 50 cycles, (2930 mAh/g).
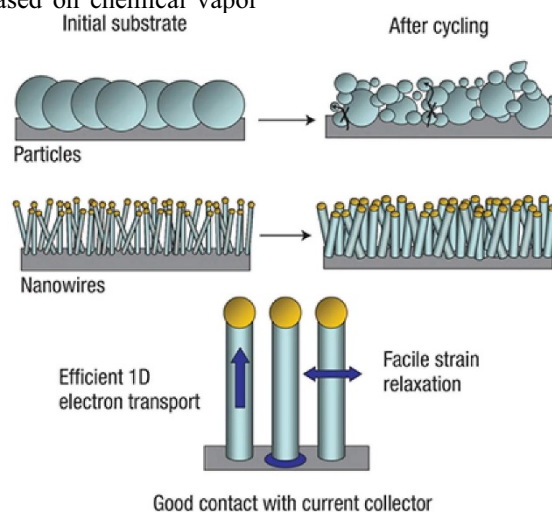

Figure 6. Schematic of morphological changesof Si nanowires and Si nanoparticle before and after cycling. Copyright 2008, American Nature Publishing Group.

To improve the mass loading of Si NWS, Hu et al. [28]   reported a 3D porous Si NWs by depositing the Si particles

from a Si ink with subsequent CVD coating of a single-layer Silicon with a network structure which increased the areal capacity from 0.6 to 2.5 mAh/cm² compared to pure Si NWs. Moreover, Leveau et al. [29] used the CVD progress with two steps (Figure 7a) to compose a new Si nano-tree structure material for anodes. The first step is conventional deposition progress (Figure 7b), while the

second step enabled the catalyst layer to evaporate on the Si NWs electrode. (Figure 7c). After the development of progress, it finally acquired a high-density Si nano-tree electrode with an area-capacity of over 7 mAh/cm² and a mass loading of 2.47mg/cm², along with increased capacity stability.
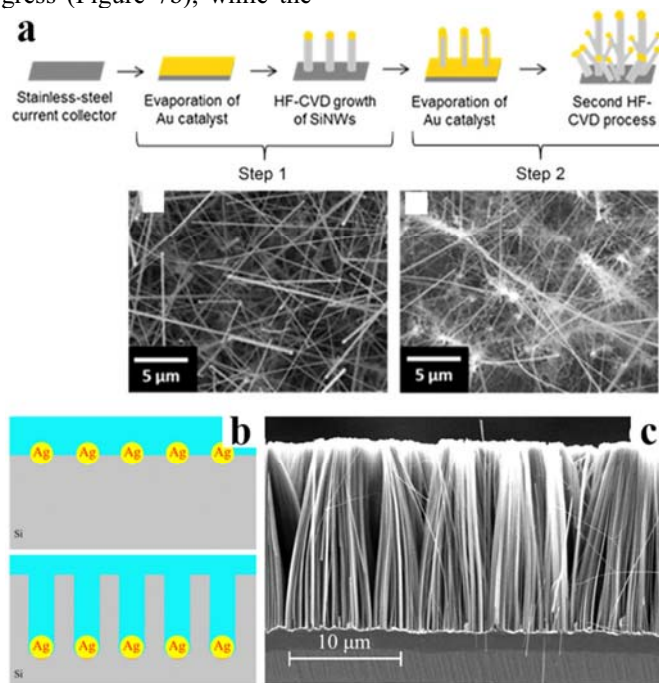

Figure 7a. Schematic illustration of the two-step progress of interconnected Si NWs. Copyright 2016, Elsevier.
7b. Schematic formation, and 7c. typical cross-sectional SEM image of Si NWs arrays.
Copyright 2008, American Institute of Physics.

