Topical Review

Challenges and prospects of nanosized silicon anodes in lithium-ion batteries

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Abstract

Batteries are commonly considered one of the key technologies to reduce carbon dioxide emissions caused by the transport, power, and industry sectors. We need to remember that not only the production of energy needs to be realized sustainably, but also the technologies for energy storage need to follow the green guidelines to reduce the emission of greenhouse gases effectively. To reach the sustainability goals, we have to make batteries with the performances beyond their present capabilities concerning their lifetime, reliability, and safety. To be commercially viable, the technologies, materials, and chemicals utilized in batteries must support scalability that enables cost-effective large-scale production.

As lithium-ion battery (LIB) is still the prevailing technology of the rechargeable batteries for the next ten years, the most practical approach to obtain batteries with better performance is to develop the chemistry and materials utilized in LIBs—especially in terms of safety and commercialization. To this end, silicon is the most promising candidate to obtain ultra-high performance on the anode side of the cell as silicon gives the highest theoretical capacity of the anode exceeding ten times the one of graphite. By balancing the other components in the cell, it is realistic to increase the overall capacity of the battery by 100%—200%. However, the exploitation of silicon in LIBs is anything else than a simple task due to the severe material-related challenges caused by lithiation/delithiation during battery cycling. The present review makes a comprehensive overview of the latest studies focusing on the utilization of nanosized silicon as the anode material in LIBs.

Keywords: lithium ion battery, anode, silicon, nanosize

(Some figures may appear in color only in the online journal)

Abbreviations

| Abbreviation | Description                  |
|--------------|------------------------------|
| ALD          | Atomic layered deposition    |
| ARC          | Accelerating rate calorimeter|
| CE           | Coulombic efficiency         |
| CNT          | Carbon nanotube              |
| CVD          | Chemical vapor deposition    |
| DEC          | Diethyl carbonate            |
| DMAA         | Dimethylacrylamide           |
| DMC          | Dimethyl carbonate           |
| dQ/dV        | Differential capacity        |
| DSC          | Differential scanning calorimetry |
| EC           | Ethylene carbonate           |
| EMC          | Ethyl methyl carbonate       |
| FEC          | Fluoroethylene carbonate     |
| ICE          | Initial Coulombic efficiency |
| LiBOB        | Lithium difluoro(oxalato)borate |
| NaCMC        | Sodium carboxymethyl cellulose |
1. Introduction

Lithium-ion batteries (LIBs) have the advantages of high operating voltage (3.0 to 3.8 V) and high energy density (100 to 250 Wh kg\(^{-1}\), 300 to 680 Wh L\(^{-1}\)) [1]. Therefore they are widely used in mobile power instruments and energy storage devices. To meet the ever-growing requirements of large-capacity and high-power batteries like in cases of electric vehicles, scientists have been continuously searching for new electrode materials with higher energy and power densities. A conventional graphite anode can intercalate one lithium per six carbon to form LiC\(_6\). The LiC\(_6\) corresponds to a gravimetric capacity of 372 mAh g\(^{-1}\) and a volumetric capacity of 719 Ah L\(^{-1}\). By comparison, silicon (Si) is considered to be a promising alternative LIB anode material. It forms Li\(_x\)Si\(_3\), Li\(_{12}\)Si\(_7\), Li\(_{13}\)Si\(_4\), Li\(_{15}\)Si\(_4\), and Li\(_{22}\)Si\(_3\) silicon-lithium alloys during the alloying process, among which Li\(_{15}\)Si\(_4\) has a capacity of 3579 mAh g\(^{-1}\) (2194 Ah L\(^{-1}\)) at room temperature, which is the highest theoretical capacity known for the anode material [2–4]. At the same time, the average voltage platform of Si (0.4 V vs. Li/Li\(^+\)) is higher than that of the graphite electrode (0.125 V vs. Li/Li\(^+\)), which makes it possible to avoid lithium plating and dendritic lithium formation on the anode material surface during the lithiation/delithiation process [4–6]. As a result, the safety performance of the battery can be significantly improved. Also, Si has the advantages of abundant reserves in the earth’s crust and low price, which fosters further the industrial interest to utilize silicon in batteries.

Despite these advantages, silicon still has severe shortcomings when used as an electrode material. The core problem for the utilization of Si in a LIB is its vast volume expansion during lithiation. Si electrode can expand by 280% (Li\(_{4}\)Si\(_4\)), which is much more than 10% for the graphite electrode. First, Si particles are gradually pulverized due to the repeated volume change and lose electrical contact between the active and other components, including conductive carbon and binder, which causes the capacity to decrease sharply and the cycle performance to decline rapidly. Secondly, the volume change also gradually causes active material to peel off the current collector, resulting in an electrical contact loss between the active material and the current collector, and the electrode capacity reduction after the initial cycle [7]. Besides, the SEI layer is fractured and reformed continuously due to the volume expansion/contraction behavior of the Si electrode during cycling, resulting in the continuous exposure of fresh Si surface to the electrolyte. As a result, electrolyte degradation takes place continually on the highly reducing fresh lithiated Si surface, thus leading to an irreversible capacity loss at each cycle and eventual cell death [8]. Both the mechanical failure and the electrolyte degradation can make the Si electrode lose its electrochemical activity very rapidly in the cycling process. Last, the semiconductor nature of Si makes it difficult to be utilized as the electrode material in the practical applications of LIBs due to the issues of low electron conductivity [9]. The electrical conductivity of Si particles is about 10\(^{-3}\) S cm\(^{-1}\) at room temperature and is sensitive to the dopant concentration [10].

