Challenges and Recent Progress in the Development of Si Anodes for Lithium-Ion Battery

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Silicon, because of its high specific capacity, is intensively pursued as one of the most promising anode material for next-generation lithium-ion batteries. In the past decade, various nanostructures are successfully demonstrated to address major challenges for reversible Si anodes related to pulverization and solid-electrolyte interphase. However, the electrochemical performance is still limited by challenges that stem from the use of nanomaterials. In this progress report, the focus is on the challenges and recent progress in the development of Si anodes for lithium-ion battery, including initial Coulombic efficiency, areal capacity, and material cost, which call for more research effort and provide a bright prospect for the widespread applications of silicon anodes in the future lithium-ion batteries.

1. Introduction

As the emerging markets of portable electronics and electric vehicles create tremendous demand for advanced lithium-ion batteries (LIBs),[1,2] there is growing interest in developing battery electrodes with high gravimetric and volumetric capacity to surpass the energy density of the current LIBs.[3–5]

Rechargeable lithium-ion batteries mainly consist of four parts: two electrodes, a separator and electrolyte. The two electrodes are divided by a separator and liquid electrolyte that permits lithium ions to shuttle back and forth between the two electrodes (Figure 1). When a battery is charged, lithium ions released from the positive electrode (cathode) will move toward the negative electrode (anode). When a battery is discharged, lithium ions will move from the anode to the cathode. Meanwhile, electrons released from lithium atoms in the anode will travel through the external circuit to the cathode, which provide electric power from chemical energy.[1]

In the case of anode, graphite is commercially used as the electrode material because of its high conductivity, good reversibility, and relatively low cost. But graphite has limited energy density because every six carbon atoms can hold only one lithium atom. Silicon is widely considered as one of the most promising anode materials.[8–10] Each silicon atom can bond to four lithium ions, which gives it ten times more capacity than graphite anode (4212 mA h g⁻¹ for Li₄Si at high temperatures and 3579 mA h g⁻¹ for Li₅Si₄ observed in room-temperature electrochemical cells,[11,12] versus 372 mA h g⁻¹ of graphite anode). Besides, silicon is attractive because of its natural abundance (the second-most abundant element in the earth’s crust), environmentally benignity and low electrochemical potential. Unfortunately, ~300% volume change of silicon during lithiation and delithiation leads to severe particle pulverization, unstable solid-electrolyte interphase (SEI) formation and loss of electrical contact in the electrode level, resulting in capacity fading and limited cycle life (Figure 1a–c). A variety of nano-sized silicon structures[13,14] such as nanoparticles,[15] nanowires,[16] nanotubes,[17] and nanoporous networks[18,19] have demonstrated enhanced mechanical integrity, which can effectively address this issue by accommodating the large volume change. The electrochemical cycling performance of these nanostructures is stable above 1000 mA h g⁻¹ in a large number of previous studies. Even though fundamental materials guidelines for designing nanostructures provide possible solution for improved gravimetric capacity and capacity retention, for practical applications, there are still many other important figures of merit to improve, including initial Coulombic efficiency (CE), areal capacity, volumetric capacity, and materials cost, which will be discussed one at a section in the rest of the article. Due to the length of this article, other factors such as binders, electrolyte, safety issues, electrode composition will be briefly mentioned instead of extensively discussed. The former four figures of merit are often impaired by the use of nanomaterials to overcome fracture problem. First, high electrode and electrolyte contact area leads to low initial Coulombic efficiency (Figure 1d), consumption of the lithium from the cathode and electrolyte, which seriously affect full cell performance. Second, tap density of nanomaterials can be limited due to much inter-particle space (Figure 1e), consequently generating low mass loading, low areal capacity, and even low volumetric capacity. Only when the highly promising electrochemical properties can still be maintained at higher areal capacity, these considerations of electrode structure design are meaningful. Third, complex synthesis procedures or expensive raw materials hinder the widespread application (Figure 1f).
There are several classical reviews about silicon anodes or alloy anodes,[20] focusing on various nanostructured materials, including 0D (nanoparticles), 1D (nanowires and nanotubes), and 2D (thin film) for stable long cycle life and increased rate performance because of superior advantages of nanomaterials.[8,14,21,22] Different from all the previous reviews, we prepare and organize this progress report by summarizing the barriers and progress toward the widespread applications of silicon anodes for next-generation lithium-ion battery.

In this progress report, we will first briefly discuss the fundamental challenges and solutions of silicon anodes, then focus on the issues and recent progress toward its commercialization, including initial Coulombic efficiency, areal capacity, and material cost. Specific examples are provided to illustrate these fundamental design principles for commercialization. In addition, we also discuss full cell performance of silicon anode and expect reliable prospect.

2. Fundamental Challenges and Solutions of Si Anodes

2.1. Material Pulverization

Silicon is an alloy anode and each silicon atom can host four lithium atoms. This mechanism of lithiation is associated with massive volume changes due to their intake of large amounts of lithium. When transforming from Si to Li$_4.4$Si, the volume mass changes due to their intake of large amounts of lithium atoms. This mechanism of lithiation is associated with massive volume changes due to their intake of large amounts of lithium. When transforming from Si to Li$_4.4$Si, the volume expansion is about 420%. This large volume expansion/contraction during lithium insertion/extraction induces large stresses, which can cause cracking and pulverization of Si, leading to loss of electrical contact and capacity fading.