2.4 Si Nano film

The Si thin film obtains the following merits: (1) accommodate and relieve the longitudinal strain caused by volume expansion; (2) increase the contact and react area between the materials and the current collector. According to S. Ohara et al., the amorphous n-type 50nm Si films obtained by vacuum deposition gain a high initial capacity of 3750 mAh/g. In contrast, the reversible capacity is close to 3800 mAh/g after 200 cycles at the 1C current rate, which shows good capacity stability. (Figure 8) [30]. However, when the thickness of Si films increases, the anode performance decreases. As the thickness of Si films increased to 150 nm, the reversible capacity goes down to near 2300 mAh/g after 200 cycles due to the lower diffusion of lithium in silicon.
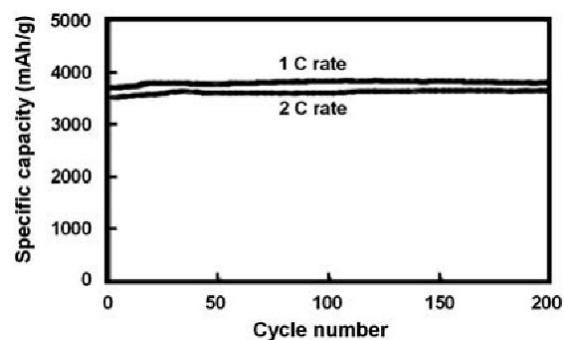

Figure 8 Capacity of a 50 nm thick amorphoussilicon electrode at 1C and 2C rates. Copyright 2011 The Royal Society of Chemistry

2.5 Other types of nanostructures.

Besides the nanostructure mentioned above, other silicon-based nanostructure materials as anode materials, including nanocomposites, nanospheres and nanoparticles, are under research. In 2006, by developing a spray-pyrolysis technique with a large operating temperature range (150-1400℃), Ng fabricated a spheroidal carbon-coated silicon nanocomposite as anode material in LIBs, which provide a high capacity of 1489 mAh/g and a high coulombic efficiency about 99.5% after 20 cycles [31]. In 2007, Ma reported a nest-like silicon nanospheres with

large specific capacity of 3628 mAh/g at 400 (0.1℃), 3291 mAh/g at 800 (0.2℃) and 3052 mAh/g at 2000 (0.5℃), shown in Figure 9 [32]. In 2013, Ge developed a novel scalable preparation to porous silicon nanoparticles, which can apply to LIBs, providing capacities of approximate 1400 mAh/g at 1A/g and 1000 mAh/g at 2A/g [33].
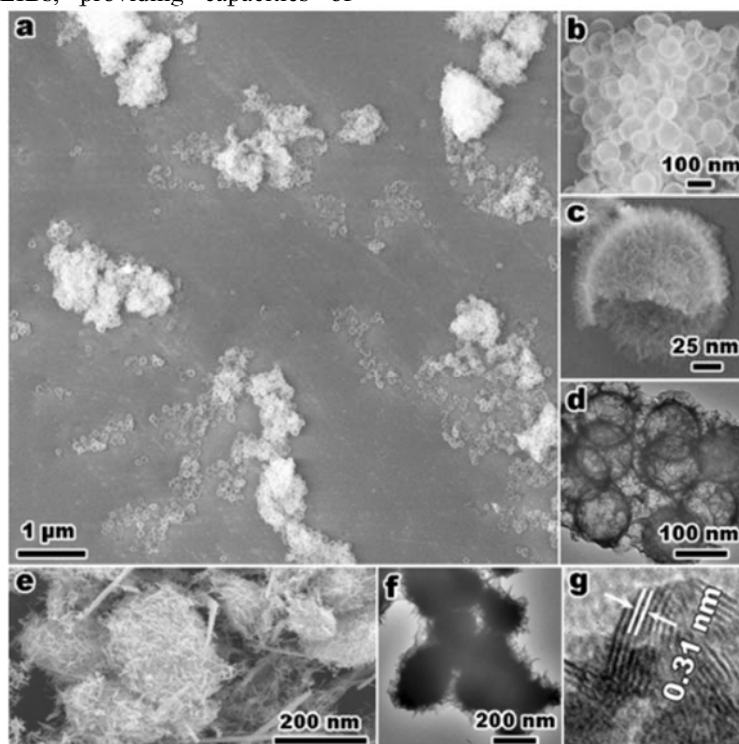

Figure 9 a–c) Scanning electron microscope (SEM) and d) transmission electron microscopy (TEM) images of nest-like Si nanospheres. e) SEM, f) TEM, and g) high resolution TEM images of coil-like Si nanospheres. Copyright 2007 Adv. Mater.

