Latest development of nanostructured Si/C materials for lithium anode studies and applications

Abstract

Silicon anodes for lithium-ion batteries have been extensively explored due to their high capacity, moderate operation potential, environmental friendliness, and high abundance. However, silicon's application as anodes is hindered by its poor capacity retention caused by the large volume change during lithium insertion and desertion process, its intrinsic low conductivity and the formation of unstable solid-electrolyte interphase (SEI) films. Recently, influential improvements have been achieved using different design methods with the purpose of increasing cycle life and increasing charging rate performance. Here, we review such design methods including the rational design of nanostructured silicon, the combination of silicon with different carbonaceous materials including traditional carbons and the utilization of nanocarbons (such as carbon nanotube, graphene and corresponding three dimensional architectures). Meanwhile, we draw the essential reason accounting for the excellent electrochemical performance of those structures. Furthermore, we selectively depict the effects of binder, conductive additives and electrolyte composition, which also play important roles in silicon based battery performance.

Keywords

Lithium ion batteries; anodes; Si/C composites; Carbon nanotubes; Graphene

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1. Introduction

Energy is one of the most important topics of the 21st century. Ever rising demands for energy coupled with the depletion of finite fossil fuel and the emission of contaminative gases have encouraged scientists to develop new energy storage and conversion technologies for renewable and clean energy sources. Among various energy storage technologies, electrochemical storage is considered as one of the most promising technologies, especially for the applications of electric vehicles (EVs), plug-in hybrid electric vehicles (PHEVs) and hybrid electric vehicles (HEVs) [1-5]. Moreover, the popularization of portable electronics and communication equipment worldwide stimulates the development of energy storage devices, such as batteries and supercapacitors with higher energy density and higher power density respectively [6]. Lithium ion batteries (LIBs) are widely used as a convenient power source for various portable electronic devices and are considered as potential energy source to power EVs, HEVs and PHEVs [7-12].

A LIB is mainly composed of an anode (negative), a cathode (positive), a separator, and a certain amount of electrolyte [13, 14]. The positive electrode materials are typically Li-containing metal oxides and the negative electrode materials include insertion-type materials (such as graphite, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), etc.), and alloying-type materials. The function of the separator is to prevent short circuiting between the cathode and anode electrodes and to provide abundant channels for

transportation of Li ion during charging/discharging. The electrolyte should be a good ionic conductor and electronic insulator and most of them are based on the solution of inorganic lithium salts dissolved in a mixture of organic solvents. Currently, most commercially available LIBs are made with graphite as the anode material and lithium metal oxides/lithium iron phosphate as the cathode material. The theoretical capacities of these anode and cathode materials are 372 mAh g^{-1} and *ca.* 200 mAh g^{-1} , respectively, resulting in energy density of *ca.* 200 Wh Kg^{-1} . However, this energy density value cannot satisfy the demands for higher energy density batteries used in emerging new-type electronic devices, advanced communication facilities, and in particular, EVs or HEVs.

The energy density of a battery is mainly determined by its output voltage and specific capacity, which are dependent on the electrochemical properties of electrode materials[15]. Alloy type anode materials with high theoretical capacity and low operation voltage, such as silicon and tin, have been intensively explored to further increase the energy densities of LIBs for the above-mentioned applications[16]. Silicon (Si) is one of the most promising alloy type high capacity alternatives to graphite anodes. Si offers a high theoretical capacity of 4200 mAh g^{-1} because each silicon atom can accommodate 4.4 lithium atoms corresponding to the formation of $\text{Li}_{22}\text{Si}_5$ alloy. This theoretical specific capacity of silicon anode is *ca.* 10 times higher than that of graphite, and *ca.* 20 times higher than that of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO). The second merit of Si anodes is its moderate operation potential versus lithium (*ca.* 370 mV above Li/Li^+) [17]. Thirdly, Si is the second most abundant element on earth and it is environmentally benign. Furthermore, there are large and mature infrastructures for its processing and there are growing approaches using cheap raw materials to fabricate nano-Si particles [18, 19]. For example, Cui and coworkers recovered Si nanoparticles directly from rice husks, an agricultural waste, in which the silicon naturally exists in the form of silica nanoparticles, which show good electrochemical properties when tested as anodes in cells [20].

However, the use of bulk Si experiences large volume changes (undergoes up to a 300% volume expansion and contraction) as Li ions enter and leave the Si lattice,

which shortens the cycle life and contributes to cell failure [16, 18]. The mechanism that affects the electrode lifespan need to be discussed first: (1) Particle pulverization: during the process that lithium ion insert into the Si lattice, the Si particle grow larger and larger and they will collide into and squeeze each other until attaining three folds of their original volume, leading to extremely large stresses, which cause cracking and pulverization of active particles. The cracking and pulverization of the Si particles can cause lithium trapping in the active material and progressively consume of active material during cycling, all of which contribute to low Coulombic efficiency and high irreversible capacity. (2) Disruption of the electron-ion transport pathways at the level of the entire electrode: The electrode is composed with Si particles as active materials, carbon black to enhance the conductivity and binder to facilitate the integrity of the whole electrode. During lithiation process, the Si particles expand, suppressing the surrounding materials expanding at the same time, which exceed the mechanical elongation of them, resulting in electrical detachment of the surrounding components with active materials. Finally, this drastic electrode morphology change combined with intrinsic low conductivity disrupt the electron-transport pathways and further contribute to capacity fade. (3) Unstable solid-electrolyte interphase (SEI): When the potential of the anode is below *ca.* 1 V versus Li/Li^+ , the decomposition of the organic electrolyte at the electrode surface is favorable, forming the SEI layer. If the SEI layer is dense and stable, it can prevent further side chemical reactions. But the SEI layer on the Si surface continuously breaks and the fresh Si unceasingly expose to electrolyte during lithium insertion and desertion, leading to extremely thick SEI layers and excessive consumption of lithium ions and electrolyte. As a consequence of this process, even if most of the Si active materials remain electrically connected, the capacity decays because of the poor electronic conductivity and the exhaustion of the electrolyte.

To overcome the drawbacks of Si as anode materials, significant number of achievements have successfully addressed the problems. There have been several special reviews on Si as anodes for LIBs in the recent two years (2014 and 2015) [21-27]. Xu et al. described the progress in Si-based materials utilized in LIBs in

terms of composite systems, nanostructure designs, material synthesis methods, and electrochemical performances [21]. Lestriez et al. summarized the influence of the different parameters of the formulation of silicon-based composite electrode on its cyclability [25]. Metal-assisted chemical etching of silicon and nanoscale silicon materials used as Li-ion battery anodes were reviewed by McSweeney's group [26]. Terranova, Su and Zhu et al. reviewed Si/C composites respectively [23, 24, 27], but they did not give specific depiction of the recently reported composites of Si with nanocarbons, especially the three dimensional nanocarbons. Also, some reviews of progress of LIB materials have mentioned the progress in Si/C composites [15, 28-30]. However, the combination of nanostructured Si and nanostructured carbon in recent years have not been systematically presented. Thus, in this review, we will first summarize the recent progress and advances in designing nanostructured Si anode electrode materials. And then, more details for the advantages of combination of above mentioned nanostructured Si with various carbons, especially the nanocarbons, will be presented. Finally, we will move to other additional aspects, such as the binder, electrolyte and electrode additives, which could also impact electrode performance.

2. Rational designs of nanoscale dimensional silicon

Nanostructured materials improve cycling stability by incorporating pores or voids to accommodate expansion along with short lithium diffusion distances within the electrode [31]. A number of nanoscale morphologies have been investigated to minimize electrode pulverization and capacity loss in silicon anodes, including zero dimensional (0D) nanoparticles, one dimensional (1D) nanowires and nanotubes, two dimensional (2D) thin films and three dimensional (3D) porous structures. In this section, we will discuss them one by one.

Nanoscale dimension particles allow quick relaxation of stress, making nanoparticles more resistant to fracture than bulk particles. Silicon with smaller diameters as anodes could cycle more reversibly with moderately higher capacity than micron-sized silicon powder anodes [32]. Some studies have been carried out for the

relationship between Si size and the cycle life of Si anode materials. Kim and coworkers reported 10 nm sized n-Si as the optimized sample because smaller Si particle encounter with larger unstable SEI and larger Si particles suffer from larger strain during volume changes [33]. Wang's group reported the critical 15 nm Si building block size with SiO as starting materials [34]. As for the preparation methods, Si nanoparticles (Si NPs) could be synthesized from reduction of silica or SiCl₄ [35], disproportion of silicon monoxide [34], ball milling from bulk Si [36]. Compared to solid structures, hollow structures provide empty interior space for the volume expansion, which offers lower diffusion-induced stresses. The finite element modeling results show that the maximum tensile stress in a hollow Si sphere is five times lower than that in a solid sphere with an equal volume of Si [37]. The lower stress values mean that the hollow nanostructures will fracture less readily. The 0D nanoparticles are most promising nanoscale design for the application of Si/C materials, which we will review in the following section. The reasons are as follows: 1) 0D nanoparticles are easier to combine with carbon materials, including traditional carbons and nanocarbons in simple methods; 2) 0D nanoparticles are easier to fabricate with low cost in easy methods.

Other than 0D nanoparticles, 1D silicon nanowires (NWs) have shown high discharge capacities and stable cycling over tens of cycles with high reversible capacities. An advanced vertical growth of NW structure design prepared via vapor-liquid-solid method not only take advantage of small NW diameter to better accommodation of the large volume changes but also electrically connect each Si NW to the current collector to prompt efficient charge transport (**Figure 1**). When those nanowires were charged with C/5 rate, the capacity was stable at *ca.* 3,500 mAh g⁻¹ for 20 cycles. Moreover, the capacity of the Si NWs at faster rates was also excellent with the capacity remained at 2,100 mAh g⁻¹ at 1C rate [38]. Hence, silicon nanowire battery electrode might make a truly promising design, which could accommodate large strains without pulverization, provide good electronic conduction, and display short lithium insertion distances. Similarly, 1D Si nanotubes, which offers lower diffusion-induced stresses for the empty space inside, show that the morphology of

the nanotubes did not change after cycling, leading to superior capacity retention of 89% after 200 cycles at a rate of 1C in practical Li-ion cells[39]. Arrays of sealed, tubular Si nanotubes, which combine the merits of nanowires and hollow spheres, was expected to further accommodate the large volume changes, exhibit high initial Coulombic efficiencies (i.e., >85%) and stable capacity retention (>80% after 50 cycles), due to an unusual, underlying mechanism that is dominated by free surfaces [40]. An active silicon nanotube surrounded by an ion-permeable silicon oxide shell can cycle over 6,000 times in half cells while retaining more than 85% of their initial capacity, resulting from a stable SEI [41]. However, such techniques do not fit with standard preparation methods for manufacturing Li-ion battery electrodes because of its high cost, low syntheses efficiency. A simple 1D free-standing carbon-coated Si nanofiber binderless electrode, which was prepared via magnesiothermic reduction of electrospun SiO₂ nanofiber paper produced by an acid catalyzed polymerization of tetraethyl orthosilicate (TEOS) in-flight, was reported with a capacity of 802 mAh g⁻¹ after 659 cycles with a Coulombic efficiency of 99.9%[42]. 1D Si nanowires are also promising in application of lithium ion batteries.