Over the past decade, researchers have explored various ways to improve the performance of silicon as the anode material, one of which is designing nanosized Si anode materials to enhance their lithium storage performance. These nanosized silicon includes Si nanoparticles [11–13], Si nanowires [14], Si nanotubes [15], Si thin flakes [16], Si nanopillars [17], Si nanofilms [18], and Si with nanoporous structure [19, 20]. For further improvement, nanosized Si is coated, encapsulated or dispersed typically in some form of carbon, thereby avoiding the direct contact of silicon with the electrolyte [21]. However, nanosized silicon still faces big challenges to be used in practical commercial cells, which require solutions at the atomic, particle, binder, electrode, electrolyte, and cell levels. A large amount of research has been devoted to this field. When searching Web of Science with entering ‘LIB’ and ‘silicon’ at the same time, it was found that more than 5000 papers had been published in the past 10 years (figure 1(a)) as well as the cited number has been increasing rapidly (figure 1(b)). In the present paper, we give a brief review of nanosized silicon anode material in terms of fundamental electrochemistry in LIBs, some key challenges, and the possible solutions that are relevant to the silicon anode researchers.

2. Electrochemistry of nanosized Si anode

2.1. Lithiation/delithiation process of nanosized silicon

Many ex-situ and in situ measurements (e.g. XRD, TEM, NMR, and Mössbauer) have been used to understand the structural changes of Si during the lithiation/delithiation process. Obrovac et al. have investigated the reaction mechanism of the Si electrode very carefully [2]. Nanosized Si is very similar to the bulk silicon in terms of electrochemistry [4]. Figure 2(a) [2] shows the voltage curve of a crystalline silicon electrode cycled vs. a lithium anode in 2320 coin cell with an electrolyte of 1 M LiPF\(_6\) in EC/DEC 1:2 by weight at 500 mA g\(^{-1}\). The voltage curves illustrate the electrochemical conversion of crystalline silicon to amorphous lithiated silicon, amorphous lithiated silicon to crystalline Li\(_{13}\)Si\(_4\), and Li\(_{15}\)Si\(_4\) back to amorphous silicon. However, the lithiated product of the Si electrode is related to the lower cutoff voltage [2].

Plateau I in figure 2(a): The first lithiation process is corresponding to the transformation from crystalline Si (cr-Si) to amorphous Li\(_x\)Si (a-Li\(_x\)Si). As shown in figure 2(a), the sloping plateau at 170 mV corresponds to the two-phase reaction between cr-Si and the heavily lithiated amorphous Li\(_x\)Si phase.

\[
\text{cr-Si} + x\text{Li} \rightarrow a-\text{Li}_x\text{Si} \quad (170 \text{ mV, two - phase region}) \quad (1)
\]
Figure 1. (a) The publication number between 1990 and 2020 when searching Web of Science with ‘lithium ion battery’ and ‘silicon’ at the same time. (b) The cited number of publications shown in figure 1(a).

Here, the term ‘Two-phase’ refers to the existence of both amorphous and crystalline phases.

Plateau II in figure 2(a): The following lithiation process occurs at and below 50 mV, corresponding to the formation of crystalline Li$_{15}$Si$_4$ (cr-Li$_{15}$Si$_4$). The tiny plateau near 50 mV corresponds to the two-phase reaction between the amorphous Li$_x$Si phase and the cr-Li$_{15}$Si$_4$ phase. It is consistent with the \textit{in situ} TEM results that present evidence for Li$_{15}$Si$_4$ as the final phase in fully lithiated nanosized Si, including nanoparticles [22] and nanowires [23].

$$\text{a-Li}_x\text{Si} + \text{Li} \rightarrow \text{cr-Li}_{15}\text{Si}_4 \quad (50 \text{ mV, two-phase region})$$  

$$\text{(2)}$$
Figure 2. (a) Typical voltage curves of Si electrode in a half cell (Li as a counter electrode). (b) The dQ/dV curves of the Si electrode shown in figure 2(a). L(cr-Si): Lithiation of crystalline silicon; D(\text{Li}_{15}\text{Si}_{4}): Delithiation of \text{Li}_{15}\text{Si}_{4}; L\text{I}(a\text{-Si}): High-voltage lithiation plateau of amorphous silicon; L\text{I}(a\text{-Si}): Low-voltage lithiation plateau of amorphous silicon; D1(a-Si): Low-voltage delithiation plateau of amorphous silicon; D2(a-Si): High-voltage delithiation plateau of amorphous silicon [2]. Copyright: The Electrochemical Society, 2017.
Plateau III in figure 2(a): The delithiation of cr-Li$_{15}$Si$_4$ occurs by a two-phase reaction where the crystalline Li$_{15}$Si$_4$ is converted to amorphous Li$_x$Si (a-Li$_x$Si). Further delithiation corresponds to a solid solution reaction where the a-Li$_x$Si phase is uniformly delithiated until amorphous Si (a-Si) is obtained [2, 4].

$$\text{cr-Li}_{15}\text{Si}_4 \rightarrow \text{a-Li}_x\text{Si} + \text{Li} \quad \text{(two-phase region)} \quad (3)$$

$$\text{a-Li}_x\text{Si} \rightarrow \text{a-Si} + \text{Li} \quad \text{(single-phase region)} \quad (4)$$

Here, the term ‘single-phase’ refers to the existence of only amorphous phases. The original crystalline Si structure is never re-established [4].

When the Si electrode is cycled above 50 mV, crystalline Li$_{15}$Si$_4$ cannot be formed. The reactions (2) and (3) are changed to (5) and (6), which are corresponding to IV and V in figure 2(a), respectively:

$$\text{a-Li}_x\text{Si} + \text{Li} \rightarrow \text{a-Li}_x\text{Si} \quad (>50 \text{ mV, single-phase region}) \quad (5)$$

$$\text{a-Li}_x\text{Si} \rightarrow \text{a-Li}_x\text{Si} + \text{Li} \quad \text{(single-phase region)} \quad (6)$$

This correlation between the lithiation/delithiation and the lower cutoff voltage is also observed in the following cycles (VI is the same as II; VII is the same as III; VIII is the same as IV).

2.2. Differential capacity analysis

Differential capacity (dQ/dV vs. V) can reveal subtle changes in slope on the voltage-composition relationship and is extremely sensitive to the changes in microstructures or nanostructures [2, 4, 24]. A sharp peak corresponds to a two-phase reaction (a plateau in voltage curve), and a broad peak corresponds to a single-phase reaction (a sloping curve in voltage curve). The peak height indicates the flatness of the plateau, and its area is a measure of the plateau’s capacity [4]. This characteristic makes differential capacity analysis to be a powerful tool to monitor the phase transformation of the Si electrode during cycling.