3 Si composites applied in lithium-ion battery

3.1. Si-C composite.

Different fabrication methodologies have been applied constitute Si-C composite anode material with a variety of architectures (such as the carbon-encapsulated silicon nanoparticles or Si-C yolk-shell structure, the lamellar structure of graphite flakes and the incorporation of carbon nanotubes in the Si/graphite composites, Figure 10) [34-36] in the pursuit of better performance. CVD (Chemical Vapor Deposition) and other deposition techniques with more practical and economic structural or hierarchical designs and fabrication processes should be applied in the large-scale production of high-performance Si-C nanocomposite anode material. Furthermore, the carbon nanotube can act as buffer that can accommodate the volume expansion because of its high-resilience characteristics. It leads to a pyrolytic carbon coated silicon/CNT composite electrode with good cyclability (discharge capacity of 727 mAh/g after 20 cycles compares to 363 mAh/g without the application of CVD but simply the pyrolytic carbon coated mixture of nanosized silicon and CNTs.
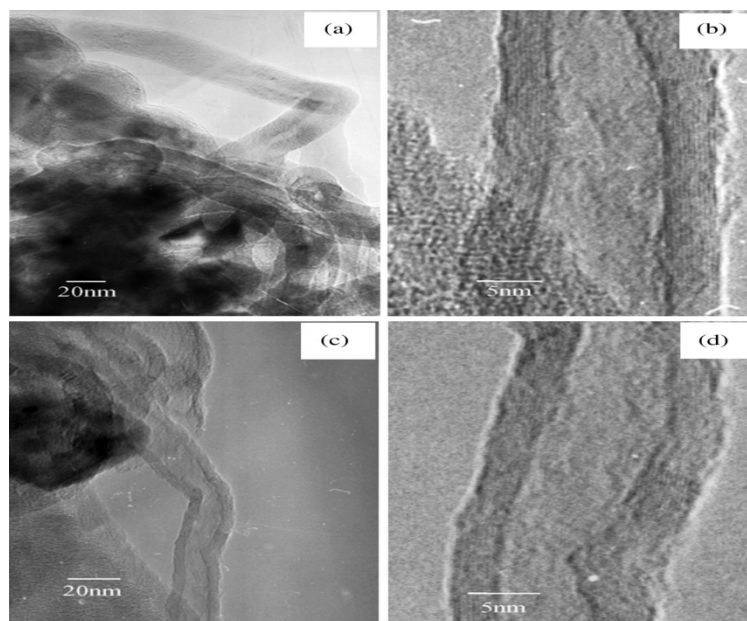
Figure 10. High resolution TEM micrographs of (a–b) Si/CNT (carbon nanotube) systems and (c–d) Si/CNT/C (pyrolytic carbon) systems. [37]. Copyright 2014 Journal of Power Sources.

More recently, a pomegranate-inspired nanoscale design of the secondary structure of the Si-C composite anode was introduced by Nian Liu and his group in 2014, as shown in Figure 11 [38]. The nanosized silicon is immune to potential fracture. The silicon anode's internal void space can accommodate the volume expansion during lithiation without changing the dimensions of the silicon particles. The carbon framework encapsulated the silicon nanoparticles can act as an electrical highway due to its excellent intrinsic conductivity and control the formation of SEI to the outer surface of the multicomponent system rather than on the individual nanosized silicon particles. Thus, the well-defined internal void spaces in the secondary particles can be retained to accommodate the volume change without cracking the outer carbon coatings and deforming the overall system as the carbon framework functions as the electrolyte-blocking barrier. Eventually, they lead to outstanding cyclability (97% capacity retention after 1,000) and volumetric capacity (1,270 mAh cm^{-3}).
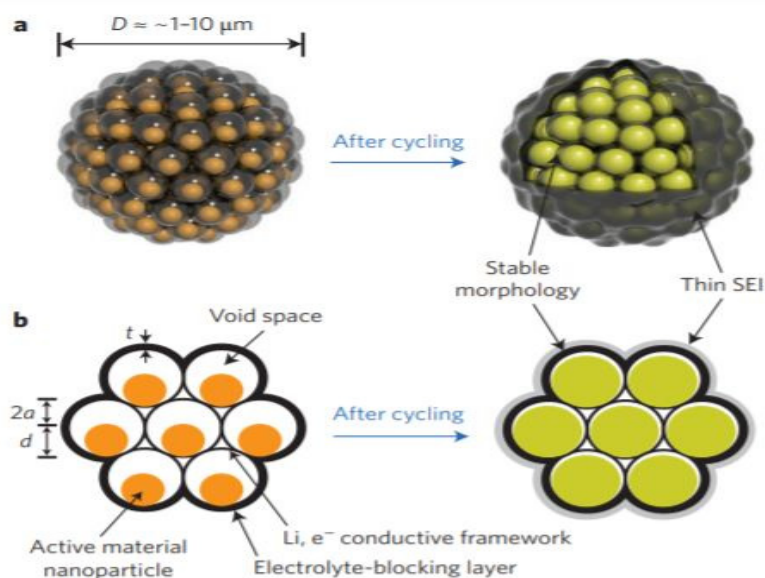