In order to solve the material pulverization problem, it is found that silicon nanowire can circumvent the issue as they can accommodate large strain without pulverization.[16] Besides, it also shortens lithium diffusion distances, and provides good electronic contact and conduction, as shown in Figure 2a.[16]

When lithium ions moved into and out of the silicon nanowires, the nanowires suffered little fracture. The theoretical charge capacity for silicon anodes is achieved with 75% capacity retention after 10 cycles. Shape and volume changes upon first lithiation on a single nanostructure level and critical size of the Si nanowires is investigated in detail.[23–27]

Meanwhile, silicon particles in the nanoscale are also free of pulverization. Huang and co-workers reported a strong size dependence of fracture by studying lithiation behavior of individual spherical Si nanoparticles.[28] It was found that a critical particle diameter (>150 nm) also existed. When the diameter of particles is below this value, the particles will neither crack nor fracture upon initial lithiation. When the diameter of particles is above this value, the particles will initially form surface cracks and then fracture because of lithiation-induced stress, presented in Figure 2b. The lithiation behavior was carefully studied using in situ transmission electron microscopy (TEM). Electrochemical lithiation of a small Si nanoparticle around the critical size showed no fracture.[28]

Particle-size-dependent fracture behaviors of Si nanoparticles provide guidance for building high-performance lithium-ion batteries with size optimization. Besides, various structures with porosity or void space control, such as yolk–shell nanostructures and porous networks have been successfully employed to provide stable interphases and structures despite the large volume expansion, leading to improved cycling performance.[30–31]
2.2. Unstable Solid-Electrolyte Interphase

Apart from pulverization, large volume change during electrochemical cycling results in another severe issue: unstable solid-electrolyte interphase.\cite{17} When the potential of the anode is below $\approx 1$ V versus Li/Li$^+$, the anode surface becomes covered by a SEI film, due to the reductive decomposition of the organic electrolyte. In order to prevent further side chemical reactions from occurring, this layer should be dense and stable, electronically insulating but ionically conducting. However, the SEI crushed due to the volume change of Si anodes during cycling. The exposed fresh electrode surface leads to very thick SEI layer, resulting in low Coulombic efficiency, low electronic conductivity and higher resistance to ionic transport of the whole electrode. So, it is a big challenge to maintain a stable SEI layer over cycling.

Nanotechnology again provides new opportunities to address the unstable SEI issue. Wu et al. have successfully designed a double-walled silicon nanotube structure to stabilize SEI and achieve long cycle life.\cite{17} Double-walled Si-SiO$_x$ nanotube was prepared by a templating method, in which Si nanotubes are confined in SiO$_x$ outer shells. The void space in the center and the outer SiO$_x$ clamping layer force the silicon tube to expand inward during lithiation, leading to the intact and thin SEI layer over thousands of cycles (Figure 2c). The average CE of the double-walled silicon nanotubes electrode from the 2nd to 6000th cycles is 99.938% and 88% retained capacity was achieved over 6000 cycles. SEI control has also been realized on silicon nanoparticles (SiNPs), which are a promising candidate because they are industrially scalable and commercially available. In the respect of silicon nanoparticles, artificial SEI layer is introduced to overcome unstable SEI layer. Liu et al. also designed a “yolk–shell” structure to achieve a stable and scalable Si anode, in which silicon nanoparticle ($\approx 100$ nm) is “the yolk” and amorphous carbon ($5$–$10$ nm thick) is “the shell”, as shown in Figure 2d.\cite{29} The outer carbon shell can conduct electron and Li ion. The rationally designed void space between the inner particles and outer shell can permit the volume expansion of Si particle, leading to stable carbon shell and SEI layer on the outer surface without breaking. In another effort, mechanically strong and ductile graphene layer can also be used to maintain stabilized SEI layer.\cite{34} Recently, in situ and operando atomic force microscopy was used for mechanical property of SEI, of which the fracture energy is estimated to be $\approx 13$ J m$^{-2}$.\cite{35}

Although nanosized materials can achieve stable long cycling electrochemical performance by addressing materials pulverization and unstable SEI problem through elegant structure designs, there are also challenges related to nanosized materials, including low initial Coulombic efficiency, low tap density leading to low electrode mass loading and low areal capacity, and high cost. In the following sections, we will summarize...
these three main issues and recent progress toward commercialization of Si anodes for lithium-ion battery.

3. Initial Coulombic Efficiency

Coulombic efficiency refers to the ratio of discharge capacity and charge capacity, and is an important metric to evaluate the reversibility of battery reaction. As mentioned above, when the potential of the anode is below 1 V during charging, electrolyte decomposes on the interphase of anode surface and electrolyte to form SEI. The ideal SEI layer can permit lithium ion transport, prevent further electrolyte decomposition on the electrode surface, and increase the electrochemical cyclability and stability. However, in the first cycle, active Li\(^+\) is consumed due to the SEI film formation, resulting in irreversible capacity and extra cathode electrode consumption. In recent years, a lot of research focused on the initial cycle of silicon electrodes to investigate the formation mechanism at the very starting of battery operation, which can accelerate the understanding of the usually observed large irreversible capacity loss.[36–40]

Edström and co-workers demonstrated the interfacial mechanisms during charge and discharge, including surface silicon oxide change transformation, Li–Si alloying reaction, and formation of SEI layer.[41] As shown in Figure 3a, at the very beginning of discharge (0.5 V vs Li\(^+\)/Li), a thin SEI layer has already formed but lithium has not yet reacted with silicon. Lithium started to react with the silicon nanoparticle after further discharge to 0.1 V vs Li\(^+\)/Li. The formation of Li\(_2\)O and Li\(_x\)Si\(_y\)O\(_z\) (most probably Li\(_4\)SiO\(_4\)) is resulted by reaction with the surface SiO\(_2\) layer. Further reaction with the silicon leads to the formation of the Li–Si alloy. After full lithiation (0.01 V vs Li\(^+\)/Li), the Li–Si alloying process is almost finished. After full delithiation (0.9 V vs Li\(^+\)/Li), lithium has been moved out of the particle, Li\(_2\)O has disappeared and the thickness of the SEI has lightly decreased. Figure 3b shows a summary of the composition on the surface of the silicon nanowire samples at different working potentials as determined from the X-ray photoelectron spectroscopy (XPS) high-resolution scans of the initial two cycles.[6] SEI layer is composed of hydrocarbons, polyethylene oxide (PEO)-type oligomers, Li\(_x\)PF\(_y\), LiF, and Li\(_x\)PF\(_y\)O\(_z\) products (0.5 V); hydrocarbons and PEO-oligomers (0.1 V); Li\(_2\)CO\(_3\) and LiF (0.01 V), respectively, with Li\(_2\)CO\(_3\) as a major element.