Figure 1 Schematic of morphological changes that occur in Si during electrochemical cycling. NWs grown directly on the current collector do not pulverize or break into smaller particles after cycling. Rather, facile strain relaxation in the NWs allows them to increase in diameter and length without breaking. This NW anode design has each NW connected with the current collector, allowing for efficient 1D electron transport down the length of every NW. The figure is reprinted from Ref. [38] with permission.

Two dimensional thin silicon films have demonstrated high capacities and long

cycle lives of Si nanostructures [43]. The thin film expands during lithiation along perpendicular direction, while contraction during delithiation occurs both perpendicular to and in plane with the substrate, leading to cracking of the film after the first discharge cycle. After the initial fracture, the active material can be cycled without additional film cracking [44]. Thickness, surface morphology, and the interfacial bonding degree between the Si and current collector all have impact on the performance of Si thin films as electrode [45-48]. The reversible capacity and cycling life decrease with increasing films thickness, whereas capacity and cycle life increase with increasing films roughness. Amorphous n-type silicon films with a thickness of 50 nm vacuum deposited onto nickel substrates exhibited an initial capacity of approximately 3750 mAh g⁻¹ and without significant capacity decay after 200 cycles at 1C [49]. Thicker film of 275 nm delivered an initial reversible capacity of about 2200 mAh g⁻¹ with capacity retention of 61.3% after 500 cycles. After annealing this sample for better interfacial adhesion between the Si thin film and the Cu substrate, the capacity retention was further improved to 78.5% for 500 cycles [50]. Nevertheless, Si thin film encounter with the trouble in production.

An advanced effective approach to improve the electrochemical performance of silicon anodes is to fabricate silicon-based 3D composites with porous nanostructures, in which the local void space could partially accommodate the large volume change, thus preventing the capacity from fading [51, 52]. A lotus-root-like mesoporous Si with carbon surface coating displayed a stable capacity of *ca.* 1500 mAh g⁻¹ for 100 cycles at 1C and a high rate capability up to 15C [53]. Macroporous silicon and carbon-silicon periodic materials based on inverse-opal structures synthesized via templating with ordered colloidal spheres and subsequent silicon deposition was demonstrated with high capacities at low currents and decent capacity retentions, but their performance is severely restricted due to the low electrical conductivity of silicon. A capacity with carbon coated could be maintained above 2100 mAh g⁻¹ for 145 cycles whereas the capacity of a silicon inverse-opal coated without amorphous carbon was completely lost by the 11th cycle [54]. Monodisperse porous silicon nanospheres (MPSSs) were synthesized via hydrolysis process with subsequent

surface-protected magnesiothermic reduction. The Li-ion battery (LIB) anodes based on MPSSs demonstrate a high reversible capacity of 1500 mAh g⁻¹ after 500 cycles at C/2 [55]. Furthermore, nest-like Si nanospheres[56] exhibit superior lithium-storage capacity, high-rate capability and long cycling properties as well.

From previous discussion, we find that even though large volume change of pure Si could be accommodated by the rational design of nano architectures, their cycling stability still much need to be further improved by the protection of carbon. Because the surface-to-volume ratio is high for these morphologies, the formation of stable SEI layers is less possible. At the same time, carbonaceous materials normally could form stable SEI layers on their own surfaces. Thus, carbon coating might offer a good choice in constructing long lifespan batteries for Si materials. Moreover, the incorporation of carbon can release stress of volume expansion contributing to long cycle life. Thus, recent progress for the roles of carbon in promoting the electrochemical performance of Si anode will be discussed more thoroughly in the following section.

3. The composite materials of nano silicon and carbon

Much effort has been not only put in preparing nanostructured silicon, but also come over constructing of nanohybrids with such as metal and carbon for their ability to accommodate the volume change and enhance electrical conductivity. Typical structures include metallic nanohybrids and carbonaceous nanohybrids. There are some examples of applying Cu and Ag coatings that have been shown to increase coulombic efficiency and improve rate capability.[57, 58] Metallic nanohybrids, due to a larger atomic density and higher cost, are practically unsuitable for the construction of electron-transport pathways. As a result, a significant amount of studies have focused on exploring lighter alternatives for the construction of similar electron-transport pathways in Si-based anodes. The most common attempt is to combine the Si structure with a conducting carbonaceous layer, which possess many merits, such as excellent flexibility, high conductivity, lightweight, electrochemical

and thermal stability, in hoping to better retain the integrity of Si particles and restrain active materials disconnected from the conductive electrode. In this section, Si/carbon composites are classified into two main classifications: (1) Si/traditional carbon (Si/TC) composites, including Si particles with deposition carbon, pyrolytic carbon and commercial bulk carbons; (2) Si/nanocarbon (Si/NC) composites, including Si particles with carbon nanotubes (CNTs), graphene and corresponding 3D architectures; and (3) Si/traditional carbon/nanocarbon (Si/TC/NC) composites. The Si/TC composites will be discussed first followed by Si/NC composites and Si/TC/NC composites.

3.1 Si/traditional carbon composites

Si/traditional carbon (Si/TC) composites using traditional carbons will be discussed on the line of their preparation methods and then some of the recent exciting and interesting design examples will be presented.

Conventionally, coating carbon on nano Si materials commonly adopted thermal decomposition or chemical vapor deposition method with precursors of acetylene [34] gas. These methods result in carbon layers of high uniformity, neat surface smoothness and high purity. Thus, the initial capacity and capacity retention of carbon coated Si nanowires, nanotubes and porous structures in this method are usually high, *ca.* 2000 mAh g⁻¹ [53, 54, 59]. The shortcomings of this method are bad operability, high cost and poor scalability.

Similarly, Si NPs could also deposited on commercial carbon structures, and these composites also show high capacities after long cycle numbers. For example, Yushin's group loaded Si NPs on a 3D spherical carbon-black scaffold. The final Si/C nanohybrid exhibited impressive electrochemical properties, including a high specific capacity above 1500 mAh g⁻¹ at a rate of 1C after 100 cycles [60]. An interesting architecture is Si nanowires internally grown from porous graphite, demonstrating a high volumetric capacity density of 1363 mAh cm⁻³ with 91% Coulombic efficiency and high rate capability of 568 mAh cm⁻³ even at a 5C rate (**Figure 2**) [61].

Figure 2 Schematic view for the synthesis process of Si nanowires internally grown in porous graphite. The figure is reprinted from Ref. [61] with permission.

A more cost efficient approach for preparing Si/C composite is mixing Si with carbon or blending with carbon precursors with following pyrolysis process. For example, directly mixing Si powder with graphite, mesocarbon microbeads (MCMB) or hard carbon could achieve stable electrode morphology even after extended cycling [62, 63] and the capacity retention could attain *ca.* 500 mAh g⁻¹ after 400 cycles (for MCMB/Si mixture) [64]. Si can also blend with carbon sources by ball-milling and then pyrolyze resulting mixture at high temperature [65]. Silicon/ carbon composites synthesized via the above methods often display reversible capacities higher than graphite [66]. When lithium metal was added in previous of ball milling, lithiated silicon-carbon composites display *ca.* 0.13% capacity loss per cycle with high specific capacity (~ 700 mAh g⁻¹) [67]. Ternary composites such as flake graphite/silicon/carbon also show good cycling retention [68, 69]. Various precursors can be used for encapsulation, including resorcinol formaldehyde gel [70], poly(vinylidene fluoride) (PVDF) [71], polystyrene [72], glucose [73], pitch [74], poly(vinyl chloride) (PVC) [75, 76] and so on. The hydrothermal method is another easy approach to homogeneously blend Si with precursors [56, 77]. Spray pyrolysis, which could blend solvent type precursors together and obtain powder product, was considered as an effective approach to synthesis various structures and composites with good electrochemical performance [78]. Spherical nanostructured Si/C composites could be prepared by spray drying technique with phenol formaldehyde resin as the carbon source, which could exhibit a relatively high reversible capacity and good cycle performance used in lithium ion batteries [79, 80]. Furthermore, spray drying technique could be applicable for the large-scale production of various Si/C composites [70].

There are some delicate designs prepared with special meaning but hard to

classify. Here we will give a brief introduction of them. A pioneer example is a yolk-shell structure design. This structure was prepared through an intermediate sacrificial silica layer with void space in between the Si particles and the carbon shell and showed excellent capacity (2833 mAh g^{-1} at C/10), long cycle life (1000 cycles with 74% capacity retention), and high coulombic efficiency (99.84%) [81]. Later, those hybrid nanoparticles are assembled into a thicker carbon layer. This microstructure could further lower the electrode-electrolyte contact area, resulting in higher Coulombic efficiency (99.87%) and volumetric capacity ($1,270 \text{ mAh cm}^{-3}$), and the cycling remains stable even when the areal capacity was increased to the level of commercial lithium-ion batteries (3.7 mAh cm^{-2}) [82].

In short, Si/TC composites are very promising for LIB anodes. But the preparation of high quality carbon in easy and cost efficient methods are still challenging.

3.2 Si/nanocarbon composites

Nanocarbons such as fullerene [83], carbon nanofibers (CNF) [84-86], carbon nanotubes (CNTs) and Graphene, intensively investigated for advanced energy storage with continuously growing academic and technological impetus, have been incorporated with Si NPs for the preparation of LIB anode materials [87-90]. Thus, the latest development for the composite anode materials of Si with these nanocarbon materials, especially CNFs/CNTs and Graphene, are discussed below.

3.2.1 Si/CNFs anode materials

One-dimensional (1-D) nanostructures have the advantages of high surface area and short ion diffusion length, and have been viewed as components for next-generation electrochemical energy conversion and storage devices. The ductile CNF matrix can buffer the Si volume expansion on the macro domain and maintain good contact with both the active materials and the electrolyte after lithium insertion and extraction cycles, resulting in high reversible capacity and fairly good cyclability

[91]. Sputter Si at CNF, the hybrid nanostructured Si/CNF anodes exhibited superior device performance to materials used in previous studies, in terms of both specific capacity and cycle life. The CNFs provide not only a good strain/stress relaxation layer but also a conductive electron pathway [44]. Vertically aligned carbon nanofiber (VACNF) provide a good lithium-ion intercalation medium and a robust conductive core to effectively connect high-capacity silicon shells for lithium-ion storage. When VACNFs coaxially coated with silicon shells, an excellent cycle stability, about 89% of the capacity retention after 100 charge–discharge cycles at the C/1 rate, has been achieved [86]. Si/C fiber paper electrode could be synthesized by simultaneously electrospraying nano-Si-PAN (polyacrylonitrile) clusters and electrospinning PAN fibers followed by carbonization with uniform incorporation of Si NPs into fiber paper. The flexible 3D Si/C fiber paper electrode demonstrated a very high overall capacity of 1600 mAh g⁻¹ with capacity loss less than 0.079% per cycle for 600 cycles and excellent rate capability [92].