Obrovac et al have used differential capacity analysis to investigate the phase formation or transformation of Si anode during cycling [2]. Figure 2(b) shows a typical dQ/dV curve of the Si electrode, whose voltage curve is presented in figure 2(a). In the first discharge process with a lower cutoff voltage below 50 mV (Top-left panel in figure 2(b)), a very sharp cathodic peak can be observed that corresponds to the transformations of crystalline Si first to amorphous Li$_x$Si (Plateau I) and then to the crystalline Li$_{15}$Si$_4$ (Plateau II). Accordingly, in the following charge process, a sharp anodic peak can be seen at 0.45 V, which corresponds to the transformation of crystalline Li$_{15}$Si$_4$ to amorphous Si. As a result, the 0.45 V peak can be a good sensor to inspect if the Li$_{15}$Si$_4$ phase is present. In the second discharge/charge process with a lower cutoff voltage of 70 mV (Top-right panel in figure 2(b)), two broad peaks can be seen in the cathodic and anodic process, respectively, and each peak corresponds to a single-phase reaction. For the lithiation process, it is the transformation from lithium less amorphous Li$_x$Si to lithium-rich amorphous Li$_x$Si phase (Sloping curve IV). For the delithiation process, it is the transformation from lithium-rich amorphous Li$_x$Si to lithium less amorphous Li$_x$Si phase (Sloping curve V). In the third cycle (Bottom-left panel in figure 2(b)), when the lower cutoff voltage was below 50 mV, a small sharp cathodic peak appeared again, indicating the formation of crystalline Li$_{15}$Si$_4$ (Plateau VI). In the following delithiation process, a sharp peak identified the two-phase reaction from crystalline Li$_{15}$Si$_4$ to amorphous Si (Plateau VII). In the fourth cycle (Bottom-right panel in figure 2(b)), when the lower cutoff voltage was changed to 70 mV, the differential curves show the same characterization as that of the second cycle. It confirms that the lithiated product of the Si electrode is related to the lower cutoff voltage.

2.3. Li$_{15}$Si$_4$ phase

The evolution and growth of Li$_{15}$Si$_4$ might be associated with high internal stresses, which can lead to particle cracking, poor electrical contact, and capacity fading [25, 26]. The suppression of Li$_{15}$Si$_4$ can lead to good cycling of the Si electrode, which means that the 0.45 V becomes broad in the dQ/dV curve. In addition to the lower cutoff voltage, many other factors also affect the Li$_{15}$Si$_4$ formation during cycling. These factors include particle size, cycling current rate, binder, and electrolyte additive. Gauthier et al have observed that the 0.45 V peak of micросized Si particles with ~10 nm nanocrystalline domains was suppressed significantly at a rate of 480 mA g$^{-1}$ (~C/7) [27]. Obrovac et al found that the Li$_{15}$Si$_4$ phase still appear at a low C-rate of C/40 [4]. Erk et al found that the presence of Li$_{15}$Si$_4$ is dependent on the lithiation rate and the binder chemistry of Si nanoparticles [28]. Chevrier et al have seen that the Li$_{15}$Si$_4$ phase gradually disappears in a 60 nm Si nanoparticle electrode with cycling at C/4 and reappears when lithiated at C/160 [29]. Nguyen et al have found high impedance may hinder the crystallization of a-Li$_x$Si to Li$_{15}$Si$_4$ phase since the ‘true’ cutoff voltage of 5 mV may not be reached at the end of discharge. The peak at ~0.5 V is sharpest for the electrolyte with 5% fluoroethylene carbonate (FEC) consistent with lower impedance. The formation of c-Li$_{15}$Si$_4$ is avoided at a higher cycling rate [30].

3. Challenges of nanosized Si anode material

Downsizing the active materials can improve the electrochemical properties of electrodes significantly by enhancing both the Li-ion diffusion kinetics and the fracture tolerance of electrodes. Reducing the Si particle size to the nanoscale can also help in mitigating the physical stresses induced by the large volume change that occurs during the lithiation/delithiation process and decreasing the electronic and ionic transport distances. Also, the high density of grain boundaries in nanomaterials provides a fast diffusion path for
lithium ions and acts as additional Li-storage sites [31]. Considerable research has been devoted to the design of nanosized Si anode in LIBs, and many excellent papers have reviewed the size, morphology, structure, fabrication methods of nanosized silicon as well as their lithium storage performance. Based on the large number of results reported, the approach of nanosizing is very successful in improving the cycle life and even rate capability of the Si electrode to some extent. However, despite the overwhelming beneficial features, the practical implementation of nanosized Si as the anode material is still impeded by some unavoidable challenges such as low initial Coulombic efficiency, high irreversible capacity, low mass loading, low thermal stability, and high cost, which are discussed in the following sections.

3.1. High irreversible capacity and low Coulombic efficiency

The irreversible capacity is seen with all electrodes and in each cycle during the lithiation/delithiation cycling process. For the anode, the SEI layer is formed on the electrode surface during the first lithiation process accompanied by the consumption of active Li$^+$ (from the electrolyte and the counter electrode of Li metal in a half cell or the cathode in a full cell) and electrolyte degradation. Ideally, the SEI layer is stable, thereby enhancing the electrode stability and cycle life. However, the formation of SEI causes some irreversible capacity of the Si electrode. Smaller particle size causes higher surface area, which can lead to a higher ICE. Compared to commercial bulk silicon (Silicon powder, -325 mesh, 1.2 m$^2$ g$^{-1}$, Sigma Aldrich), commercial nanosized Si has a much larger surface area. Si nanopowder with an average particle size of 30–50 nm (Nanosstructured & Amorphous Materials, Inc.) has a specific surface area in the 70–80 m$^2$ g$^{-1}$ range; Si nanopowder (Nanosstructured & Amorphous Materials, Inc.) with an average particle size of 100 nm range has a specific surface area of approximately 50 m$^2$ g$^{-1}$. Nanosized Si consumes much more Li$^+$ to form the SEI layer, leading to a high irreversible capacity and a low ICE.