While nanosized silicon has been effective to address pulverization problem for long cycling performance, large surface area of nano-Si leads to low initial Coulombic efficiencies due to the formation of SEI, resulting in irreversible capacity loss. Figure 3c presents the calculated surface area in contact with the electrolyte for secondary particles composed of 80 nm primary nanoparticles, with different size of secondary particles. The specific SEI area, which is the surface area in contact with the electrolyte divided by the mass of silicon, increases from...
1.5 m² g⁻¹ for 10 µm secondary particles to 15 m² g⁻¹ for 1 µm secondary particles and to 90 m² g⁻¹ for single yolk–shell particles.\(^{[42]}\) Large surface area leads to severe SEI formation in the first cycle and results in low initial Coulombic efficiency, and consumption of the lithium from the cathode and electrolyte during cycling. Besides, we should concern more about increased and accelerated native oxide surface derived from nanosized silicon materials with large surface area, which can affect the electrochemical performance and induce the inevitable use of hydrofluoric acid (HF).\(^{[43,44]}\)

The first-cycle Coulombic efficiency of silicon anode is typically in the range of 65–85%, far below that of commercial graphite anodes (90–94%). Below we will summarize the recent progress to achieve high initial Coulombic efficiency from three aspects, including secondary structure design, prelithiation, and electrolyte additive.

### 3.1. Secondary Structure Design

As mentioned above in Figure 3c, the electrode/electrolyte surface area can be tuned by forming secondary structures with nanoscale building blocks. Higher initial Coulombic efficiency is achieved by designing microstructures with electrolyte blocking layers in the outer surface, which decrease side reaction between electrode surface and electrolyte.\(^{[45,46]}\) We present four notable designs, including a pomegranate-inspired nanoscale design, porous silicon with graphene coating, micrometer-sized silicon with graphene cage, and silicon-nanolayer-embedded graphite.

In the pomegranate-inspired structure designed by Liu et al. (Figure 4a), secondary silicon particle of micrometer size is made up with yolk–shell silicon nanoparticle through a self-assembly process, where single silicon nanoparticle is
encapsulated by a conductive carbon layer with void space for volume expansion and the whole microsized particle is then encapsulated by a thicker carbon layer as an electrolyte barrier.\cite{42} The pomegranate design affords remarkable high initial Coulombic efficiency because of decreased surface area and outer electrolyte blocking layer. Besides, the self-supporting conductive carbon framework can hold electrochemical activity of silicon nanoparticle and facilitate lithium transport throughout the whole particle. At the same time, a high tap density is achieved for high areal capacity, which will be discussed later.

Besides electrolyte blocking layer of carbon shell, the graphene coated porous silicon particles\cite{48} have also been used to enable high Coulombic efficiency. The porous silicon particles were produced by two steps: ball milling the mixture of low grade silicon and water for silicon oxide (SiO\textsubscript{x}) particles, and then convert SiO\textsubscript{x} particles to mixed crystalline (Si) and amorphous (SiO\textsubscript{2}) phases by thermal disproportionation.\cite{48} This structure offers several unique features. Porous silicon with continuous and precise porosity control can offer a stable structure despite 400% volume change. Also the graphene shell can offer a stable interphase layer for stabilizing SEI formation, while increasing the electrical conductivity of whole structures. In addition, different from amorphous carbon layer, graphene shell will not trap the lithium ions, which is beneficial for high initial Coulombic efficiency. Therefore, porous/graphene composite can offer high CE of the first cycle, stable cycling performance, as well as superior rate performance, ideal for the next-generation lithium-ion batteries.

Instead of building secondary structure with nanoparticle building block, there are also some progress to use micrometer-sized Si as source materials. As discussed above, there are huge challenges associated with micrometer-sized Si due to particle pulverization. During repeated electrochemical cycling, Si microparticles rupture due to volume change, resulting in electrical contact failure. Besides, freshly exposed surfaces of silicon microparticle repeatedly react with the electrolyte, leading to a thick and ionically insulating SEI film. The destruction of electronic and ionic pathways causes critical cell decay. Li et al. introduced the conformal conductive graphene cage as an encapsulation layer in order to stabilize the Si microparticles electrodes over battery operations (Figure 4b).\cite{49} The mechanically strong and flexible graphene cage with a pre-designed void space can confine all the broken Si pieces within and provide
undamaged electrically pathways to the ruptured pieces. Most importantly, graphene cage can act as the electrolyte blocking layer, leading to SEI formation mainly on the surface of outer graphene cages. Efficient SEI formation on the microscale and graphite-like surface of the graphene cage reduces irreversible lithium ion consumption, and enhances initial Coulombic efficiency.

Si-containing graphite composites have been intensively pursued as one of the most promising anode materials for practical applications. Figure 4c shows the schematic and detailed structure of Si-nanolayer-embedded graphite/carbon hybrids (SGC).\(^{47}\) The Si nanolayer through chemical vapor deposition (CVD) process is both beneath inner pores of graphite particle and on the surface of graphite. The thickness of silicon layer is less than 20 nm, which can relieve the stress induced by volume change and permit fast lithium ion transportation, while homogeneous carbon coating layer from the last synthetic steps can further promote stable SEI formation. The unique Si-nanolayer-embedded graphite/carbon hybrids play a beneficial role for improved reversible specific capacity and initial Coulombic efficiency.