The carbon nanofibers can not only serve as the conductive matrix, but also encapsulate Si NPs into them. Here are two interesting examples. Hwang et al. developed an electrospinning process to produce core–shell fiber electrodes with Si NPs as core wrapped in the carbon shell. This core–shell structure exhibited high gravimetric capacity of 1384 mAh g⁻¹, excellent cycle life of 300 cycles with almost no capacity loss [93]. Later, Lee's group demonstrated the almost full accommodation of all the volumetric changes of Si by embedding Si NPs into a tunable cyclized-polyacrylonitrile (cPAN) fiber network bonded together by a cPAN coating [94].

3.2.2 Si/CNTs anode materials

Due to their excellent conductivity, high surface area, mechanical flexibility, and chemical stability [95, 96], CNTs, including single wall CNTs and multiwall CNTs [97], are considered as promising materials to improve the performance of silicon anode materials. There are many studies combining CNT with Si in mainly two forms,

considering the relative position of Si particles and CNTs: Si NPs on the inner walls of CNTs and Si NPs on the outer walls of CNTs [95, 98-102].

When Si film was deposited on and weakly bonded to the inner surface of a nano confined and size-preserving tubular material, Si deforms upon electrochemical alloying and dealloying without cracking. This model was verified by Yushin's group, who utilized carbon nanotubes (CNTs) with an inner Si coating. The composite samples with a Si content of 46 wt% showed a capacity of 2100 mAh g^{-1} , very close to the theoretical maximum predicted, assuming Si's contribution to be 4200 mAh g^{-1} . Furthermore, a stable SEI layer on the carbon layer impermeable to solvent molecules serves as a barrier to electrolyte decomposition and leads to a Coulombic efficiency $> 99.9\%$ after the first cycle (**Figure 3**) [103]. Cheng's group revealed the confinement effect of CNTs when Si NPs encapsulated within the hollow core of the CNTs. The volume expansion of the lithiated Si NPs is restricted by the walls of the CNTs (**Figure 4**) [104].

Figure 3. Electron microscopy of the composite Si-in-C tubes: (a) scanning electron microscopy (SEM) of one of the synthesized samples, (b) SEM of the electrode attached to a Cu current collector, (c) TEM and (d) its schematic of the sample after Li extraction at the 10th cycle. The figure is reprinted from Ref. [103] with permission.

Figure 4. Dynamic structural changes of a Si NP-filled CNT under electrochemical lithiation/delithiation. (a-d) Lithiation of a Si NP-filled CNT. (e-h) Delithiation of the same Si NP-filled CNT. (i) Illustration of the lithiation/delithiation of Si NP-filled CNTs. The figure is reprinted from Ref. [104] with permission.

As another combination method, Si NPs on the outer walls of CNTs take advantage of both the voids between the CNTs/N-CNTs and the tubular voids, thus effectively release the volume change of Si [105]. Vertical aligned Si/CNTs composite can be prepared via a two-step CVD method: CVD growth of CNTs array on substrate and deposition of Si NPs on it [106-108]. The covalent bonding of CNTs to Si NPs can further enhance the electronic pathway to the active material particles and helps to prevent the detachment of Si from CNTs upon repeated lithium insertion/extraction [99]. The capacity of the composite can reach 2000 mAh g^{-1} with 0.15% decay per cycle in 25 cycles [109]. The gravimetric capacity is high, but volumetric (areal) capacity of Si/CNTs composite is relatively low. When the vertically aligned CNTs utilized as the conductive core and coated with pore size-graded Si film, this $4 \mu\text{m}$ thick electrode deliver a high volumetric (areal) capacity and good cycle stability [101]. Volumetric (areal) capacity could also be increased through preparing a multilayer Si/CNT coaxial by a layer-by-layer assembling technique [110].

Generally speaking, Si/CNTs is a good candidate for LIB anodes and the encapsulation technique is an effective way to prevent pulverization and stabilize SEI layer, mainly because of the significantly enhanced conductivity and structural

durability. Major concerns for this composite material are: 1) the complicated fabrication process, which significantly increase the fabrication cost, and thus prevent its commercial application and 2) the loose binding between silicon and CNTs and the binding construction between them is also expensive and time consuming.

3.2.3 Si/Graphene anode materials

Graphene plays important roles in electrode materials investigation, due to that it could provide a conductive channel for electron transport, optimize electrical contact between the electrode components and also act as a buffer to volume changes during cycling, which are all benefiting from the graphene's large surface area, mechanical flexibility, chemical stability and excellent conductivity. Scientists have developed several methods to fabricate composites of silicon nano particles/wires and graphene (Si/Graphene) composites for LIB recently.

Graphene in Si/Graphene composites include the graphene reduced from graphene oxide, exfoliated graphene [111] and CVD growth of graphene [112], among which reduced graphene oxide (RGO) is the most common used graphene. Si/Graphene composites can be developed through a simple facile way by filtering the silicon/graphene oxide solution to film with a following reduction treatment [113]. The reversible specific capacity of this free standing Si composites can reach 1500 mAh g⁻¹ after 200 cycles. Another interesting self-supporting binder-free silicon based anode was prepared by double encapsulation of silicon nanowires (SiNWs) with two kinds of graphene (overlapping graphene (G) sheaths and reduced graphene oxide (RGO) overcoats) (**Figure 5**). This resulted structure (SiNW@G@RGO) have a high reversible specific capacity of 1600 mAh g⁻¹ at 2.1 A g⁻¹, 80% capacity retention after 100 cycles, and superior rate capability (500 mAh g⁻¹ at 8.4 A g⁻¹) [114].

Figure 5. Schematic of the fabrication (upper panel) and adapting (lower panel) of SiNW@G@RGO. The fabrication process mainly includes (I) chemical vapor deposition (CVD) growth of overlapped graphene sheets on as-synthesized silicon nanowires (SiNWs) to form SiNW@G nanocables, and (II) vacuum filtration of an aqueous SiNW@G-graphene oxide (GO) dispersion followed by thermal reduction. The resulting SiNW@G@RGO can transform between an expanded state and a contracted state during lithiation/delithiation cycles, thus enabling the stabilization of the silicon material. The figure is reprinted from Ref. [114] with permission.

Though both the filtration-directed assembly approach and simple mixing method have obtained improvements on lithium storage, they do not provide good dispersion of Si NPs between graphene sheets and good interfacial connection between Si NPs and graphene sheets. An electrostatic attraction-directed self-assembly approach was developed with uniform dispersion of Si NPs on graphene sheets [115]. This approach realizes an uniform dispersion of Si NPs between two layers of graphene sheets. The as-obtained composite exhibits stable cycling performance (approximately 1205 mAh g⁻¹ after 150 cycles) and excellent rate capability. The interfacial contact between graphene and other materials could be connected by mechanical or chemical interaction [116]. Dual chemical cross-linking and hydrogen bonding interactions between surface-modified Si NPs and graphene oxide (GO) exhibited an outstanding capacity retention capability and good rate performance, delivering a reversible capacity of 1000 mAh g⁻¹ after 400 cycles at a

current of 420 mA g^{-1} with almost 100% capacity retention [117]. Furthermore, Si wrapped in graphene sheets can also be synthesized by a simple spray drying process. This simple but effective nano/micro-assembly technology can be used for large-scale production of various graphene-based composite materials with high performance for electrochemical energy storage and conversion [70].

To further improve the electrochemical properties of Si/Graphene composites, works with delicate control of Si nanoparticle size and coating graphene layers have been conducted. Si NPs downsized to *ca.* 3nm silicon quantum dots and anchored on GNS, this Si/Graphene composite exhibited an extraordinary rate capability due to the surface-controlled lithium storage behavior rather than conventional diffusion-controlled mechanisms[118]. Another example is graphene sheets of 2-10 layers directly grown on Si particles and the graphene layers rooted on the Si particles. This structure can accommodate the large volume change of Si particle via a sliding process between adjacent graphene layers. Thus, cells using the above composite as anode could reach a high volumetric energy densities of 972 and 700 Wh L^{-1} at first and 200th cycle, respectively [119].

The multilayer C/Si/C microtubes exhibited synergistic properties and superior electrochemical performance when used as anodes for LIBs because its rolled-up layer by layer structure could buffer the strain of volume changes, and delay the pulverization of the electrode materials [120]. When the carbon layer in the roll to roll nanomembranes was replaced by RGO layer, the sandwiched Si/RGO nanoarchitecture demonstrates long cycling life of 2000 cycles at 3 A g^{-1} with a capacity degradation of only 3.3% per 100 cycles. The inner void space inside the configuration together with the mechanical feature of the amorphous Si nano membranes can buffer the strain of lithiation/delithiation against pulverization to extend cycling life. The alternatively aligned RGO layers in this nanostructure can facilitate electron transport, accommodate the volume change of Si layers and prevent their aggregation. Furthermore, the RGO layers can protect the nanomembranes from the excessive formation of thick SEI layer to suppress the capacity degradation (**Figure 6**) [121].

Figure 6. Schematic fabrication process of the rolled-up Si/rGO bilayer nanomembranes. The figure is reprinted from Ref. [121] with permission.

Si/Graphene composite is another good candidate for LIB anodes and the combination structure is effective to prevent the mechanical pulverization, mainly because of the flexibility and high specific area of graphene. However, the capacity is still inevitably decaying, and the proposed reasons are as follows: 1) the low conductive connection between graphene and Si, especially during the lithium insertion and desertion process; 2) not yet refined structural morphology of the composite.

Three-dimensional structures of active materials provide large surface area, well defined pathways for the access of electrolyte and mechanical stability for the integrity of electrodes [122]. Taking advantages of such extraordinary properties of graphene offers excellent opportunities for building attractive matrices, which not only accommodate the Si volume change, but also provide unobstructed electron and ion pathways.

Si on 3D graphene framework composites could be prepared through constructing 3D architectures, and then Si NPs or Si precursors being loaded on the as formed framework. The first example is a hierarchical 3D mesoporous carbon-coated Si@graphene foam nanoarchitecture, which was prepared via magnesiothermic reduction of silica on the three dimensional matrix and exhibited superior electrochemical performance including a high lithium storage capacity of 1,200 mAh g⁻¹ at the current density of 1 A g⁻¹ [123]. Another example is the amorphous Si NPs coated on backbone-graphene nanocomposite architecture. The electrode facilitates

the electron transport and lithium diffusion, resulting in remarkable first-cycle Coloumbic efficiency of 92.5% with a high specific reversible capacity of 2858 mAh g⁻¹, excellent power capability, and outstanding cycling stability (**Figure 7**) [124].

Figure 7. Schematic view of a-SBG nanocomposites before and after electrochemical cycling. The figure is reprinted from Ref. [124] with permission.

Compared with simple graphene sheets, which are easy to restack, hierarchical three-dimensional architectures could more effectively buffer the strain from the volume change of Si during the charging discharging process and preserve the high electrical conductivity of the overall electrode, representing a new direction for fabricating robust, high-performance lithium-ion batteries and related energy storage applications with advanced nanostructured materials [125].

3.3 Si/traditional carbon/nanocarbon composites

Traditional carbon coating of nanocarbon/Si composite could further effectively alleviate the aggregation of Si NPs by separating them from each other and help nanocarbons build more efficient 3D conducting networks. In the hybrid of graphene/carbon-coated Si NPs, the Si NPs are wrapped between graphene and amorphous carbon coating layers. These two layers work together to effectively suppress the aggregation and destruction of Si NPs, keeping the overall electrode highly conductive and active in Li storage [126]. Another graphene/Si-C hybrid (G/Si-C) is reported having a high areal capacity of 3.2 mA h cm⁻² after 100 cycles with high coulombic efficiency [127]. These findings demonstrate the importance of building a conductive network in the electrode level for efficient material utilization and may suggest future designs of Si-based anodes [128-130].