Another contribution to the high irreversible capacity and low ICE of nanosized Si anode is due to the irreversible reactions between lithium-ions and silicon oxide on the silicon surface. It is well-known that the native surface of silicon is made up of silicon oxide (Si-O-Si) and silanol (Si-OH) bonds [32–34]. Thus, no matter whether it is Si nanoparticle, Si nanowire, or Si wafer, there is always a covering native oxide layer on the surface of Si. In this case, the electrolyte contacts with silicon oxide directly instead of Si. The irreversible reactions between lithium and SiO$\text{2}$ to form Li$_2$O and Li$_4$SiO$_4$, or Li$_2$Si$_2$O$_5$ are shown below [35–38]:

\[
\begin{align*}
\text{SiO}_2 + 4\text{Li}^+ + 4e^- & \rightarrow 2\text{Li}_2\text{O} + \text{Si} \\
2\text{SiO}_2 + 4\text{Li}^+ + 4e^- & \rightarrow \text{Li}_4\text{SiO}_4 + \text{Si} \\
5\text{SiO}_2 + 4\text{Li} & \rightarrow 2\text{Li}_2\text{Si}_2\text{O}_5 + \text{Si}
\end{align*}
\]

The reactions (7) and (8) are irreversible and parallel, and (9) is also irreversible as reported in some nanostructured SiO$_2$ film electrodes [37, 38]. In contrast, the reaction (10) is responsible for the reversible capacity. As a result, for the nanosized silicon materials, it is not surprising to have low ICE and large irreversible capacity in the first lithiation process.

Some very recent studies have been done to investigate the source of the irreversible capacity of the Si electrode. Lee et al. used an electrochemical approach (depth of discharge test) to indicate four different contributions in the charge-discharge capacities of crystalline silicon electrodes [39]: (a) SEI formation (scales with surface area, about 10 mAh per square meter of the active material surface), (b) lithium accommodation in carbon black and binder, (c) lithiation and delithiation of the Si active material (the intrinsic coulombic efficiency for the crystalline-to-amorphous transition in the first cycle is about 90%, which is independent of the particle size), and (d) capacity loss associated with particle cracking and isolation (This can be observed when the binder amount is <20 wt%. Insignificant contribution from mechanical strains in the electrode when the binder amount >20 wt%) [39]. Therefore, to reduce the irreversible capacity of Si electrodes further, it is essential to adopt Si particles with low surface area, appropriate amounts of carbon black and binder, and a strong binder that can tolerate the volume change of silicon.

The ICE of nanosized Si anode is generally in the range of 65%–85%, far below that of commercial graphite anodes (90%–94%) [40]. Such a low ICE can be a severe problem for nanosized Si electrodes to obtain high energy density in LIBs. Obrovac et al. have calculated the effect of Si anode irreversible capacity on the full cell energy density [4]. The maximum energy value of a full cell can be achieved when the cathode and anode have an equal irreversible capacity. If the irreversible capacity of the anode is increased further, the energy density of the full cell reduces. A Si anode with a >25% irreversible capacity (ICE < 75%) does not show any advantages in terms of energy density compared to a conventional graphite cell [4].

The effect of CE during cycling is also significant for the design and development of high energy density anode material. As discussed in the previous section, the SEI of nanosized Si is not stable due to the fracture of Si particles caused by large volume changes during cycling. Thus, reversible capacity loss occurs in each cycle. When assuming the cathode CE is 100%, the capacity fade in a full cell can still quickly become unacceptable even the anode CE has tiny changes. For example, Coulombic efficiencies of 99.99% and 99.95% in each cycle can lead to 5% and 22% capacity loss after 500 cycles, respectively [4]. Lin et al. have done more calculation of CE in a theoretical full cell, and the results were surprising: Coulombic efficiency of 99% in each cell gets capacity retention of 0.00% at the 1000th cycle. They also found that CE of 99.96% is required to achieve capacity retention of 80% at the 500th cycle for commercialization [41].
3.2. Low mass loading

The silicon mass loading is one of the critical factors that determine the specific energy density of the battery. The high gravimetric capacity and excellent cycle performance have been achieved for a lot of nanosized Si electrodes; however, most of them were performed with Si loading less than 1 mg cm\(^{-2}\), which is merely one-tenth of the commercial graphite anode (10–15 mg cm\(^{-2}\)) \([42]\). Wei \textit{et al} have studied the crucial relationship between the Si mass loading and specific energy density in a Si/Li(Ni\(_x\)Co\(_y\)Mn\(_z\))O\(_2\) (x + y + z = 1) full cell (figure 3). They found that the energy density of this full cell is below 250 Wh kg\(^{-1}\) when the Si loading is 1 mg cm\(^{-2}\) at maximum. There is a plateau in the specific energy density for Si anode battery after \(\sim 5\) mg cm\(^{-2}\). It is because the cathode material also limits the specific energy density of the battery in addition to the Si mass loading. Therefore, increasing the Si loading to 5 mg cm\(^{-2}\) is crucial for practical applications of Si anode. As demonstrated, when the Si loading reaches 5 mg cm\(^{-2}\), the specific energy density can exceed 400 Wh/kg\(^{1}\), which makes it possible that the driving range of the electric vehicles could catch up with that of the gasoline vehicles \([42]\).

3.3. Poor thermal stability (safety issue)

The high surface area of Si nanoparticles results in significantly high side reactions with the electrolyte on the anode surface. The high surface area is associated with increased reactivity with electrolyte, leading to thermal instability.

Park \textit{et al} have compared the thermal stability of lithiated Si powders having particle sizes of 15 \(\mu\)m (S1), 5 \(\mu\)m (S2), and 30–50 nm (S3) \([43]\). Figure 4 shows the significant impact of particle size and surface area on the thermal stability of lithiated Si. Micrometer-sized Si was found to be more thermally stable than graphite, but nanosized Si was less thermally stable than graphite \([43]\).