3.2. Prelithiation

Prelithiation presents exciting opportunities for next-generation high-capacity anodes with an alternative lithium source for high initial Coulombic efficiency, which prevents the lithium in the cathode from being consumed during side reactions of SEI formation. There are three main ways to prestore lithium in anodes. The first approach is to incorporate a temporary cell to realize electrochemical prelithiation by contacting lithium foil with electrolyte-wetted anodes.\(^{50,51}\) The second approach is to prelithiate silicon with microscale stabilized lithium metal powder through mechanical activation.\(^{52,53}\) The third one is to apply Li\(_x\)Si nanoparticles from chemical synthesis as a potential prelithiation reagent.\(^{54}\) We will discuss the three main methods one by one.

Electrochemical prelithiation stores lithium in advance to form a SEI layer through electrochemical reactions. As shown in Figure 5a, in the prelithiation process, silicon anodes were in contact with a piece of Li metal foil in liquid environment of electrolyte through a temporary cell under inert atmosphere. Potential difference between the two electrodes can

![Figure 5](image-url)

**Figure 5.** Prelithiation improves initial Coulombic efficiency: Schematic of a) electrochemical prelithiation, b) microscale stabilized lithium metal powder, c) ambient-air stable prelithiation with polymer coating, and d) Li\(_x\)Si nanoparticles. a) Reproduced with permission.\(^{55}\) Copyright 2016, American Chemical Society. b) Reproduced with permission.\(^{55}\) Copyright 2014, American Chemical Society. c) Reproduced with permission.\(^{56}\) Copyright 2016, American Chemical Society. d) Reproduced with permission.\(^{54}\) Copyright 2014, Nature Publishing Group.
sponsor spontaneous prelithiation for SEI formation, because of an external short circuit built between lithium metal foil and c-SiO₂ electrode. Proper electrochemical prelithiation requires a delicate control, since insufficient lithiumation cannot improve the initial Coulombic efficiency enough due to remaining Li trapping sites, while overlithiation reduces the lithium ion accommodation in the real first lithiation process. Choi et al. introduced a roll-to-roll scalable and delicate prelithiation process based on electrochemical reactions with lithium metal. The degree of prelithiation can be precisely controlled via a voltage monitoring process. The roll-to-roll electrochemical prelithiation process is consistent with the current manufacturing route and have the possibility to be employed in the next-generation lithium-ion battery with higher initial Coulombic efficiency.

Microscale stabilized lithium metal powder (SLMP) can serve as another sacrificial lithium source. It is necessary to mechanically activate the SLMP to fully employ lithium, after depositing the SLMP onto the Si anode. The pressure-activation process of SLMP through rolling compression is demonstrated as a cartoon in Figure 5b. By compressing the SLMP onto the surface of silicon with mechanical forces, the contact area between the Si surface and the SLMP is maximized. This step guarantees proper lithium diffusion into the silicon, which promotes stable SEI formation on the surface of silicon anode. The whole process is consistent with the present battery fabrication.

The whole prelithiation process should be finished under inert atmosphere because of the low potential and high chemical reactivity of lithium metal with H₂O and O₂. Combining above two prelithiation methods, Yang and co-workers proposed an active material/polymer/lithium anode trilayer structure with uniform distribution of lithium source, which is stable in ambient air. As illustrated in Figure 5c, lithium is deposited on a Cu foil, and then lithium is coated with a protective polymer layer (polymethyl methacrylate, PMMA) to make it ambient-air-stable. Then, the anode materials, deposited on the top of the polymer layer, can be integrated with electrolyte and conventional cathode materials to make up a real battery. As the polymer coating layer dissolves in the electrolyte, the anode materials contact lithium directly. As a result of pressure inside the cell caused by cell assembly process, lithium metal is activated and forms an in situ lithiated silicon anode.

The third excellent prelithiation reagent is Li₃Si nanoparticles, proposed by Zhao et al. for the first time. Compared with microscale stabilized lithium metal powder, Li₃Si nanoparticles show multiple excellent properties: First, nanoscale Li₃Si particles with size around 100–200 nm can distribute homogeneously in the entire electrode structure for a uniform and fast prelithiation. Second, the surface of Li₃Si nanoparticle can be modified to realize ambient air compatibility. Third, Li₃Si nanoparticle is compatible with the existing battery manufacturing environment and can be mixed with various anode materials during slurry processing and serves as an excellent prelithiation reagent. Figure 5d demonstrated Li₃Si–Li₂O core–shell nanoparticles synthesized from a one-step thermal alloying process with simple experimental setups. Si nanoparticles react with molten Li to form Li₃Si nanoparticles. As the nanoparticles react with limited oxygen, a dense Li₂O passivation layer is formed on the surface of Li₃Si. As-synthesized Li₃Si–Li₂O core–shell nanoparticles can be used as a localized prelithiation reagent in the mixture of electrode slurry and is activated at the presence of carbonate electrolyte, resulting lithium diffusion into anode materials. In the follow-up study, concept of artificial SEI layer is built to improve air stability. A continuous and uniform artificial SEI coating consisting of Li alkyl carbonate and LiF with long hydrophobic carbon chains is formed on the surface of Li₃Si nanoparticles by using 1-fluorodecanec. The coated Li₃Si nanoparticles showed improved air stability at a low-humidity level (<10% relative humidity). Furthermore, ambient air stable Li–Si–O anode is demonstrated with low-cost SiO and SiO₂ starting materials. As-synthesized Li₃Si/Li₂O composites provided a unique structure combining homogeneously dispersed active Li₃Si nanodomains embedded in a robust Li₂O matrix. The Li₂O matrix is highly crystalline and contact area between Li₃Si nanodomains and Li₂O matrix is increased, which is beneficial for stability in dry air and even ambient air compatibility (~40% RH). Besides, Li₃Si/graphene composite can serve as an alternative for air stable and free-standing lithium metal anode.

3.3. Electrolyte Additive

Electrolyte additive plays a significant role in passivating the Si/electrolyte interphase during the initial lithiation process. Aiming to form a stable SEI layer on the surface and improve the cycle life of Si electrodes, additives/cosolvents including fluoroethylene carbonate (FEC), propylene carbonate (PC), vinylene carbonate (VC), lithium bis(oxalate)borate (LiBOB), lithium difluoro(oxalate) borate (LiDFOB), and succinic anhydride have been introduced into the electrolyte solutions for anodes materials.