Table 1. Electrical properties of Si anodes with Si/TC/NC composites.

Anode material	Preparation method	Si wt. %	Q_{r1} (mAh g^{-1}) (initial CE)	Current density ($A\ g^{-1}$)	Q_dN (mAh g^{-1}) (N)	C.R.N	Ref.
Si /C/RGO	Si @PANI @RGO, pyrolysis	66%	1184 (73.2%)	2	900 (300)	76%	[131]
Si/C/RGO	Si&PANI&RGO, pyrolysis	70%	1630 (81.1%)	0.9	1121 (230)	68.8%	[128]
Si/C/RGO	PAN add into GO&Si, coat on Cu foil, pyrolysis	39.3%	1711 (78%)	0.1	1357 (50)	79.3%	[132]
Si/CNT/RGO	CNT&RGO—freeze dry--annealing	60%	2186 (79.5%)	1	1160 (500)	88.5%	[133]
Si/C/RGO	Si & PDA & GO mix -- pyrolysis	82.2%	2590 (87%)	0.2C 0.5C	1900 (100) 1400 (100)	73% 54%	[19]
Si/C/RGO	Si&GO&RF ---80°C---annealing	52.2%	1425 (87.8%)	0.5	749 (100)	85.2%	[130]
Si@C @Void@RGO	Si&PVP&GO---Spry pyrolysis---annealing	75%	2498 (71.4%)	7	966 (500)	84%	[129]
Si/Polymer/CNT	Si & Py & CNT -- in-situ polymerization -- coat on Cu foil	70% (binder free)	3600 (78.2%)	3.3	1600 (1000)	86%	[125]

Si wt. %: mass loading of anode material; Q_{r1} : the first reversible capacity; CE: Coulombic efficiency; $Q_dN(N)$: discharge capacity in Nth cycle; C.R.N.: capacity retention in Nth cycle. PANI: polyaniline; PDA: polydopamine; RF: resorcinol (R) and formaldehyde (F); PVP: polyvinylpyrrolidone; Py: Pyrrole.

Table 1 lists some combination works of Si NPs with TC and NC, in form of preparation methods and electrochemical properties, in which Si/TC/RGO composites are more intensively investigated than Si/TC/CNT. This may be resulted from that GO, precursor of RGO, has functional groups and negatively charged that could chemically bond or electrostatically connect with other carbon source or modified Si NPs. Most of Si/TC/RGO composite can be prepared via simple mixing of Si NPs with carbon source (carbon sources are usually positive charged, serving as an intermedia layer to electrostatically attract with negatively charged Si NPs and GO)

and GO, and then annealing at high temperature to pyrolysis carbon source and reduce GO at the same time. Thus, the pyrolytic carbon, encapsulating Si NPs, was anchored on the walls of RGO. Pyrolytic carbon plays three important roles in Si/TC/NC composite: 1) provide electrical conductivity; 2) reduce direct exposure of Si to electrolyte, thus decrease the unstable SEI growth; 3) serve as a glue to connect Si NPs with RGO. The RGO play key roles in: 1) provide good electrical contact and 2) provide large void spaces to accommodate the volume change of Si. In the Si/Polymer/CNT composites, CNTs and PPy work together to improve conductivity and provide space for volume change [125]. Si/Polymer/CNT composites possess an advantage over Si/TC/RGO in that they do not need annealing at high temperature to recover the conductivity of RGO.

Furthermore, Silicon could also be well-anchored onto 3D NT/TC frameworks. For example, Si @ 3D graphene/carbon nanotube (CNT)/ aerogels framework (CAs) nanohybrids could make use of both NT/TC layers and the balanced open voids, with a high reversible capacity of 1011 mAh g^{-1} , and excellent capacity retention of 96% [134]. However, the preparation method above was not satisfying for the complicate fabrication of 3D supporting framework and deposition of Si. Therefore, some simple methods for the preparation of high performance Si on 3D network anode composites were also reported. Our group fabricated a ternary Si-based composite Si@C/GF through simple hydrothermal reaction and thermal reduction, in which Si NPs were coated by a thin carbon layer by pyrolysis of phenolic resin and encapsulated in a graphene framework (GF). As a result, the double-protected Si NPs have a much improved cycle stability as well as high specific capacity and good rate performance [135]. Another simple method of preparation of 3D framework composite is Si NPs impregnated assemblies of templated carbon bridged oriented graphene, which was prepared by a modified vacuum filtration process followed by thermal treatment (**Figure 8**). When used as LIB anodes, the 3D framework exhibited high gravimetric capacity (1390 mAh g^{-1} at 2 A g^{-1} with respect to the total electrode weight), high volumetric capacity (1807 mAh cm^{-3}), superior rate capability (900 mAh g^{-1} at 8 A g^{-1}) and excellent cyclic stability (0.025% decay per cycle over 200 cycles) [136].

Figure 8. Electrode design and fabrication. (a) Schematic of the configuration of silicon nanoparticle-impregnated assemblies of templated carbon bridged oriented graphene (TCG-Si). (b) Schematic illustration showing the structure of TCG obtained by removing the Si template from the TCG-Si. (c) Schematic illustration of the fabrication process for TCG-Si, where bovine serum albumin (BSA)-coated silicon nanoparticles and graphene oxide (GO) are assembled via electrostatic interactions during vacuum filtration, thus enabling the successful fabrication of TCG-Si. The figure is reprinted from Ref. [136] with permission.

Table 2. Preparation methods and electrical properties of Si anodes with Si disperse in 3D frameworks.

Anode material	Preparation method	Si wt. %	Q_{ri} (mAh g ⁻¹) (initial CE)	Current density (A g ⁻¹)	Q_{dN} (mAh g ⁻¹) (N)	C.R.N	Ref.
3D mesoporous silicon @ graphene foam nanoarchitecture	PU as template to get GF --TEOS load SiO ₂ -- Mg reduction -- C ₂ H ₂ to carbon coating	56%	1,480 (66%)	0.1	1318 (200)	89.1%	[137]
a-Silicon @ backboned graphene nanocomposite (a-SBG)	Reduction of freeze-dried GO -- decomposition of SiH ₄	82 %	2858 (92.5%)	14	1103 (1000)	ca. 100%	[124]

Si @ 3D graphene/carbon nanotube (CNT) aerogels	Polymerization of RF with CNT/G --freeze-dried --decomposition of SiH ₄	50%	1698 (53.7)	0.4	1011 (270)	96%	[134]
Si-PPy-CNT	Si&Py&CNT -- in-situ polymerization -- coat on Cu foil	70% (binder free)	3600 78.2%	3.3	1600 (1000)	86%	[125]
Nano Si -3D graphene-PF pyrolytic carbon	HT -- add P/F -- HT --annealing	65%	3062 (61.5%)	1	650 (200)	85.1%	[135]
Si @ templated carbon-bridged oriented graphene	Si mixed with BSA -- mixed with GO -- filtration -- annealing	62%	2170 (72%)	2	1390(200)	95%	[136]

Si wt.%: mass loading of anode material; Q_{r1} : the first reversible capacity; CE: Coulombic efficiency; $Q_dN(N)$: discharge capacity in Nth cycle; C.R.N.: capacity retention in Nth cycle; RF: resorcinol (R) and formaldehyde (F).

We can summarize from table 2, a-Silicon @ backboned graphene nanocomposite (a-SBG) is the most effective approach to improve the performance of Si/C materials, for it show a high initial Coulombic efficiency of 92.5% and a high capacity of 1103 mAh g⁻¹ at 14 A g⁻¹ after 1000 cycles with nearly 100% capacity retention. However, the Si coating process is not commercially viable for applications in large batteries using similar scalable technology. So the simple method of preparing 3D framework composite with easy mixing, filtration and annealing process is attractive, and this composite has a relatively high initial Coulombic efficiency of 72% and a high capacity of 1390 mAh g⁻¹ at 2 A g⁻¹ after 200 cycles with 95% capacity retention. Simultaneously, the in-situ polymerization of the mixture of Si, Py and CNT, and coating on the current collector for cell fabrication is also a good method to prepare the Si anode materials.

In brief, Si NPs on frameworks of TC and NC is an excellent candidate for LIB anodes. The TC and NC framework could work together to provide both superior and robust conductivity and sufficient pores. Furthermore, the 3D framework could provide not only superior conductivity but also sufficient pores for lithium ion pathways and volume change buffer. Thus, the construction of effective 3D TC/NC architecture with Si NPs encapsulated in it simultaneously and with low cost may be a research direction in the future.

4. Other factors

It is noteworthy that the binders, electrolyte composition and conductive additives also play important roles in improving the electrochemical performance of Si based LIB anodes besides the morphology and composition of Si materials. Here, we will describe the noteworthy progress in these aspects.

4.1 Binders

The type of binder used in particulate electrodes could greatly influence the cycling lifetime. Poly(vinylidene) difluoride (PVDF) and carboxymethylcellulose (CMC) are the most frequently used binder in bulk powder electrodes, but these binders cannot sustain the elongation that occurs during volumetric expansion, leading to rapid capacity fade [25, 138-141]. Poly(acrylic) acid (PAA) [142] possessing certain mechanical properties comparable to those of CMC but containing a higher concentration of carboxylic functional groups, has been shown to improve cycle life by enhancing the adhesion of electrode active materials to copper current collectors. Alginate, a natural polysaccharide extracted from brown algae, was introduced as binder for Si NPs in LIBs and the capacity of Si NPs has been significantly improved to 2000 mAh g⁻¹ at a high charge rate of 1 C [143]. Although the linear, one dimensional (1D), backbones represent a significant progress in the Si anode research, the multidimensional hyperbranched β -CD polymer with three dimensional backbones was reported to enhance Si-binder interactions as well as improve mechanical stability of the electrode and therefore resolving the chronic insufficient cycle lives of Si anode [144]. After the concept of combining binding and conducting properties in the binder molecules [145, 146] with poly(9,9-dioctylfluorene-co-Suorenone-comethylbenzoic acid) (PFFOMB) binder[147] as an example, self-healing polymers (SHPs), which can mechanically and electrically heal cracks and damages, had been also demonstrated as effective binder to stabilize low-cost Si microparticle (SiMP) anodes. Compared with traditional polymer binders, the self-healing chemistry is designed to enable spontaneous repair of the mechanical

damage in the electrode and thus increase the lifetime of the SiMP anode [148, 149]. In-situ polymerization of conducting polymer hydrogel is another effective novel binder conception, which forms a continuous three-dimensional (3D) pathway for electronic conduction and provide sufficient voids for the expansion of Si (**Figure 9**) [150]. By taking advantage of the conductive polymer matrix, which provides fast electronic and ionic transfer channels, as well as free space for Si volume changes, the electrode could be continuously deeply cycled up to 5,000 times without significant capacity decay. The following research could concentrate on the fabrication of binders with high mechanical strength, excellent electrical conductivity and more importantly, simple preparation process with low cost.