Solvent and salt in the electrolyte can affect the thermal stability of Si anode. Wang \textit{et al} have compared the thermal stability of Li\(_x\)Si (x = 1, 2, 3, respectively) and Li\(_{0.81}\)C\(_6\) in 1 M LiPF\(_6\) EC/DEC (V/V 1:2) electrolyte solution by using an ARC \([44]\). They have found lower self-heating rates for all lithiated Si samples than for lithiated graphite in this electrolyte system, even though the specific surface area of Li\(_x\)Si was about twice as large \([44]\). Wang \textit{et al} and Profatilova \textit{et al} have found the reactivity of lithiated Si was significantly reduced by the presence of LiPF\(_6\) or LiBOB as the decomposition products from LiPF\(_6\) form a protective film and suppress the reaction between the Li in the active material and the solvent \([45, 46]\). On the other hand, Profatilova \textit{et al} have studied the effect of FEC and VC on the thermal stability of lithiated nano Si. It was found that FEC or VC delays the onset of significant exothermic reactions from 153 °C to 200 °C and 214 °C, respectively \([47]\).

These results indicate that with appropriate electrolyte and additives, the composite electrodes using Si-based materials could be as safe as or safer than corresponding graphite electrodes in full-scale LIBs. However, it is essential to study the thermal stability of various nanostructured Si
electrodes, especially the nano Si electrodes of long-term cycling LIBs.

4. Methods to improve nanosized Si anode performance

4.1. Size control

As mentioned earlier, many different forms of Si nanostructures have been prepared using various methods. The conclusions that nanosized particles would limit particle fracture and pulverization have been confirmed in many in situ TEM experiments in terms of the size dependence of Si particle fracturing. The obtained results indicate that Si nanowires/nanopillars and nanoparticle have a critical size of approximately 300 and 150 nm, respectively, and the fracturing can be avoided during lithiation when the particle size is below these values \([22,48]\). Liu et al have investigated the effect of silicon particle size on the structural stress release by using in situ TEM. They proposed that the stored strain energy from electrochemical reactions is not enough to drive crack propagation if the diameter of the Si particle is smaller than 150 nm \([22]\).

Previous studies based on the calculated misfit stress energies of partially delithiated particles have suggested that the particles with 10 nm diameters less than do not crack \([49]\). Kim et al investigated the size effects of nanosized Si on the electrochemical performance. They found that 5 nm Si nanoparticles have lower specific capacities than 10 nm and 20 nm Si nanoparticles in the first 40 cycles. The 10 nm Si nanoparticles coated with a carbon shell with CVD showed minimal capacity decay over 40 cycles \([50]\).

4.2. Oxygen control

There is always a native silicon oxide layer on the Si surface as the surface oxidation of Si can easily take place from the preparation to the storage. The exact composition of the oxidation layer is affected by the reaction conditions and time. The oxygen content in silicon directly affects the electrochemical properties of the Si electrode, such as electrical conductivity, structural stability, and irreversible/reversible capacity.

Kim et al have prepared nonstoichiometric silicon oxide nanoparticles by using inductively coupled plasma. They examined the chemical composition of these silicon oxides with EDS as well as studied the effect of oxidation on the Si electrode. Their results showed that the appropriate oxygen concentration was lower than 18 at%, and high oxygen content could result in low capacity \([51]\). Abel et al have also made partially oxidized Si nanofilms (13 at% oxygen) that delivered a capacity of 2200 mAh g\(^{-1}\) with a small fading in the first 120 cycles \([52]\). Lee et al have prepared SiO\(_x\) with different oxygen contents with the magnesiothermic reduction of SiO\(_2\). The theoretical capacities of these Si/SiO\(_x\) composites were calculated based on the Si/SiO\(_x\) composition estimated by using
4.3. Prelithiation

One of the methods to reduce the irreversible capacity in the first cycle is prelithiation. Various prelithiation techniques have been investigated, including electrochemical prelithiation, chemical prelithiation, additive prelithiation, and lithium metal prelithiation [55]. Here, the review focuses on the commercially available prelithiation agent or the ones with commercial potential.

In 2005, Jarvis et al introduced the stabilized lithium metal powder (SLMP) into the anode prelithiation in LIB [56, 57]. There are various methods to perform prelithiation with SLMP. One of the popular routes is spreading SLMP particles on the electrode surface, followed by a pressing process to activate the SLMP [40]. Forney et al have used SLMP for the prelithiation of the Si-CNT anodes in the battery making process by the pressure-activation, and the prepared Si-CNT anodes showed the capacities of 1500–2500 mAh g⁻¹, which removed the 20%–40% initial irreversible capacity loss. After the prelithiation, the full LiNiCoAlO₂ (NCA)/Si-CNT battery can perform over 1000 cycles at 20% depth-of-discharge [58]. SLMP can be doped precisely and seems to be an attractive commercial product for prelithiation. Nevertheless, it has a high cost and remains challenging to be distributed in the electrode homogeneously. Additionally, safety and aging behavior need to be evaluated in more detail, asking for further research [55].

Instead of using lithium metal, lithiated active materials can also be used for the anode prelithiation. These additive materials can be as additives that are embedded in the electrode during the electrode preparation process. Zhao et al have used dry-air-stable lithium silicide-lithium oxide (Li₄Si-Li₂O) to prelithiate the Si electrode. First, they prepared the Li₄Si-Li₂O nanoparticles by mixing Si nanoparticles and Li metal foil mechanically in an Ar-filled glove box to obtain the core–shell nanoparticles. Here the oxygen of the Li₂O might be from the SiOₓ surface of Si or the trace oxygen in the glove box. Then, they added the Li₄Si-Li₂O particles to the electrode slurry for prelithiation. They found that the prelithiated electrode showed a high ICE of 94% in half cells [59].