Among all the additives, FEC shows the great promise. There are two main degradation routes for FEC additive: defluorination and ring-opening. FEC degrades at a higher reduction potential, prior to ethylene carbonate (EC)/diethyl carbonate (DEC), to form an initial SEI layer combining LiF and other organic species (–CHF–OCO₂-type compounds). Furthermore, the initially formed SEI can substantially limit the degradation of EC/DEC and thus prevent the excess formation of an inhomogeneous SEI layer, and enhance the initial Coulombic efficiency. Density functional theory simulation based molecular dynamics shows lithium fluoride (LiF), the most plausible product of the FEC reductive decomposition, adsorbs the organic SEI film components through the F–Li bindings, which demonstrate the role of glue within the SEI film for stabilizing SEI. However, much attention should be paid to optimize amount of FEC because residual FEC results in gas evolution and HF formation, which causes significant dissolution of cathode materials in full cell, especially at elevated temperatures.

We summarize the initial Coulombic efficiency in Figure 6 by comparing the three main improve methods with original nanostructured silicon anodes. The enhancement of initial Coulombic efficiency is quite obvious. The first-cycle Coulombic efficiency of silicon anode is typically in the range of 65–80%, such as 65% for core–shell silicon nanoparticles and 73% for silicon nanowire, far below that of commercial graphite anodes (90–94%). FEC electrolyte additive can increase...
the initial Coulombic efficiency to 81% of silicon film\(^{[66]}\) and 87% of silicon particle\(^{[61]}\) due to the prior formed SEI layer by FEC and the limited degradation of EC/DEC. The secondary structure design can further improve the initial Coulombic efficiency comparable to the level of commercial graphite (90%). For example, because of reduced surface area between silicon and electrolyte and the outer electrolyte blocking layer, as presented in the Figure 6, pomegranate Si microparticle,\(^{[43]}\) porous Si with graphene coating,\(^{[48]}\) silicon-nanolayer-embedded graphite,\(^{[47]}\) multiscale hyperporous Si flake,\(^{[97]}\) and micrometer-sized Si particles of graphene cages\(^{[49]}\) show initial Coulombic efficiencies of 82%, 89.5%, 92%, 92.7%, and 93.2%, respectively. Furthermore, initial Coulombic efficiency with pretreatment method is above the commercial standard. The three main approaches of pretreatment can prestore Li and realize initial Coulombic efficiency of 90% (Li metal powder),\(^{[55]}\) 94.9% (electrochemical pretreatment),\(^{[50]}\) >100% (Si/polymer/lithium),\(^{[56]}\) and >100% (Li, Si nanoparticles).\(^{[54]}\)

In summary, the main three methods indeed improve the initial Coulombic efficiency of silicon anode. Through structure design and sacrificial lithium, the initial Coulombic efficiency can reach or exceed the commercial level of state-of-the-art graphite anodes (90%) step by step. The pretreatment procedure, such as Li, Si nanoparticle, is compatible with the existing battery manufacturing process. The challenge of initial Coulombic efficiency can be solved by combining the above method considering the scalable production and feasible operations.

4. Areal Capacity

Practical application requires high areal capacity, the capacity on a unit area of electrode, to minimize the weight percentage of metal foil current collectors in the battery. The large volume changes of silicon anode makes it challenging to achieve stable cycling at high areal capacity, even though it cycles stably at low areal capacity. In thick electrode, silicon spheres expand vertically during lithiation, resulting in the increase of electrode thickness. During delithiation, as lithium extracts, silicon particles contract resulting in destruction of electrical pathways to their surrounding particles and current collectors. As exemplified in Figure 7a, the original electrode consisted of 6 × 6 grid of cubic close-packed Si spheres.\(^{[68]}\) After 270% expansion, silicon spheres are displaced vertically to accommodate the horizontal expansion. This drastic electrode morphology change can lead to electrical isolation of active material, electrode failure, and capacity fading (Figure 1c). Thus, it is urgently needed to maintain the electrical connection at the electrode level and the integrity of the morphology electrodes over cycling. Tarascon et al. use a simple mode with geometrical considerations to suggest that in order to avoid particle rearrangement due to volume change of the silicon, the volumetric percentage of silicon in single layer sphere is only 14%, as presented in Figure 7b, as enough void space is necessary to accommodate the volume change. In the bulk-nanoporous-silicon negative electrode, there are many nanopores surrounding the Si nanoligaments, which can accommodate large volume changes. The accommodation limit up to porosity is quite important since low porosity can lead to fractures the Si nanoligaments (Figure 7c).\(^{[66]}\) Therefore, the areal mass loading is severely limited by the low silicon proportion and low electrode thickness for all the reasons listed above.

Although nanostructure silicon materials have been effective to solve silicon pulverization problem, the reduced size creates more interparticle space and surface, giving rise to low tap density and high interparticle resistance. The low tap density causes low volumetric capacity and long electron pathway for the same mass loading, which makes it difficult to maintain electrical and ionic pathways during cycling. The large interparticle resistance also creates barriers for the electron transport between current collectors and active materials. Low areal mass loading and low tap density altogether hinder the achievement of high areal capacity. In this section, we will summarize the recent effort to improve areal capacity from the two aspects of higher mass loading and higher tap density through structure designs and employing conductive binders.

4.1. Structure Design

As discussed in section 3.1, silicon particle with large size (micrometer) can reduce surface area. In addition, the tap density of micrometer-sized particles is generally higher than that of nanoparticles due to the reduced interparticle space. Higher tap density can decrease the electrode thickness and shorten the electron pathway for the same mass loading.