Figure 9. Schematic illustration of 3D porous SiNP/conductive polymer hydrogel composite electrodes. Each SiNP is encapsulated within a conductive polymer surface coating and is further connected to the highly porous hydrogel framework. The figure is reprinted from Ref. [150] with permission.

4.2 Electrolyte and electrode additives

The incorporation of additives into electrolytes has been considered for enhancing the stability of the passivation layer because additives can alter the composition of SEI. Lithium bis(oxalato) borate (LiBOB), fluoroethylene carbonate (FEC) and vinylene carbonate (VC), undergoing reductive decomposition at the silicon surface at higher potentials than commonly-used ethylene carbonate (EC), is proposed to improve cycling stability by encouraging the formation of a stable SEI layer with a lowered resistance for the diffusion of lithium ions on the surface of silicon electrodes. This avoids not only the decomposition of electrolyte but also the oxidation of the Si electrode [151-154]. As evidenced by the difference of SEI layer

of Si film anode formed in VC-free and VC-containing electrolytes, the SEI layer formed in VC-containing electrolyte possessed better properties, which was impermeable to electrolyte and the impedance kept almost invariant upon cycling. In addition, SEM imaging revealed that the electrode cycled with VC had a smooth surface with small cracks believed to form during delithiation, compared to a much rougher surface with protruding crystallites and an inhomogeneous appearance without VC [155]. Detailed investigations are needed to guide our further advancement of electrolyte additives.

The choice of the conductive additive and the quantities of additive added into the electrode can have a significant impact on electrochemical performance. The addition of carbon nanotubes and reduced graphene, which have larger theoretical surface area compared to the active material (such as super P and acetylene black), were shown to enhance both capacity and cycling stability by forming a more efficient percolation pathway compared that when larger later active additive particles were used [156-160]. It is also found that the amount of conductive additive can have a profound effect on the cycle life of the electrode, which increases with increasing conductive additive content [161]. For example, Si NPs with a mean diameter of 78 nm that were mixed with carbon black in a 1 : 1 weight ratio showed a reversible capacity above 1700 mAh g⁻¹ over ten cycles [162]. To obtain high energy density in practice, addition of less advanced additive and attain better electrochemical performance is attractive.

5. Conclusion and perspective

The discussion in this review has illustrated that significant amount of researches are devoted into overcoming the challenges of using silicon anodes in practical lithium ion batteries. Rational designs of nanoparticles are effective to accommodate the large volume change, but they are relatively expensive and must incorporate with carbon to attend acceptable capacity retention. Si/C composite could not only address the volume problems but also help to stabilize the SEI layers. Nano carbons features

their remarkable properties and are more attractive in constructing of Si composite to further improve the cycling stability. Battery composites other than electrode materials, such as electrolyte additives and conductive additives, are also play important roles in improving the cycle stability of Si anodes.

Even though considerable improvements has been achieved, future research is still necessary along the following directions for their practical application in commercial LIBs: (1) To the electrode material aspect: we should explore more structurally and compositionally complex hierarchical composite nanostructures with not only internal void/pore space to buffer the large volume change but also good conductivity to attend high capacity retention during long cycle life; the manufacture process of those nanomaterials should be simple and liable and the cost of raw nanomaterials should be also accessible. (2) To other aspects: new low cost, effective binders, electrode and electrolyte additives are needed to maintain efficient electronic and ionic conduction from silicon to the current collectors and stabilize the SEI layers during cycling. (3) To practical fabrication aspect: the scalability, manufacturability, and cost of the nanomaterials are crucially important to the eventual success in the practical applications. Furthermore, the volumetric capacity, as an important parameter, should be given more attention in future research and practical manufacture.

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References

- [1] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, Nano-sized transition-metaloxides as negative-electrode materials for lithium-ion batteries, *Nature* 407 (2000) 496-499.
- [2] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat. Mater.* 7 (2008) 845-854.
- [3] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature* 414

(2001) 359-367.

- [4] M. Armand, J.M. Tarascon, Building better batteries, *Nature* 451 (2008) 652-657.
- [5] H. Li, H. Zhou, Enhancing the performances of Li-ion batteries by carbon-coating: present and future, *Chem. Commun.* 48 (2012) 1201-1217.
- [6] Y. Lu, G. Long, L. Zhang, T. Zhang, M. Zhang, F. Zhang, Y. Yang, Y. Ma, Y. Chen, What are the practical limits for the specific surface area and capacitance of bulk sp² carbon materials?, *Sci. China Chem.* (2015) 1-7.
- [7] P. Simon, Y. Gogotsi, B. Dunn, Where Do Batteries End and Supercapacitors Begin?, *Science* 343 (2014) 1210-1211.
- [8] H. Wang, H. Dai, Strongly coupled inorganic-nano-carbon hybrid materials for energy storage, *Chem. Soc. Rev.* 42 (2013) 3088-3113.
- [9] P.G. Bruce, B. Scrosati, J.M. Tarascon, Nanomaterials for rechargeable lithium batteries, *Angew. Chem. Int. Edit.* 47 (2008) 2930-2946.
- [10] E. Yoo, J. Kim, E. Hosono, H. Zhou, T. Kudo, I. Honma, Large reversible Li storage of graphene nanosheet families for use in rechargeable lithium ion batteries, *Nano Lett.* 8 (2008) 2277-2282.
- [11] B. Dunn, H. Kamath, J.M. Tarascon, Electrical Energy Storage for the Grid: A Battery of Choices, *Science* 334 (2011) 928-935.
- [12] B. Kang, G. Ceder, Battery materials for ultrafast charging and discharging, *Nature* 458 (2009) 190-193.
- [13] L. Ji, Z. Lin, M. Alcoutlabi, X. Zhang, Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries, *Energy Environ. Sci.* 4 (2011) 2682-2699.
- [14] C. Liu, F. Li, L.P. Ma, H.M. Cheng, Advanced materials for energy storage, *Adv. Mater.* 22 (2010) E28-E62.
- [15] N. Nitta, G. Yushin, High-Capacity Anode Materials for Lithium-Ion Batteries: Choice of Elements and Structures for Active Particles, *Part. Part. Syst. Char.* 31 (2014) 317-336.
- [16] X.L. Wu, Y.G. Guo, L.J. Wan, Rational design of anode materials based on Group IVA elements (Si, Ge, and Sn) for lithium-ion batteries, *Chemistry, an Asian journal* 8 (2013) 1948-1958.
- [17] M.N. Obrovac, L. Christensen, Structural Changes in Silicon Anodes during Lithium Insertion/Extraction, *Electrochem. Solid St.* 7 (2004) A93-A96.
- [18] H. Wu, Y. Cui, Designing nanostructured Si anodes for high energy lithium ion batteries, *Nano Today* 7 (2012) 414-429.
- [19] L. Wang, B. Gao, C. Peng, X. Peng, J. Fu, P.K. Chu, K. Huo, Bamboo leaf derived ultrafine Si nanoparticles and Si/C nanocomposites for high-performance Li-ion battery anodes, *Nanoscale* 7 (2015) 13840-13847.
- [20] N. Liu, K. Huo, M.T. McDowell, J. Zhao, Y. Cui, Rice husks as a sustainable source of nanostructured silicon for high performance Li-ion battery anodes, *Sci Rep* 3 (2013) 1919.
- [21] B. Liang, Y. Liu, Y. Xu, Silicon-based materials as high capacity anodes for next generation lithium ion batteries, *J. Power Sources* 267 (2014) 469-490.
- [22] D. Ma, Z. Cao, A. Hu, Si-Based Anode Materials for Li-Ion Batteries: A Mini Review, *Nano-Micro Lett.* 6 (2014) 347-358.
- [23] X. Su, Q. Wu, J. Li, X. Xiao, A. Lott, W. Lu, B.W. Sheldon, J. Wu, Silicon-Based Nanomaterials for Lithium-Ion Batteries: A Review, *Adv. Energy Mater.* 4 (2014) 1300882.
- [24] M.L. Terranova, S. Orlanducci, E. Tamburri, V. Guglielmotti, M. Rossi, Si/C hybrid nanostructures for Li-ion anodes: An overview, *J. Power Sources* 246 (2014) 167-177.

- [25] D. Mazouzi, Z. Karkar, C. Reale Hernandez, P. Jimenez Manero, D. Guyomard, L. Roué, B. Lestriez, Critical roles of binders and formulation at multiscales of silicon-based composite electrodes, *J. Power Sources* 280 (2015) 533-549.
- [26] W. McSweeney, H. Geaney, C. O'Dwyer, Metal-assisted chemical etching of silicon and the behavior of nanoscale silicon materials as Li-ion battery anodes, *Nano Res.* 8 (2015) 1395-1442.
- [27] X. Zhu, D. Yang, J. Li, F. Su, Nanostructured Si-Based Anodes for Lithium-Ion Batteries, *J. Nanosci. Nanotechnol.* 15 (2015) 15-30.
- [28] M. Ko, P. Oh, S. Chae, W. Cho, J. Cho, Considering Critical Factors of Li-rich Cathode and Si Anode Materials for Practical Li-ion Cell Applications, *Small* 11 (2015) 4058-4073.
- [29] P. Roy, S.K. Srivastava, Nanostructured anode materials for lithium ion batteries, *J. Mater. Chem. A* 3 (2015) 2454-2484.
- [30] H. Zhao, W. Yuan, G. Liu, Hierarchical electrode design of high-capacity alloy nanomaterials for lithium-ion batteries, *Nano Today* 10 (2015) 193-212.
- [31] Y. Yin, L. Wan, Y. Guo, Silicon-based nanomaterials for lithium-ion batteries, *Chinese Sci. Bull.* 57 (2012) 4104-4110.
- [32] S.H. Ng, J.Z. Wang, D. Wexler, K. Konstantinov, Z.P. Guo, H.K. Liu, Highly reversible lithium storage in spheroidal carbon-coated silicon nanocomposites as anodes for lithium-ion batteries, *Angew. Chem. Int. Edit.* 45 (2006) 6896-6899.
- [33] H. Kim, M. Seo, M.H. Park, J. Cho, A critical size of silicon nano-anodes for lithium rechargeable batteries, *Angew. Chem. Int. Edit.* 49 (2010) 2146-2149.
- [34] R. Yi, F. Dai, M.L. Gordin, H. Sohn, D. Wang, Influence of Silicon Nanoscale Building Blocks Size and Carbon Coating on the Performance of Micro-Sized Si-C Composite Li-Ion Anodes, *Adv. Energy Mater.* 3 (2013) 1507-1515.
- [35] N. Lin, Y. Han, L. Wang, J. Zhou, J. Zhou, Y. Zhu, Y. Qian, Preparation of nanocrystalline silicon from SiCl₄ at 200 degrees C in molten salt for high-performance anodes for lithium ion batteries, *Angew. Chem. Int. Edit.* 54 (2015) 3822-3825.
- [36] B. Zhu, Y. Jin, Y. Tan, L. Zong, Y. Hu, L. Chen, Y. Chen, Q. Zhang, J. Zhu, Scalable Production of Si Nanoparticles Directly from Low Grade Sources for Lithium-Ion Battery Anode, *Nano Lett.* 15 (2015) 5750-5754.
- [37] Y. Yao, M.T. McDowell, I. Ryu, H. Wu, N. Liu, L. Hu, W.D. Nix, Y. Cui, Interconnected Silicon Hollow Nanospheres for Lithium-Ion Battery Anodes with Long Cycle Life, *Nano Lett.* 11 (2011) 2949-2954.
- [38] C.K. Chan, H. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins, Y. Cui, High-performance lithium battery anodes using silicon nanowires, *Nat. Nano.* 3 (2008) 31-35.
- [39] M.-H. Park, M.G. Kim, J. Joo, K. Kim, J. Kim, S. Ahn, Y. Cui, J. Cho, Silicon nanotube battery anodes, *Nano Lett.* 9 (2009) 3844-3847.
- [40] T. Song, J. Xia, J.-H. Lee, D.H. Lee, M.-S. Kwon, J.-M. Choi, J. Wu, S.K. Doo, H. Chang, W.I. Park, Arrays of sealed silicon nanotubes as anodes for lithium ion batteries, *Nano Lett.* 10 (2010) 1710-1716.
- [41] H. Wu, G. Chan, J.W. Choi, I. Ryu, Y. Yao, M.T. McDowell, S.W. Lee, A. Jackson, Y. Yang, L. Hu, Y. Cui, Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control, *Nat Nano* 7 (2012) 310-315.
- [42] Z. Favors, H.H. Bay, Z. Mutlu, K. Ahmed, R. Ionescu, R. Ye, M. Ozkan, C.S. Ozkan, Towards Scalable Binderless Electrodes: Carbon Coated Silicon Nanofiber Paper via Mg Reduction of