Over-lithiated cathode additives or lithium-rich cathode materials can also help the prelithiation of the anode in the LIB. The cathode additive ranges from binary compounds, such as Li₂S, Li₂N, LiNiO₂, Li₂O₂, and LiF, to ternary compounds, such as LiₓFeOₓ, LiₓNiO₂, LiₓCoO₂, and LiₓMoO₃ [55]. Theoretically, these additives can be added to any cathode material to compensate anode material for its lithium loss during electrochemical cycling. However, the prelithiation additive can cause the weight increase to the cathode side when the additive decomposes incompletely during delithiation. Also, the effect of gas generation due to the decomposition of the prelithiation additives needs to be considered carefully [55]. For the lithium-rich cathodes, the ‘lithium reservoir’ is released in the first cycle to compensate for the lithium loss in the anode side. LiNiCoMnO₂ (NMC) and NCA materials with different Ni, Co, Mn, or Al ratios showing a lithium-rich characteristic can be used for prelithiation. One part of the charge capacity delivered in the first cycle for this type of cathode cannot be recovered in the following discharge process due to a kinetic limitation of the re-lithiation process. This ‘no recovered’ capacity can compensate the anode for its lithium loss [55]. The lithium-rich spinels Li₃+xMn₂O₄ and Li₁+xNi₀.₅Mn₁₋ₓO₂ have been investigated as prelithiation cathode materials. LiNi₀.₅Mn₁₋ₓO₂ (LNMO) is a 5 V cathode material, which makes lithium-rich Li₁+xNi₀.₅Mn₁₋ₓO₂ possible to be used in a commercial high voltage LIB. Gabrielle et al have studied LNMO materials with different lithium degrees using the Si/C composite anode in full cells [60]. The found that the improvement of the specific energy for optimized Si/C-LMNO was 25%, where the LMNO cathodes fully compensated the Si/C anode for its irreversible capacity [60].

4.4. Li trapping control

In the leading theory, the capacity loss of the Si electrode during cycling is explained by large volume expansion/contraction during the lithiation/delithiation process as well as the irreversible formation of SEI. Lithium trapping, another failure mechanism, was proposed by Rehnlund et al for the capacity loss in alloy electrodes, which has mainly been neglected [61, 62]. Li trapping is caused by a two-way diffusion process (figure 5 [62]): (a) In the first lithiation process, the deposited lithium diffuses towards the particle center (steps 1–4). In the following delithiation process, the deposited lithium diffuses towards both the surface and center of the electrode particle (steps 5–8). This two-way diffusion can cause some lithium to remain in the electrode particle even after the delithiation step (step 8). (b) In the second lithiation process, the deposited lithium diffuses inwards to the particle center; the lithium in the particle center diffuses outwards to the particle surface (step 1b). The lithium can diffuse too deep in the electrode to be recovered in the following delithiation step [62]. As a result, a small part of the deposited lithium is trapped in the electrode on each cycle. The trapping effect is decided by the experiment time scale and the electrode dimensions (i.e. the active layer thickness and the particle) [62]. Rehnlund et al have reported
that Li trapping in Si anode contributes to about 30% of the lithium loss in the first cycle, thus leading to accelerated capacity decay of Si anode in the following cycles [62]. However, very little research has been done on this issue. Zhu et al have studied the Li trapping in the Si electrode by using both the theoretical calculation and experimental methods. They found that by introducing Ge substitution to Si with reasonable compositional control, the energy barrier of lithium diffusion was significantly reduced due to the lattice expansion. Also, the isovalent isomorphism can reduce the Li trapping by ~70% and improve the ICE to over 90% [61]. Ai et al have synthesized LiAlO$_2$ coated Si nanoparticles, in which LiAlO$_2$ serves as an artificial SEI film with higher lithium-ion conductivity compared to the naturally formed SEI layer, thus enhancing lithium-ion diffusing into Si nanoparticles with deeper lithiation. The electrode delivered a capacity of 1050 mAh g$^{-1}$ at 4000 mA g$^{-1}$ and retention of 90.9% after 500 cycles. This work provided a practical strategy to reduce the lithium trapping of Si anode during cycling [63].

4.5. Nanoporous Si design

The principle of using porous Si designs to enhance the performance of Si anodes is similar to that of hollow core–shell structures and yolk-shell structures, in which the void space can allow the silicon to expand during lithiation with little or no change in the volume of the entire particle. The minimized volume expansion and shrinkage can prevent particle fracture and lead to a stable SEI layer on the particle surface that can keep all or most of the particles in contact with conductive pathways [64]. Based on the calculation, Ikonen et al have found that when the porosity of the particles is 50%, the etched mesoporous Si particles with parallel pores can accommodate the volume change of the particle due to lithiation in two dimensions [20]. Considerable research has been performed on the design of porous nanosized Si or nanoporous Si electrodes, and multiple methods have been investigated to create various porous structures in silicon.

Liu et al have developed a novel method to produce mesoporous Si nanoparticles from the cheap and plentiful husks of rice. In the first step, they prepared nano-SiO$_2$ at 700 °C by acid washing of rice husks and calcinating of the leached product. In the following step, they produced Si nanoparticles with a magnesiothermic reduction of the nano-SiO$_2$ powder. The obtained Si has particle sizes ranging from 10 to 40 nm and shows the surface area of 245 m$^2$ g$^{-1}$ and a pore volume of 0.74 cm$^3$ g$^{-1}$. When cycled in a half cell, the first discharge capacity of the Si electrode was 2790 mAh g$^{-1}$, and a capacity of ~1700 mAh g$^{-1}$ remained after 300 cycles at the C/2 rate. The capacity was ~2200 mAh g$^{-1}$ after 100 cycles at the C/5 rate. They attributed the superior capacity and rate capability to nanoparticle sizes, large surface area, and the presence of mesopores that can accommodate the volume expansion of Si during lithiation [65].

Ikonen et al have prepared silicon microparticles containing nanosized pores by electrochemical etching and investigated the effects of Si particles’ porosity on battery performance. The optimal particle size was between 10 and 20 μm; The porosity of 50% was estimated to be the lowest value for the Si electrode that still can accommodate the substantial volume change during the lithiation process. They have also found that the thermally carbonized surface of porous silicon (TCP$\text{Si}$) could enhance the lithiation kinetics of the Si electrode at 2 A g$^{-1}$ [20]. In the following work, they prepared TCPSi-CNT hybrid anode material through conjugation and the subsequent succinic anhydride treatment to saturate the remaining carboxyl groups. They attributed the improved electrode performance to the right polarity of the conjugation and the succinic anhydride, which is not only as an electrolyte additive but passively as a reagent to change the surface chemistry [60].