To follow up with the pomegranate-inspired design, industrially mature mechanical based approach is used to densely pack primary building blocks (Figure 8a).\(^{[70]}\) A high tap density of 0.91g cm\(^{-3}\) and stable cycling with over 2 mg cm\(^{-2}\) of...
areal mass loading (≈ 3.5 mA h cm$^{-2}$) is achieved (Figure 8d). Besides, mesoporous Si sponge with diameter over 20 µm showed an area-specific-capacity of ≈1.5 mA h cm$^{-2}$ and 92% capacity retention over 300 cycles.\cite{71} The highly porous structure with thin crystalline Si walls surrounding large pores can help to accommodate volume change (Figure 8b,c,e).

Apart from the silicon/carbon nanocomposite, alloying silicon with other inactive metals to form micron-sized particles is another route to increase tap density. Lithium-inactive metal silicides have good electrical conductivity and can buffer the volume expansion from lithiation of silicon, providing stable electrochemical performance. The microscale alloy particle size leads to improved tap density compared to silicon nanoparticles. FeCuSi ternary composite with an average diameter of 6.5 µm demonstrates the tap density of 0.8 g cm$^{-3}$.\cite{72}

Besides, the tap density of SiNiSi$_2$Al$_2$O$_3$@C composite was measured to be 1.34 g cm$^{-3}$ due to the higher density of NiSi$_2$ (4.83 g cm$^{-3}$) compared to that of Si (2.33 g cm$^{-3}$).\cite{73}

Tap density of various Si-based anode materials can be found in Figure 9. Compared with the low tap density of silicon nanoparticles (0.16 g cm$^{-3}$), the tap density of Si–C composite with granule hierarchical bottom-up assembly\cite{74} Si–C composite from SiO disproportionation,\cite{75} nano/microstructured Si/C,\cite{46} and pomegranate Si microparticle\cite{42} are 0.49, 0.78, 0.81, and 0.53 g cm$^{-3}$, respectively. Si-containing graphite composites also have shown great potential for practical application. For example, Si-nanolayer-embedded graphite/carbon hybrids show the tap density of 1.0 g cm$^{-3}$.\cite{47} Therefore, it is confirmed that secondary microstructure composites could improve tap density by reducing interparticle space.

### 4.2. Conductive Binder

Polymer binder is necessary for making slurry and maintaining the integrity of the structure, and therefore critical for stable electrochemical performance. Traditionally, the following categories of binders have been shown effective for Si anode: carboxymethyl cellulose (CMC) and alginate, conventional synthetic polymer such as poly(acrylic acid) and polyimide. Recent works have demonstrated that the polymeric binders with high electronic conductivity and binding affinity with Si can help achieve high areal capacity for silicon anodes.\cite{76–79}

Self-healing binders (SHP) have both electrical and mechanical healing capabilities, which heal the damages caused by fracture of silicon microparticles during battery cycling.\cite{80} Figure 10a presents schematic illustration and cycling behavior of a conventional microparticle silicon electrode and a self-healing electrode. In a traditional silicon-based anode, the silicon particles are surrounded by polymer binder to maintain electrical connections between active materials and the current collector. During cycling, large volume change results in fracture of polymer binder and silicon particles and the loss of electrical contact. However, self-healing binder is stretchable and...
can repair spontaneously the mechanical destruction of anodes. As shown in Figure 10b, dynamic reassociation of hydrogen bonds due to amorphous structure and low glass-transition temperature lead to spontaneous self-healing, which results in more stable electrical and mechanical connections among the anodes. Besides, good mechanical property of conductive polymer binder is essential to accomplish the calendering or winding during manufacturing process. The good mechanical stretchability of crosslinked network of SHP enables structural integrity when it is stretched to three times of its initial length. Besides, the resistance of SHP/CB did not change significantly even though the composite was subjected to a 100% strain, in order to retain electrical conductivity.

Another functional conductive polymer binder, poly(9,9-dioctylfluorene-co-fluorenone-co-methylbenzoic ester) (PFM) has also been developed to provide electronic connections between the conductive polymer matrix and active materials at molecular-level, because of electrical conduction and tightly adhesion (Figure 10c).\[^{[55]}\] Chemical structure of the PFM functional conductive polymer binder is presented in Figure 10d, in which the blue shadow highlights the ester group for adhesion bonds formation with the SiOH surface. Figure 10e shows the transesterification reaction between the ester functional group of the PFM binder and the SiOH surface group during the electrode drying process, which provides strong adhesion. In addition, poly(1-pyrenemethyl methacrylate-co-methacrylic acid) (PPyMAA) is used for a high tap density nanoSi anode.\[^{[77]}\] PPyMAA can bind to nanoSi with strong affinity and polymer is electronically conductive at the presence of pyrene. High electronic conductivity together with mechanical binding of polymer can help to significantly improve electrode areal capacity. Detailed mechanical property of these polymers needs to be further studied to ensure the requirement of calendering or winding during manufacturing process. We summarize the specific areal capacity and mass loading of several representative works in Table 1, which is divided into three main categories. First, all of the selected designs with microscale secondary structures present areal capacities above
and mechanical binding of polymer improve electrode areal capacity significantly. Siliconself healing polymer/carbon black composite (Si-SHP/CB) have exhibited high areal capacity (above 3 mA h cm\(^{-2}\)) and stable cycling for more than 140 cycles using low-cost large Si particles.\(^{[83]}\) Although areal capacity and mass loading is drastically improved, weight proportion of conductive polymer is still high. Weight ratio between active materials and polymer component is 2:1 for PPy and Si-SHP/CB, 1:1 for self-healing SIMP. Future study should focus on reducing conductive polymer binder amount and study volumetric or gravimetric energy density considering all components.