Electrospun SiO₂ Nanofibers, *Sci. Rep.* 5 (2015) 8246.

[43] J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, C.D. Evans, Thin-film lithium and lithium-ion batteries, *Solid State Ionics* 135 (2000) 33-45.

[44] P.-C. Chen, J. Xu, H. Chen, C. Zhou, Hybrid silicon-carbon nanostructured composites as superior anodes for lithium ion batteries, *Nano Res.* 4 (2010) 290-296.

[45] Y.S. Choi, M. Pharr, K.H. Oh, J.J. Vlassak, A simple technique for measuring the fracture energy of lithiated thin-film silicon electrodes at various lithium concentrations, *J. Power Sources* 294 (2015) 159-166.

[46] J. Graetz, C.C. Ahn, R. Yazami, B. Fultz, Highly reversible lithium storage in nanostructured silicon, *Electrochem. Solid St.* 6 (2003) A194-A197.

[47] H. Haftbaradaran, Solute segregation and stress intensity factors at the edge of elastic thin-film electrodes under chemical equilibrium, *J. Power Sources* 288 (2015) 278-287.

[48] H. Haftbaradaran, X. Xiao, M.W. Verbrugge, H. Gao, Method to deduce the critical size for interfacial delamination of patterned electrode structures and application to lithiation of thin-film silicon islands, *J. Power Sources* 206 (2012) 357-366.

[49] S. Ohara, J. Suzuki, K. Sekine, T. Takamura, A thin film silicon anode for Li-ion batteries having a very large specific capacity and long cycle life, *J. Power Sources* 136 (2004) 303-306.

[50] L.B. Chen, J.Y. Xie, H.C. Yu, T.H. Wang, An amorphous Si thin film anode with high capacity and long cycling life for lithium ion batteries, *J. Appl. Electrochem.* 39 (2009) 1157-1162.

[51] L. Ji, X. Zhang, Fabrication of porous carbon/Si composite nanofibers as high-capacity battery electrodes, *Electrochem. Commun.* 11 (2009) 1146-1149.

[52] H. Kim, B. Han, J. Choo, J. Cho, Three-dimensional porous silicon particles for use in high-performance lithium secondary batteries, *Angew. Chem. Int. Edit.* 47 (2008) 10151-10154.

[53] H. Jia, P. Gao, J. Yang, J. Wang, Y. Nuli, Z. Yang, Novel Three-Dimensional Mesoporous Silicon for High Power Lithium-Ion Battery Anode Material, *Adv. Energy Mater.* 1 (2011) 1036-1039.

[54] A. Esmanski, G.A. Ozin, Silicon Inverse-Opal-Based Macroporous Materials as Negative Electrodes for Lithium Ion Batteries, *Adv. Funct. Mater.* 19 (2009) 1999-2010.

[55] W. Wang, Z. Favors, R. Ionescu, R. Ye, H.H. Bay, M. Ozkan, C.S. Ozkan, Monodisperse porous silicon spheres as anode materials for lithium ion batteries, *Sci. Rep.* 5 (2015) 8781.

[56] H. Ma, F. Cheng, J.Y. Chen, J.Z. Zhao, C.S. Li, Z.L. Tao, J. Liang, Nest-like Silicon Nanospheres for High-Capacity Lithium Storage, *Adv. Mater.* 19 (2007) 4067-4070.

[57] Y. Yu, L. Gu, C. Zhu, S. Tsukimoto, P.A. van Aken, J. Maier, Reversible storage of lithium in silver-coated three-dimensional macroporous silicon, *Adv. Mater.* 22 (2010) 2247-2250.

[58] B.D. Polat, O. Keles, K. Amine, Silicon-Copper Helical Arrays for New Generation Lithium Ion Batteries, *Nano Lett.* 15 (2015) 6702-6708.

[59] H. Wu, G. Chan, J.W. Choi, I. Ryu, Y. Yao, M.T. McDowell, S.W. Lee, A. Jackson, Y. Yang, L. Hu, Y. Cui, Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control, *Nat. Nano.* 7 (2012) 310-315.

[60] A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala, G. Yushin, High-performance lithium-ion anodes using a hierarchical bottom-up approach, *Nat. Mater.* 9 (2010) 353-358.

[61] S. Jeong, J.P. Lee, M. Ko, G. Kim, S. Park, J. Cho, Etched graphite with internally grown Si nanowires from pores as an anode for high density Li-ion batteries, *Nano Lett.* 13 (2013) 3403-3407.

[62] N. Dimov, S. Kugino, M. Yoshio, Mixed silicon-graphite composites as anode material for lithium ion batteries, *J. Power Sources* 136 (2004) 108-114.

- [63] M. Holzapfel, H. Buqa, W. Scheifele, P. Novak, F.M. Petrat, A new type of nano-sized silicon/carbon composite electrode for reversible lithium insertion, *Chem. Commun.* (2005) 1566-1568.
- [64] M. Yoshio, T. Tsumura, N. Dimov, Silicon/graphite composites as an anode material for lithium ion batteries, *J. Power Sources* 163 (2006) 215-218.
- [65] Y. Chen, S. Zeng, J. Qian, Y. Wang, Y. Cao, H. Yang, X. Ai, Li(+)-conductive polymer-embedded nano-Si particles as anode material for advanced Li-ion batteries, *ACS Appl Mater Interfaces* 6 (2014) 3508-3512.
- [66] M.K. Datta, P.N. Kumta, Silicon and carbon based composite anodes for lithium ion batteries, *J. Power Sources* 158 (2006) 557-563.
- [67] M.K. Datta, P.N. Kumta, In situ electrochemical synthesis of lithiated silicon-carbon based composites anode materials for lithium ion batteries, *J. Power Sources* 194 (2009) 1043-1052.
- [68] J. Lai, H. Guo, Z. Wang, X. Li, X. Zhang, F. Wu, P. Yue, Preparation and characterization of flake graphite/silicon/carbon spherical composite as anode materials for lithium-ion batteries, *J. Alloy. Compd.* 530 (2012) 30-35.
- [69] J.-H. Lee, W.-J. Kim, J.-Y. Kim, S.-H. Lim, S.-M. Lee, Spherical silicon/graphite/carbon composites as anode material for lithium-ion batteries, *J. Power Sources* 176 (2008) 353-358.
- [70] Y.-S. He, P. Gao, J. Chen, X. Yang, X.-Z. Liao, J. Yang, Z.-F. Ma, A novel bath lily-like graphene sheet-wrapped nano-Si composite as a high performance anode material for Li-ion batteries, *RSC Adv.* 1 (2011) 958-960.
- [71] Y. Liu, Z.Y. Wen, X.Y. Wang, A. Hirano, N. Imanishi, Y. Takeda, Electrochemical behaviors of Si/C composite synthesized from F-containing precursors, *J. Power Sources* 189 (2009) 733-737.
- [72] H. Wu, G. Zheng, N. Liu, T.J. Carney, Y. Yang, Y. Cui, Engineering empty space between Si nanoparticles for lithium-ion battery anodes, *Nano Lett.* 12 (2012) 904-909.
- [73] V.G. Khomenko, V.Z. Barsukov, Characterization of silicon- and carbon-based composite anodes for lithium-ion batteries, *Electrochim. Acta* 52 (2007) 2829-2840.
- [74] Z. Luo, D. Fan, X. Liu, H. Mao, C. Yao, Z. Deng, High performance silicon carbon composite anode materials for lithium ion batteries, *J. Power Sources* 189 (2009) 16-21.
- [75] Y. Liu, K. Hanai, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, Silicon/Carbon Composites as Anode Materials for Li-Ion Batteries, *Electrochem. Solid St.* 7 (2004) A369-A372.
- [76] C. Ma, C. Ma, J. Wang, H. Wang, J. Shi, Y. Song, Q. Guo, L. Liu, Exfoliated graphite as a flexible and conductive support for Si-based Li-ion battery anodes, *Carbon* 72 (2014) 38-46.
- [77] Y.S. Hu, R. Demir-Cakan, M.M. Titirici, J.O. Muller, R. Schlogl, M. Antonietti, J. Maier, Superior storage performance of a Si@SiO_x/C nanocomposite as anode material for lithium-ion batteries, *Angew. Chem. Int. Edit.* 47 (2008) 1645-1649.
- [78] D.S. Jung, Y.N. Ko, Y.C. Kang, S.B. Park, Recent progress in electrode materials produced by spray pyrolysis for next-generation lithium ion batteries, *Adv. Powder Technol.* 25 (2014) 18-31.
- [79] L. Chen, X. Xie, B. Wang, K. Wang, J. Xie, Spherical nanostructured Si/C composite prepared by spray drying technique for lithium ion batteries anode, *Mat. Sci. Eng. B-Solid.* 131 (2006) 186-190.
- [80] M. Li, X. Hou, Y. Sha, J. Wang, S. Hu, X. Liu, Z. Shao, Facile spray-drying/pyrolysis synthesis of core-shell structure graphite/silicon-porous carbon composite as a superior anode for Li-ion batteries, *J. Power Sources* 248 (2014) 721-728.
- [81] N. Liu, H. Wu, M.T. McDowell, Y. Yao, C. Wang, Y. Cui, A yolk-shell design for stabilized and scalable li-ion battery alloy anodes, *Nano Lett.* 12 (2012) 3315-3321.