An et al have prepared ant-nest-like porous silicon from magnesium-silicon alloy with a scalable top-down method. The obtained ant-nest-like porous silicon includes three-dimensional interconnected silicon nanoligaments; This bicontinuous nanopore can accommodate volume expansion during lithiation and prevent pulverization. With carbon coating, this ant-nest-like porous silicon anode showed a capacity of 1271 mA g$^{-1}$ at a cycling rate of 2100 mA g$^{-1}$; and the capacity retention was 90% after 1000 cycles. Meanwhile, this electrode showed a low electrode swelling of 17.8% at a high areal capacity of 5.1 mA cm$^{-2}$. The full cell, including the prelithiated silicon anode paired with a Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ cathode, delivered a high energy density of 502 Wh Kg$^{-1}$ and the capacity retention was 84% after 400 cycles [66]. This work provided insights to design and optimize high energy density Si batteries.

The high cost and low yield of nanoporous silicon fabrication often limit its practical application. Very recently, Wang et al have developed three-dimensional nanoporous silicon microparticles through a scalable, low-cost, and high yield (90.4%) fluoride-free approach (Mg$_2$Si + O$_2$ → 2MgO + Si). The obtained porous silicon electrode delivered an ICE of 84.3% and a reversible capacity of 3033 mAh g$^{-1}$ compared to 73.1% and 2418 mAh g$^{-1}$ of commercial nano Si electrode. They attributed the excellent electrode performance to the low oxygen content reducing SEI formation and three-dimensional porous architecture buffering volume expansion and providing good electrical conductivity. This work sheds light on the rational design of Si anodes for practical high-energy LIBs [67].

4.6. Surface modification of nanosized silicon

Surface modifications discussed in this section refer to that made for the Si active material before it is included in the slurry. Compared to bulk silicon, the nanosized silicon is considered more reactive due to its small size and higher surface area, as discussed in 3.1. This highly reactive silicon surface is likely to trigger many electrolyte decompositions during cycling, and thus the surface of nanosized Si needs further modification to keep SEI stable when cycling the electrode. Different coating materials and coating techniques have been used for the surface modification of nanosized Si.
Different organic functional groups have different effects on the electrochemical performance of the nano Si electrode. Li et al have grafted three different functional groups, including silanol, carboxyl, and siloxane, on the surface of 40 nm Si particles, and cycled these surface-modified Si particles in a half cell, respectively. They found that the hydroxyl group on the surface of Si (silanol) was decomposed with electrolyte, and cycling capacity was declined (retention: 50% at 150 cycles), but siloxane-Si formed excellent SEI and cycling performance. For carboxyl-Si, the formation of thinner SEI provided high initial capacity (2093 mA g\(^{-1}\)), but the lack of stability resulted in the capacity fading (retention: 64.27% at 150 cycles) [68].

Carbon coating has been widely used to prepare Si-based anode materials for LIBs, as it stabilizes the Si-electrolyte interface, promotes the formation of stable SEI, and extends...
the cycle life. Carbon coating can be achieved via the pyrolysis of organic precursors and physical or chemical vapor deposition.

Pitch is an economical raw material, and it is obtained as an industrial by-product. Pitch as a carbon precursor allows the synthesis of high value-added storage materials. Escamilla-Perez et al have prepared carbon-coated silicon nanoparticles by the pyrolysis of a low-cost carbon source: petroleum pitch under argon atmosphere by a laser pyrolysis technique. The carbon coating can enhance the cycling stability of silicon nanoparticles as anode material in the LIB. The optimized carbon-coated silicon nanoparticles homogeneously dispersed into the amorphous carbon matrix showed a coulombic efficiency of 81.44%, and high stability over cycling was observed (over 1100 mAh g\(^{-1}\) after 100 cycles at a relatively high current density of 716 mA g\(^{-1}\)) [69].

CVD can be used for carbon coating of Si nanoparticles, and the carbon layer thickness could easily be adjusted by controlling the deposition conditions. Yu et al have deposited a uniform carbon layer on Si nanoparticles surface with CVD, and they have found that the prepared Si@C composite electrodes showed better cycle reversibility and rate capability compared to the pristine Si electrode. The Si@C sample with a carbon layer thickness of about 12 nm delivered a relatively stable specific capacity of about 1600 mAh g\(^{-1}\) at 0.3 A g\(^{-1}\) for 70 cycles. Its capacity remained at 750 mAh g\(^{-1}\) at 5 A g\(^{-1}\) in multi-rate cycling, compared to 240 mAh g\(^{-1}\) for pristine Si [70].

In addition to the carbon coating, silicon carbide coating has also been reported. Ikonen et al have also found that the presence of a silicon carbide layer enhanced the kinetics of lithiation in the mesoporous Si electrode [20]. Despite the general agreement that the SiC phase is inert in Si-C composites and it should be avoided, it has been reported that some forms of SiC are active toward lithiation [71, 72]. Kumari et al have reported that n-SiC prepared by CVD delivered a reversible capacity of 1332 mAh g\(^{-1}\) with little capacity fade after 200 cycles [72]. However, the effect of the SiC coating layer on the electrochemical performance of the nano-Si electrode has not been intensely investigated. Further research should be done to understand the SiC coating and its lithiation mechanism.