Figure 11. Illustrations the of the pomegranate-inspired design. (3D simulation for 'a' and cross-sectional 2D view for 'b'). Copyright 2014 National Nanotechnology.

3.2 Coated Si nanomaterials

To solve the pulverization of silicon particles during lithium intercalation/ deintercalation, coated silicon nanostructure materials are highly demanded to study [39-41]. Therefore, coating silicon-based anode materials with layers nanostructure can help to deal with these problems. A molecule layer was coated on the surface of silicon

particles, playing a role as a glue to prevent particles from pulverization. As a result, the stability of anode materials is improved after cycles of charge/discharge [42]. Figure 12 shows a schematic of the bonding of the aluminum with the Si surface, and Figure 13 shows different behaviors of silicon nanoparticles under different coating conditions of lithiation/delithiation [43]. Several materials have been applied in coated silicon anode materials, such as carbon-based materials, metal particles, metal oxide particles, and so on [44]. By coating this material on Si NPs as an anode, it showed a stable cycling behavior with discharge capacities of 1020mAh/g after 200 cycles and 650mAh/g after 500 cycles at 0.36A/g. Meanwhile, the initial discharge capacity is 3300mAh/g. Copper has also been used as a coating material. Sethuraman developed a copper-coated silicon anode, achieving an available capacity decrease of 8% with 40nm copper-coated silicon electrode between 3C and C/8 discharge rates. In comparison, equivalent silicon thin-film electrode makes a decrease of 18%. Tang developed titanium nitride coated silicon nanoparticles by reduction of TiO_2 coated silicon. This anode material exhibits remarkable cycling stability, whose reversible specific capacity is 1900mAh/g at a 0.1 C rate after 100 cycles. Apart from those materials, lithium fluoride and silicon nitride have also been used as coating materials. Lin fabricated LiF coated silicon nanocolumns in LIBs, achieving a superior rate capacity and high cycling stability [45]. Wu synthesized silicon nitride coated silicon in LIBs, getting a capacity of 1121mAh/g after 200 cycles, only 0.2% of decrease during each cycle [46]. However, by adapting coated silicon anodes, the negative impacts of high cost and low yield as well as complex and dangerous preparation process can be relieved. Thus, many factors such as thickness, chemical activity, and ion transport velocity impact the electrochemical properties of batteries in this technique and need to be further studied.
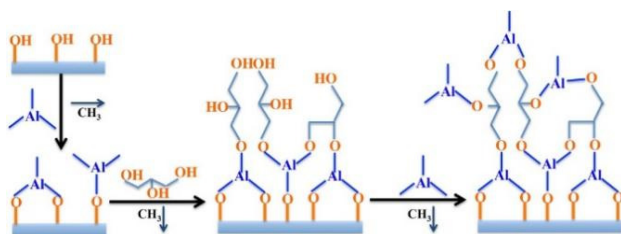

Figure 12 Schematic drawing showing the bonding of the alucone with the Si surface. Copyright 2014 ACS Nano

Figure 13 Schematic of surface reactions and cycle behaviors of silicon nanoparticles with different coating conditions and captured in situ TEM images of the alucone-coated Si nanoparticles during the lithiation/delithiation behaviour. Copyright 2014 ACS Nano

3.3 Si-Metal nanomaterials

The Si-metal (M-Si) composite material, as one of the potential materials to improve the performance of anodes of LIBs, is being widely investigated because metal has superiorities in good conductivity and high mechanical strength. Compared with other silicon composites, the Si in M-Si has stronger adhesion with the substrates, which results in better stability of the electrode structure and cycling performance. M can be inert to Li-ion, such as Fe, Cu, and Mn, or react with Li-ion, like Ca, Mg or Sn. Many metals are easy to form alloy phase with Si, which can effectively buffer the volume expansion of Si during the charge-discharge process by using ball milling as a traditional synthesis method. In addition to the ball milling method, there are other methods like vacuum sputtering and electroless plating [47,48].