- [82] N. Liu, Z. Lu, J. Zhao, M.T. McDowell, H.-W. Lee, W. Zhao, Y. Cui, A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes, *Nat. Nano.* 9 (2014) 187-192.
- [83] M. Joe, Y.-K. Han, K.-R. Lee, H. Mizuseki, S. Kim, An ideal polymeric C60 coating on a Si electrode for durable Li-ion batteries, *Carbon* 77 (2014) 1140-1147.
- [84] J. Guo, A. Sun, X. Chen, C. Wang, A. Manivannan, Cyclability study of silicon-carbon composite anodes for lithium-ion batteries using electrochemical impedance spectroscopy, *Electrochim. Acta* 56 (2011) 3981-3987.
- [85] J.Y. Howe, D.J. Burton, Y. Qi, H.M. Meyer, M. Nazri, G.A. Nazri, A.C. Palmer, P.D. Lake, Improving microstructure of silicon/carbon nanofiber composites as a Li battery anode, *J. Power Sources* 221 (2013) 455-461.
- [86] S.A. Klankowski, R.A. Rojas, B.A. Cruden, J. Liu, J. Wu, J. Li, A high-performance lithium-ion battery anode based on the core-shell heterostructure of silicon-coated vertically aligned carbon nanofibers, *J. Mater. Chem. A* 1 (2013) 1055-1064.
- [87] X. Ji, K.T. Lee, L.F. Nazar, A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries, *Nat. Mater.* 8 (2009) 500-506.
- [88] X. Huang, X. Qi, F. Boey, H. Zhang, Graphene-based composites, *Chem. Soc. Rev.* 41 (2012) 666-686.
- [89] G.L. Che, B.B. Lakshmi, E.R. Fisher, C.R. Martin, Carbon nanotube membranes for electrochemical energy storage and production, *Nature* 393 (1998) 346-349.
- [90] S. Guo, S. Dong, Graphene nanosheet: synthesis, molecular engineering, thin film, hybrids, and energy and analytical applications, *Chem. Soc. Rev.* 40 (2011) 2644-2672.
- [91] Q. Si, K. Hanai, T. Ichikawa, A. Hirano, N. Imanishi, Y. Takeda, O. Yamamoto, A high performance silicon/carbon composite anode with carbon nanofiber for lithium-ion batteries, *J. Power Sources* 195 (2010) 1720-1725.
- [92] Y. Xu, Y. Zhu, F. Han, C. Luo, C. Wang, 3D Si/C Fiber Paper Electrodes Fabricated Using a Combined Electrospray/Electrospinning Technique for Li-Ion Batteries, *Adv. Energy Mater.* 5 (2015) 1400753.
- [93] T.H. Hwang, Y.M. Lee, B.-S. Kong, J.-S. Seo, J.W. Choi, Electrospun Core-Shell Fibers for Robust Silicon Nanoparticle-Based Lithium Ion Battery Anodes, *Nano Lett.* 12 (2012) 802-807.
- [94] D.M. Piper, J.H. Woo, S.-B. Son, S.C. Kim, K.H. Oh, S.-H. Lee, Hierarchical Porous Framework of Si-Based Electrodes for Minimal Volumetric Expansion, *Adv. Mater.* 26 (2014) 3520-3525.
- [95] T. Kim, Y.H. Mo, K.S. Nahm, S.M. Oh, Carbon nanotubes (CNTs) as a buffer layer in silicon/CNTs composite electrodes for lithium secondary batteries, *J. Power Sources* 162 (2006) 1275-1281.
- [96] S. Talapatra, S. Kar, S.K. Pal, R. Vajtai, L. Ci, P. Victor, M.M. Shaijumon, S. Kaur, O. Nalamasu, P.M. Ajayan, Direct growth of aligned carbon nanotubes on bulk metals, *Nat. Nano.* 1 (2006) 112-116.
- [97] R. Epur, M. Ramanathan, M.K. Datta, D.H. Hong, P.H. Jampani, B. Gattu, P.N. Kumta, Scribable multi-walled carbon nanotube-silicon nanocomposites: a viable lithium-ion battery system, *Nanoscale* 7 (2015) 3504-3510.
- [98] K. Fu, O. Yildiz, H. Bhanushali, Y. Wang, K. Stano, L. Xue, X. Zhang, P.D. Bradford, Aligned carbon nanotube-silicon sheets: a novel nano-architecture for flexible lithium ion battery electrodes, *Adv. Mater.* 25 (2013) 5109-5114.
- [99] C. Adv., Funct., Mater., Martin, O. Crosnier, R. Retoux, D. Bélanger, D.M. Schleich, T. Brousse, Chemical Coupling of Carbon Nanotubes and Silicon Nanoparticles for Improved Negative Electrode

- Performance in Lithium-Ion Batteries, *Adv. Funct. Mater.* 21 (2011) 3524-3530.
- [100] W. Wang, P.N. Kumta, Reversible high capacity nanocomposite anodes of Si/C/SWNTs for rechargeable Li-ion batteries, *J. Power Sources* 172 (2007) 650-658.
- [101] X. Wang, L. Sun, R. Agung Susantyoko, Y. Fan, Q. Zhang, Ultrahigh volumetric capacity lithium ion battery anodes with CNT-Si film, *Nano Energy* 8 (2014) 71-77.
- [102] X. Li, J.-H. Cho, N. Li, Y. Zhang, D. Williams, S.A. Dayeh, S.T. Picraux, Carbon Nanotube-Enhanced Growth of Silicon Nanowires as an Anode for High-Performance Lithium-Ion Batteries, *Adv. Energy Mater.* 2 (2012) 87-93.
- [103] B. Hertzberg, A. Alexeev, G. Yushin, Deformations in Si- Li Anodes Upon Electrochemical Alloying in Nano-Confined Space, *J. Am. Chem. Soc.* 132 (2010) 8548-8549.
- [104] W.-J. Yu, C. Liu, P.-X. Hou, L. Zhang, X.-Y. Shan, F. Li, H.-M. Cheng, Lithiation of Silicon Nanoparticles Confined in Carbon Nanotubes, *ACS Nano* 9 (2015) 5063-5071.
- [105] W.J. Lee, T.H. Hwang, J.O. Hwang, H.W. Kim, J. Lim, H.Y. Jeong, J. Shim, T.H. Han, J.Y. Kim, J.W. Choi, S.O. Kim, N-doped graphitic self-encapsulation for high performance silicon anodes in lithium-ion batteries, *Energy Environ. Sci.* 7 (2014) 621-626.
- [106] A. Gohier, B. Laik, K.H. Kim, J.L. Maurice, J.P. Pereira-Ramos, C.S. Cojocaru, P. Van Tran, High-rate capability silicon decorated vertically aligned carbon nanotubes for Li-ion batteries, *Adv. Mater.* 24 (2012) 2592-2597.
- [107] G.K. Simon, B. Maruyama, M.F. Durstock, D.J. Burton, T. Goswami, Silicon-coated carbon nanofiber hierarchical nanostructures for improved lithium-ion battery anodes, *J. Power Sources* 196 (2011) 10254-10257.
- [108] T.D. Bogart, D. Oka, X. Lu, M. Gu, C. Wang, B.A. Korgel, Lithium ion battery performance of silicon nanowires with carbon skin, *ACS nano* 8 (2013) 915-922.
- [109] W. Wang, P.N. Kumta, Nanostructured hybrid silicon/carbon nanotube heterostructures: reversible high-capacity lithium-ion anodes, *Acs Nano* 4 (2010) 2233-2241.
- [110] Q. Xiao, Y. Fan, X. Wang, R.A. Susantyoko, Q. Zhang, A multilayer Si/CNT coaxial nanofiber LIB anode with a high areal capacity, *Energy Environ. Sci.* 7 (2014) 655-661.
- [111] W. Wei, G. Wang, S. Yang, X. Feng, K. Mullen, Efficient coupling of nanoparticles to electrochemically exfoliated graphene, *J. Am. Chem. Soc.* 137 (2015) 5576-5581.
- [112] F. Xia, S. Kwon, W.W. Lee, Z. Liu, S. Kim, T. Song, K.J. Choi, U. Paik, W.I. Park, Graphene as an Interfacial Layer for Improving Cycling Performance of Si Nanowires in Lithium-Ion Batteries, *Nano Lett.* 15 (2015) 6658-6664.
- [113] J.K. Lee, K.B. Smith, C.M. Hayner, H.H. Kung, Silicon nanoparticles-graphene paper composites for Li ion battery anodes, *Chem. Commun.* 46 (2010) 2025-2027.
- [114] B. Wang, X.L. Li, X.F. Zhang, B. Luo, M.H. Jin, M.H. Liang, S.A. Dayeh, S.T. Picraux, L.J. Zhi, Adaptable Silicon-Carbon Nanocables Sandwiched between Reduced Graphene Oxide Sheets as Lithium Ion Battery Anodes, *ACS nano* 7 (2013) 1437-1445.
- [115] X. Zhou, Y.-X. Yin, L.-J. Wan, Y.-G. Guo, Self-Assembled Nanocomposite of Silicon Nanoparticles Encapsulated in Graphene through Electrostatic Attraction for Lithium-Ion Batteries, *Adv. Energy Mater.* 2 (2012) 1086-1090.
- [116] X. Zhou, Y.X. Yin, L.J. Wan, Y.G. Guo, Facile synthesis of silicon nanoparticles inserted into graphene sheets as improved anode materials for lithium-ion batteries, *Chem. Commun.* 48 (2012) 2198-2200.
- [117] C. Sun, Y. Deng, L. Wan, X. Qin, G. Chen, Graphene Oxide-Immobilized NH₂-Terminated

Silicon Nanoparticles by Cross-Linked Interactions for Highly Stable Silicon Negative Electrodes, *ACS Appl. Mater. Inter.* 6 (2014) 11277-11285.

[118] B. Wang, X. Li, B. Luo, L. Hao, M. Zhou, X. Zhang, Z. Fan, L. Zhi, Approaching the downsizing limit of silicon for surface-controlled lithium storage, *Adv. Mater.* 27 (2015) 1526-1532.

[119] I.H. Son, J. Hwan Park, S. Kwon, S. Park, M.H. Rummeli, A. Bachmatiuk, H.J. Song, J. Ku, J.W. Choi, J.-m. Choi, S.-G. Doo, H. Chang, Silicon carbide-free graphene growth on silicon for lithium-ion battery with high volumetric energy density, *Nat. Commun.* 6 (2015) 7393.

[120] J. Deng, H. Ji, C. Yan, J. Zhang, W. Si, S. Baunack, S. Oswald, Y. Mei, O.G. Schmidt, Naturally rolled-up C/Si/C trilayer nanomembranes as stable anodes for lithium-ion batteries with remarkable cycling performance, *Angew. Chem. Int. Edit.* 52 (2013) 2326-2330.

[121] X.H. Liu, J. Zhang, W.P. Si, L.X. Xi, B. Eichler, C.L. Yan, O.G. Schmidt, Sandwich Nano architecture of Si/Reduced Graphene Oxide Bilayer Nanomembranes for Li-Ion Batteries with Long Cycle Life, *ACS nano* 9 (2015) 1198-1205.

[122] Z.N. Yu, L. Tetard, L. Zhai, J. Thomas, Supercapacitor electrode materials: nanostructures from 0 to 3 dimensions, *Energy Environ. Sci.* 8 (2015) 702-730.