Based on the areal capacity and electrode thickness, volumetric-based information is calculated and summarized, which is more important than the gravimetric capacity for certain applications. Self-healing SEI-based silicon and silicon/graphitic carbon nanowire array present volumetric capacity of 1100 mA h cm\(^{-3}\) (100th cycle) and 1500 mA h cm\(^{-3}\) (after 200 cycles), which is higher than graphite of 550 mA h cm\(^{-3}\). Therefore, higher tap density with close packing of anode materials demonstrate high volumetric capacity. Taking the self-healing SEI-based Si@TiO\(_2\) electrode as an example, the electrode thickness involved in volumetric capacity is the one containing electrode materials before cycling. The electrode thickness of Si@TiO\(_2\) is 14.7 µm before cycling, with 25.5% increment after 100 cycles.

Figure 9. Tap density of various Si-based anodes.

Figure 10. Polymer binder for higher areal capacity: a) Schematic illustration of the design and behavior of a conventional silicon electrode and stretchable self-healing electrode. b) Chemical structure of the self-healing polymer. c) Schematic of an electrode design with low concentration of functional conductive polymer binder. d) Chemical structure of the PFM functional conductive polymer binder. e) Transesterification reaction between the ester functional group of the PFM binder and the SiOH surface group. a, b) Reproduced with permission.\(^{[84]}\) Copyright 2013, Nature Publishing Group. c–e) Reproduced with permission.\(^{[55]}\) Copyright 2014, American Chemical Society.
at delithiated state. Hence, the electrode swelling should also be taken into account when considering the volumetric-based information. Setting testing criteria to characterize volumetric capacity is quite important to compare the performances of different electrodes directly. Because of volumetric expansion, it is important to clarify the state of electrode (lithiated or delithiated) and cycling number when calculating the volumetric capacity. At the aspect of energy density, SGC[49] demonstrate energy density of 1043 W h L⁻¹ (after 100 cycles) in a full coin cell configuration with LiCoO₂ cathode. In addition, monodisperse porous silicon nanospheres[87] and graphene coated silicon particle with SiC-free graphene[87] growth can reach energy density of 850 and 700 W h L⁻¹ (200th cycle).

### 5. Low Raw Material Cost

While nanostructured silicon anodes show great potential in lithium-ion battery, the commercial application can be limited by high cost related to the complex fabrication and expansive raw materials. Traditionally, silicon nanostructures are fabricated either from top-down (chemical etching) or bottom-up (CVD) method, which typically involve either toxic silane precursors or expensive high purity silicon sources. Recently, it is found that various low grade silicon[5,48,88,90] and natural sources[91–96] can serve as cost-effective sources to produce nanostructured silicon for lithium-ion battery.

#### 5.1. Low Grade Silicon

Low-grade silicon is an attractive material choice because of its abundance and cheap price. Several low-grade silicon sources, such as metallurgical-grade silicon (M-Si, ≈98 wt% Si, $1 kg⁻¹) and ferrosilicon (Fe-Si, ≈83.4 wt% Si, $0.6 kg⁻¹) provide annual global production over six million tones.[90] It is found that Si nanoparticles with controlled size can be produced at large-scale through a simple and scalable high energy mechanical milling process.[90] The size of obtained nanoparticles is ≈150 nm, which provides stable electrochemical performance (Figure 11a).[89] It is found that inactive FeSi₂ is formed in nanoparticles produced from ferrosilicon sources, which can serve as a buffer layer to alleviate the volume change during cycling. Whereas, nanoparticles from metallurgical Si sources have higher capacity and better kinetic properties due to higher purity source materials and better electronic transport properties. The purity of these obtained nanoparticles can also be improved by acid etching processes up to 99.999% (wt%).[7] During high energy ball-milling processes, the impurity-rich regions containing Fe, Al, and Ca are mechanically weak, can be easily exposed on the surface, and be effectively removed through acid etching. Therefore, it can be easily understood that the purity goes up with the smaller size of Si particles in this nanopurification process (Figure 11b).

Morphology control in porous network is also important to buffer the volume expansion. A unique nanoperforation process is developed to produce porous Si particles, combining modified ball milling, annealing, and acid treating, with a precise and continuous porosity control (from 17 to 70%) (Figure 11c).[48] Metal-assisted chemical etching has also been useful for porous silicon networks with low grade silicon source (Figure 11d).[90] The similar structure is demonstrated by Zhou and co-workers and Wehrspohn and co-workers.[88,97] Above all, these results show great potentials of recycling low grade silicon for commercial silicon anodes.

#### 5.2. Natural Source

Silicon is the second most abundant element on earth, widely distributed in rocks, sands, and soils as various forms of silicates or Si dioxide. Recently, there is progress in low-cost

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**Table 1. Areal capacity and mass loading of different kinds of structures.**