Sun et al. prepared copper silicon core-shell conical nanostructured anode materials for free-standing LIBs [49]. The copper core was used as both supporter and current collector while the amorphous Si shells acted as the active material of the negative electrode, as is shown in Figure 14a). As shown in Figure 14b, the unsealed copper nanotubes provided a larger volume for the inward expansion of Si. In addition, the top of the copper core contacts both sides of the amorphous silicon so that the expansion force might be released on the side wall of the core, which earned a long cycle life performance. After 400 charge-discharge cycles, the fading rate of less than 0.1% and a specific capacity of 1506 mAh/g showed a good performance in capacity retention and structural stability. Song et al. prepared a Si-Ge composite material used as an anode electrode of LIBs. The discharge capacity maintained 1346 mAh/g with a coulombic efficiency of 94.4% in the first cycle. After 50 cycles, the Si-Ge NWs remained the capacity retention of 72.4% with an improved rate capability at all current [50].
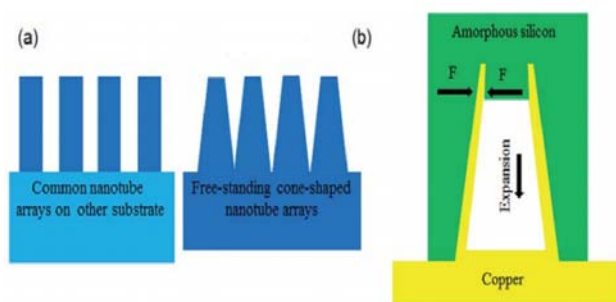
Figure 14 (a) Comparison between tradition structure and Sun`s structure. (b) Cross section of Sun`s core-shell structure. Copyright Journal of Materials Chemistry A, 2014

4 Conclusion and outlook

In this review, silicon-based anode materials of LIBs, including both silicon nanostructure and silicon composited, are summarized and discussed. In addition, challenges of each anode material are also addressed, and further study on overcoming the drawback is needed. As for Si nanostructures, nano porous, nanosheets, nano wires, nano films, and nanoparticles and nanospheres are summarized to improve the electrochemical performance. However, an interconnected nanopore surrounding the Si nano ligaments network structure is considered an effective method to deal with the problems. Silicon nanosheets relieve the pulverization of anode materials, but the preparation process still suffers from toxic precursors and cost. Silicon nano wires (NWs) provide a higher transport speed of particles and good adaption to volume variation, which reduces the decay of specific capacity after long term cycling. Si nano films applied on anode materials contribute to larger specific capacity, better stability, and longer service time. Silicon nanospheres and nanoparticles have also been used to improve the specific capacity and cyclability of silicon-based anode LIBs. In terms of silicon composite anode materials. Si-C composites, coated silicon materials, metal oxide composites are included. Si-C composite, using carbon, which has good intrinsic conductivity and ability to stabilize SEI, to tackle the problem of volume change of anode materials during the process of charge/discharge, is an ideal alternative anode material of LIBs providing a remarkable reversible capacity and cycling performance. Coated silicon materials using various materials, including carbon-based materials, metal particles, and metal oxide, coated silicon nanostructures like glue, also relieve the negative impact of volume change on anode materials. In addition, Si and metal oxide composite taking superiorities of metal such as Fe, Cu, and Mn, into usage effectively improve the performance of anodes in LIBs. All those novel materials and nanostructures, all aiming to improve the specific capacity and relieving the impact of volume change on anode materials, are promoted to a stable behavior of LIBs after long term cycling. However, these techniques suffer from challenges including toxic, high cost, and low yield preparation procedure, and the cycle time is also a limitation towards commercial application.

In the future, a study on the wild preparation procedure, a novel fabrication process technique with non-toxic, low cost, and high yield, should be further conducted. Besides, research on the combination of multiple nanostructure and materials needs to be carried out to take advantage of various techniques. With these considerations, Si as high energy anode materials can be widely used in commercial and electrical vehicle batteries more efficiently.

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