[123] S. Chen, P. Bao, X. Huang, B. Sun, G. Wang, Hierarchical 3D mesoporous silicon@graphene nanoarchitectures for lithium ion batteries with superior performance, *Nano Research* 7 (2013) 85-94.

[124] M. Ko, S. Chae, S. Jeong, P. Oh, J. Cho, Elastic a-Silicon Nanoparticle Backboned Graphene Hybrid as a Self-Compacting Anode for High-Rate Lithium Ion Batteries, *ACS nano* 8 (2014) 8591-8599.

[125] B. Liu, P. Soares, C. Checkles, Y. Zhao, G. Yu, Three-dimensional hierarchical ternary nanostructures for high-performance Li-ion battery anodes, *Nano Lett.* 13 (2013) 3414-3419.

[126] M. Zhou, T. Cai, F. Pu, H. Chen, Z. Wang, H. Zhang, S. Guan, Graphene/carbon-coated Si nanoparticle hybrids as high-performance anode materials for Li-ion batteries, *ACS Appl. Mater. Inter.* 5 (2013) 3449-3455.

[127] R. Yi, J. Zai, F. Dai, M.L. Gordin, D. Wang, Dual conductive network-enabled graphene/Si-C composite anode with high areal capacity for lithium-ion batteries, *Nano Energy* 6 (2014) 211-218.

[128] N. Lin, J. Zhou, L. Wang, Y. Zhu, Y. Qian, Polyaniline-assisted synthesis of Si@C/RGO as anode material for rechargeable lithium-ion batteries, *ACS Appl. Mater. Inter.* 7 (2015) 409-414.

[129] S.H. Choi, D.S. Jung, J.W. Choi, Y.C. Kang, Superior lithium-ion storage properties of si-based composite powders with unique Si@carbon@void@graphene configuration, *Chem.-Eur. J.* 21 (2015) 2076-2082.

[130] J. Kim, C. Oh, C. Chae, D.-H. Yeom, J. Choi, N. Kim, E.-S. Oh, J.K. Lee, 3D Si/C particulate nanocomposites internally wired with graphene networks for high energy and stable batteries, *J. Mater. Chem. A* 3 (2015) 18684-18695.

[131] Z.F. Li, H. Zhang, Q. Liu, Y. Liu, L. Stanciu, J. Xie, Novel pyrolyzed polyaniline-grafted silicon nanoparticles encapsulated in graphene sheets as Li-ion battery anodes, *ACS Appl Mater Interfaces* 6 (2014) 5996-6002.

[132] Q. Yun, X. Qin, W. Lv, Y.-B. He, B. Li, F. Kang, Q.-H. Yang, "Concrete" inspired construction of a silicon/carbon hybrid electrode for high performance lithium ion battery, *Carbon* 93 (2015) 59-67.

[133] X. Wang, G. Li, F.M. Hassan, M. Li, K. Feng, X. Xiao, Z. Chen, Building sponge-like robust architectures of CNT-graphene-Si composites with enhanced rate and cycling performance for lithium-ion batteries, *J. Mater. Chem. A* 3 (2015) 3962-3967.

[134] S. Jing, H. Jiang, Y. Hu, J. Shen, C. Li, Face-to-Face Contact and Open-Void Coinvolved Si/C

- Nanohybrids Lithium-Ion Battery Anodes with Extremely Long Cycle Life, *Adv. Funct. Mater.* 25 (2015) 5395-5401.
- [135] F. Zhang, X. Yang, Y. Xie, N. Yi, Y. Huang, Y. Chen, Pyrolytic carbon-coated Si nanoparticles on elastic graphene framework as anode materials for high-performance lithium-ion batteries, *Carbon* 82 (2015) 161-167.
- [136] M. Zhou, X. Li, B. Wang, Y. Zhang, J. Ning, Z. Xiao, X. Zhang, Y. Chang, L. Zhi, High-Performance Silicon Battery Anodes Enabled by Engineering Graphene Assemblies, *Nano Lett.* 15 (2015) 6222-6228.
- [137] S. Chen, P. Bao, X. Huang, B. Sun, G. Wang, Hierarchical 3D mesoporous silicon@ graphene nanoarchitectures for lithium ion batteries with superior performance, *Nano Research* 7 (2014) 85-94.
- [138] J.S. Bridel, T. Azaïs, M. Morcrette, J.M. Tarascon, D. Larcher, Key Parameters Governing the Reversibility of Si/Carbon/CMC Electrodes for Li-Ion Batteries†, *Chem. Mater.* 22 (2009) 1229-1241.
- [139] L. Chen, X. Xie, J. Xie, K. Wang, J. Yang, Binder effect on cycling performance of silicon/carbon composite anodes for lithium ion batteries, *J. Appl. Electrochem.* 36 (2006) 1099-1104.
- [140] B. Lestriez, S. Bahri, I. Sandu, L. Roue, D. Guyomard, On the binding mechanism of CMC in Si negative electrodes for Li-ion batteries, *Electrochem. Commun.* 9 (2007) 2801-2806.
- [141] D. Munao, J.W.M. van Erven, M. Valvo, E. Garcia-Tamayo, E.M. Kelder, Role of the binder on the failure mechanism of Si nano-composite electrodes for Li-ion batteries, *J. Power Sources* 196 (2011) 6695-6702.
- [142] A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzberg, R. Burtovyy, C.F. Huebner, T.F. Fuller, I. Luzinov, G. Yushin, Toward Efficient Binders for Li-Ion Battery Si-Based Anodes: Polyacrylic Acid, *ACS Appl. Mater. Inter.* 2 (2010) 3004-3010.
- [143] I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burtovyy, I. Luzinov, G. Yushin, A Major Constituent of Brown Algae for Use in High-Capacity Li-Ion Batteries, *Science* 334 (2011) 75-79.
- [144] Y.K. Jeong, T.W. Kwon, I. Lee, T.S. Kim, A. Coskun, J.W. Choi, Hyperbranched beta-cyclodextrin polymer as an effective multidimensional binder for silicon anodes in lithium rechargeable batteries, *Nano Lett.* 14 (2014) 864-870.
- [145] H. Zhao, Z. Wang, P. Lu, M. Jiang, F. Shi, X. Song, Z. Zheng, X. Zhou, Y. Fu, G. Abdelbast, X. Xiao, Z. Liu, V.S. Battaglia, K. Zaghib, G. Liu, Toward practical application of functional conductive polymer binder for a high-energy lithium-ion battery design, *Nano Lett.* 14 (2014) 6704-6710.
- [146] M. Wu, X. Xiao, N. Vukmirovic, S. Xun, P.K. Das, X. Song, P. Olalde-Velasco, D. Wang, A.Z. Weber, L.W. Wang, V.S. Battaglia, W. Yang, G. Liu, Toward an ideal polymer binder design for high-capacity battery anodes, *J. Am. Chem. Soc.* 135 (2013) 12048-12056.
- [147] G. Liu, S. Xun, N. Vukmirovic, X. Song, P. Olalde-Velasco, H. Zheng, V.S. Battaglia, L. Wang, W. Yang, Polymers with tailored electronic structure for high capacity lithium battery electrodes, *Adv. Mater.* 23 (2011) 4679-4683.
- [148] Z. Chen, C. Wang, J. Lopez, Z. Lu, Y. Cui, Z. Bao, High-Areal-Capacity Silicon Electrodes with Low-Cost Silicon Particles Based on Spatial Control of Self-Healing Binder, *Adv. Energy Mater.* 5 (2015) 1401826.
- [149] C. Wang, H. Wu, Z. Chen, M.T. McDowell, Y. Cui, Z. Bao, Self-healing chemistry enables the stable operation of silicon microparticle anodes for high-energy lithium-ion batteries, *Nat. Chem.* 5 (2013) 1042-1048.
- [150] H. Wu, G. Yu, L. Pan, N. Liu, M.T. McDowell, Z. Bao, Y. Cui, Stable Li-ion battery anodes by

in-situ polymerization of conducting hydrogel to conformally coat silicon nanoparticles, *Nat. Commun.* 4 (2013) 1943.

[151] M.D. Bhatt, C. O'Dwyer, Solid electrolyte interphases at Li-ion battery graphitic anodes in propylene carbonate (PC)-based electrolytes containing FEC, LiBOB, and LiDFOB as additives, *Chem. Phys. Lett.* 618 (2015) 208-213.

[152] N.-S. Choi, K.H. Yew, K.Y. Lee, M. Sung, H. Kim, S.-S. Kim, Effect of fluoroethylene carbonate additive on interfacial properties of silicon thin-film electrode, *J. Power Sources* 161 (2006) 1254-1259.

[153] S. Dalavi, P. Guduru, B.L. Lucht, Performance Enhancing Electrolyte Additives for Lithium Ion Batteries with Silicon Anodes, *J. Electrochem. Soc.* 159 (2012) A642-A646.

[154] V. Etacheri, O. Haik, Y. Goffer, G.A. Roberts, I.C. Stefan, R. Fasching, D. Aurbach, Effect of fluoroethylene carbonate (FEC) on the performance and surface chemistry of Si-nanowire Li-ion battery anodes, *Langmuir* 28 (2012) 965-976.

[155] L. Chen, K. Wang, X. Xie, J. Xie, Effect of vinylene carbonate (VC) as electrolyte additive on electrochemical performance of Si film anode for lithium ion batteries, *J. Power Sources* 174 (2007) 538-543.

[156] W.-R. Liu, Z.-Z. Guo, W.-S. Young, D.-T. Shieh, H.-C. Wu, M.-H. Yang, N.-L. Wu, Effect of electrode structure on performance of Si anode in Li-ion batteries: Si particle size and conductive additive, *J. Power Sources* 140 (2005) 139-144.

[157] B.P.N. Nguyen, N.A. Kumar, J. Gaubicher, F. Duclairoir, T. Brousse, O. Crosnier, L. Dubois, G. Bidan, D. Guyomard, B. Lestriez, Nanosilicon-Based Thick Negative Composite Electrodes for Lithium Batteries with Graphene as Conductive Additive, *Adv. Energy Mater.* 3 (2013) 1351-1357.

[158] J.E. Trevey, K.W. Rason, C.R. Stoldt, S.-H. Lee, Improved Performance of All-Solid-State Lithium-Ion Batteries Using Nanosilicon Active Material with Multiwalled-Carbon-Nanotubes as a Conductive Additive, *Electrochem. Solid St.* 13 (2010) A154-A157.

[159] X.L. Wang, W.Q. Han, Graphene enhances Li storage capacity of porous single-crystalline silicon nanowires, *ACS Appl. Mater. Inter.* 2 (2010) 3709-3713.

[160] Z. Li, W. Wang, Z. Li, Z. Qin, J. Wang, Z. Liu, Bridging porous Si-C composites with conducting agents for improving battery cycle life, *J. Power Sources* 286 (2015) 534-539.

[161] J.R. Szczech, S. Jin, Nanostructured silicon for high capacity lithium battery anodes, *Energy Environ. Sci.* 4 (2011) 56-72.

[162] H. Li, X. Huang, L. Chen, Z. Wu, Y. Liang, A high capacity nano Si composite anode material for lithium rechargeable batteries, *Electrochem. Solid St.* 2 (1999) 547-549.