<table>
<thead>
<tr>
<th>Active materials</th>
<th>Mass loading [mg cm⁻²]</th>
<th>Initial areal capacity [mA h cm⁻²]</th>
<th>Areal capacity [mA h cm⁻²]</th>
<th>No. cycles</th>
<th>Applied current density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano/microstructured Si/C[46]</td>
<td>3.1 (Si/C)</td>
<td>2.25</td>
<td>&gt;2</td>
<td>200</td>
<td>0.2 A g⁻¹</td>
</tr>
<tr>
<td>Mesoporous silicon sponge[71]</td>
<td>3.5–4 (electrode)</td>
<td>10</td>
<td>4.2</td>
<td>35</td>
<td>0.5 mA cm⁻² for lithiation, 0.75 mA cm⁻² for delithiation</td>
</tr>
<tr>
<td>Nonfilling carbon coating[82]</td>
<td>2.01 (Si/C)</td>
<td>3.22</td>
<td>2.84</td>
<td>100</td>
<td>0.05 mA cm⁻² for first 3 cycles, 0.25 mA cm⁻² for later cycles</td>
</tr>
<tr>
<td>Secondary Si particle by mechanical pressing[78]</td>
<td>2.02 (electrode)</td>
<td>3.5</td>
<td>2.3</td>
<td>100</td>
<td>0.1 mA cm⁻² for first 3 cycles, 0.5 mA cm⁻² for later cycles</td>
</tr>
<tr>
<td>Pomegranate Si microparticle[42]</td>
<td>3.12 (Si/C)</td>
<td>3.67</td>
<td>&gt;3</td>
<td>100</td>
<td>0.03 mA cm⁻² for first 3 cycles, 0.7 mA cm⁻² for later cycles</td>
</tr>
<tr>
<td>FeCuS[72]</td>
<td>–</td>
<td>3.08</td>
<td>1.968</td>
<td>300</td>
<td>1C (1C = 3 mA h cm⁻²)</td>
</tr>
<tr>
<td>Si–NiSi₂–Al₂O₃@C[76]</td>
<td>1.65 (active)</td>
<td>1.2</td>
<td>0.96</td>
<td>200</td>
<td>200 mA g⁻¹</td>
</tr>
<tr>
<td>PPyrMAA binder[77]</td>
<td>–</td>
<td>2.35</td>
<td>2</td>
<td>120</td>
<td>420 mA g⁻¹</td>
</tr>
<tr>
<td>PPyr[78]</td>
<td>1.34 (Si)</td>
<td>2.7</td>
<td>2.5</td>
<td>40</td>
<td>0.226 cm⁻²</td>
</tr>
<tr>
<td>Self-healing SiMP[80]</td>
<td>0.704 (Si)</td>
<td>2.06</td>
<td>2.02</td>
<td>8</td>
<td>1/30C (1C = 4200 mA h g⁻¹)</td>
</tr>
<tr>
<td>Si-SiHP/CF[81]</td>
<td>1.6 (Si)</td>
<td>4.16</td>
<td>&gt;3</td>
<td>140</td>
<td>0.1 mA cm⁻² for first 3 cycles, 0.3 mA cm⁻² for later cycles</td>
</tr>
</tbody>
</table>
synthesis of porous Si nanomaterials from magnesiothermic reduction with abundant and low-cost SiO\textsubscript{2} sources, such as rice husk and sand.

As a widespread food crop for human sustenance, rice is widespread with massive annual production near 10\textsuperscript{8} tons worldwide. As demonstrated in Figure 12a, rice husk is built up with interconnected nanoporous structure to ventilate air and moisture and contains ≈15–20 wt\% silica.\cite{91} Sand is a naturally abundant raw material with annual worldwide production over 115.0 million metric tons and cost lower than $10 per ton. The detailed fabrication process of turning low cost silicon contended sources into functional silicon anodes is presented in Figure 12b.\cite{96} The obtained 3D porous silicon shows stable electrochemical performance, which prove that the infinite natural source can easily satisfy the high and growing demand for energy-storage in the next decades.

6. Challenges of Full Cells

Most works still focus on half-cells with Li metal as the counter electrode for studying the electrochemical behavior of latest synthesized materials. In half-cell configuration, lithium amount in Li foil counter electrode is exhaustless, while lithium amount is limited by cathode and electrolyte in full cell. The drain of recyclable lithium is the main reason for the performance degradation of the full cell. To some extent, long-term cycling performance of silicon anode half-cell cannot provide enough information since fading of lithium metal counter electrode had effect on the whole performance. Therefore, testing silicon anodes in full cell configuration is important for serious evaluation and trouble-shooting toward practical application. Energy and power density of full cells have a higher commercial relevance.

In a full coin cell configuration with LiCoO\textsubscript{2} cathode, self-healing SEI-based silicon electrode demonstrates two times higher gravimetric capacity (762 mA h g\textsuperscript{-1}) and volumetric capacity (1100 mA h cm\textsuperscript{-3}), compared with graphite of 340 mA h g\textsuperscript{-1} and 550 mA h cm\textsuperscript{-3}.\cite{84} Besides, binder component and electrolyte additive are systematically studied to further understand silicon-based full cell system.\cite{98,99} At aspect of energy density, Si-nanolayer-embedded graphite/carbon hybrids\cite{47} and monodisperse porous silicon nanospheres\cite{86} can reach 1043 and 850 W h L\textsuperscript{-1}, respectively. Much effort should
be conducted to achieve high energy density and long cycle life required for practical LIBs, through matching suitable high capacity cathodes with silicon-based anodes. With full cell configuration, parameters such as the average lithiation/delithiation voltage and the Coulombic efficiency are more appropriate to provide detailed electrochemical performance. Therefore, full cell performance provides a more reliable and relevant prospect of the practical applications of a specific material.

7. Conclusion and Outlook

Silicon has been intensively pursued as one of the most promising anode materials for the next-generation lithium-ion battery primarily because of high specific capacity. In past decades, various nanostructures have been demonstrated to address major challenges for stable electrochemical performance. However, the widespread commercial application is still limited due to some new issues resulted by nanomaterials. In this review, we focus on the issues and recent progress toward commercialization of Si anodes for lithium-ion battery, including initial Coulombic efficiency, areal capacity, and material cost. The principles for structure designs in addressing these challenges were discussed in detail and typical examples were provided to illustrate these principles.

Despite great progresses, there are still problems remained to be addressed. As discussed earlier, none of the structures can solve all the three problems at the same time. Future work on designing a new structure or combining the above possible solutions is expected, which can simultaneously provide high energy density and long cycle life.
initial Coulombic efficiency, high areal capacity, and low cost. All-solid state lithium-ion microbatteries with silicon anodes show great potential in systems-on-a-chip.[100,101] Since the metal current collector on the anode side is usually a 10 μm thick copper foil with an areal density -10 mg cm⁻², which is much larger in weight than silicon active materials, there are many research progresses to avoid the use of heavy current collector to enhance the overall gravimetric energy density.[102,103] On the other hand, reports on freestanding or binder-free electrode structures should also mention the electrode thickness and areal capacity, for comprehensive evaluation of the pros and cons. Even though there is still much room to further improve the areal capacity; freestanding or binder-free electrode structures also show great potential application in flexible devices. It is expected that, with extensive efforts, high energy density and power density silicon-based lithium-ion battery can provide better service in practical application.

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Conflict of Interest
The authors declare no conflict of interest.

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