Some metal oxides are also used to stabilize the surface of nano Si anode, including Al\(_2\)O\(_3\) and TiO\(_2\). A growing number of papers have reported Al\(_2\)O\(_3\) coated Si [73]. However, most of them have adopted ALD to deposit Al\(_2\)O\(_3\) on the Si
particle surface. It causes a very high cost that is not practical in the battery industry. Lower cost technique are needed to develop high-quality Al2O3 coating on Si. TiO2 coating on nano Si has also been investigated. Jin et al have designed a unique yolk-shell Si@TiO2 anode with >50 wt% Si (Si-majority anode, SiMA), in which there is a void between nano Si particle and TiO2 layer accommodating the volume expansion. TiO2 layer can be an artificial SEI during cycling to protect Si surface even it is partially cracked during the slurry making process. Also, they compressed the Si@TiO2 yolk-shell powders to achieve an industrially relevant compressed density of 1.4 g cm−3, improving the volumetric capacity of electrodes. The half-cell with the SiMA (mass loading: 0.8 mg cm−2) showed a gravimetric capacity of 990 mAh g−1 after 1500 cycles. The full cell with the Si@TiO2 cluster anode (mass loading: 2.1 mg cm−2) paired with a lithium cobalt oxide cathode delivered above 1.6 mAh cm−2 after 100 cycles at 0.7 mA cm−2, which was corresponding to a volumetric capacity of 993 mAh cm−3. A stabilized coulombic efficiency exceeding 99.9% was obtained for these cells. They attributed this excellent cycling stability to the self-repair mechanism of the mechanically robust TiO2 nanoshells [74].

4.7 Nanosized silicon/graphite composite electrode design

The sole utilization of Si to improve the LIB energy density is regarded as an awkward task in practice because, in that case, large amounts of binder and conductive materials are required, as well as the battery faces severe electrode swelling issue [75]. One of the methods is combing silicon and carbon, in which carbon provides a conductive network for Si. Different types of carbon materials, such as graphite, graphene, andCNT, have been investigated to make Si/C composite electrodes. Compared to CNT or graphene, graphite has a considerable cost advantage in those carbon-rich Si/C electrodes. So far, graphite is still the most widely used commercial anode material in the LIB industry. The co-utilization of graphite can cause a relatively low specific gravimetric capacity; however, graphite can improve the volumetric energy density. This co-utilization of graphite and silicon in anodes makes it possible to use the current battery manufacturing equipment and processes and not require significant new investments [75]. It is an essential aspect of commercial applications.

Dash et al have investigated the theoretical limit of the energy density of a Si/graphite anode with a rational model [76]. This theoretical model is based on the practical standard that the external dimension increase of the LIB cannot be beyond 5%. The volume expansion of 5% is to accommodate the generated gas from electrolyte decomposition [76, 77]. The weight fraction of Si is decided by the porosity of lithiated anode, conductive material amount, and binder amount. However, to obtain the highest volumetric capacity (876 mAh/L), the maximum value for the Si content is 12 wt% for the anode with a 5 wt% SBR binder but without any carbon black (figure 6) [76]. The threshold value of the Si amount decreases from 12.0 wt% to 10.2 wt%, 8.3 wt%, and 6.4 wt% for the anodes with the porosities of 10%, 20%, and 30%, respectively [76].

Recently Chae et al have discussed the necessity and performance metric of the Si/graphite anodes and reviewed their development in commercial batteries [75]. They also summarized the synthetic methods to produce the Si/graphite composite electrodes, including ball milling, spray drying, CVD, and liquid solidification [75]. High-energy ball milling has been used to make fine particles by pulverizing bulk materials with rotating balls. This method is quite promising due to the simplicity and cost-effectiveness that make it reasonable for commercial production. However, the ball-milling technique has some challenges for commercial applications. For example, the surface area of Si/graphite electrode materials can be increased significantly, and the structure of graphite can be damaged after ball milling. As a result, it causes a higher irreversible capacity and a lower ICE than that without ball milling [75]. Spray drying has been used to make Si/graphite composites from Si nanoparticles, graphite, and carbon additives. Some significant advantages can be seen from this method. First, the volume change of the Si electrode can be alleviated by the internal pores generated during the spray drying process. Second, the battery energy density can be improved by the high density of the composite material [75]. Last, this method makes the practical application of Si in battery anode possible due to the scalable synthesis. The CVD is a facile method to make Si/graphite composite electrode for LIBs. This method can make nanosized Si particles deposited on the graphite surface very uniformly [75]. As well, there is an extreme adhesion between these Si particles and the graphite matrix, which helps maintain good electrical contact during the electrode cycling. Liquid solidification is another method to prepare Si/graphite composite electrode. With this method, the electrochemical performance of the Si/graphite composites can be easily controlled by adjusting the mixing order, the raw particle size, and the additive features. Due to the simplicity of this method, it is highly promising for the commercial applications of the Si/graphite electrodes [75].

Various high-performance Si/graphite electrode materials have been synthesized. Table 1 shows the information collected from several representative studies published since 2017 [78–87].

4.8. Calendering of nanosized Si/graphite composite electrode

Calendering can be used to improve the homogeneous distribution and interconnectivity between the electrode component particles. During calendering, the electrodes are compressed by driving them through two massive cylindrical rolls [88]. For the graphite electrode, the porosity can be reduced from 60% to around 20% after calendering [89]. Calendering improves the adhesion and density of electrode materials, resulting in better binding and electrical conduction between the particles as well as a lower cell impedance. However, higher electrode density results in less available active surface area of the active material. Besides, lower porosity hinders electrolyte transport [90]. Therefore, the calendering of the electrode should be applied with caution,
| Electrode                        | Si:Graphite ratio (by weight) | Mass loading (mg cm\(^{-2}\)) | ICE    | Reversible capacity (mAh g\(^{-1}\)) in the 1st cycle | Areal capacity (mAh cm\(^{-2}\)) | Cycle number | Capacity retention | Voltage range/1 C                       | Reference/Year |
|---------------------------------|-------------------------------|--------------------------------|--------|-----------------------------------------------------|----------------------------------|--------------|-------------------|----------------------------------------|----------------|
| Si:graphite                     | 37.5:62.5                    | 1                               | 77%    | 1001 at 0.1 A/g                                      | –                                | 100          | 850 mAh g\(^{-1}\), >80%, at 0.25 A g\(^{-1}\), 800 mAh g\(^{-1}\) at 5 A/g | 1st cycle: 0.005–0.9 V after 1st cycle: 0.05–0.9 V | [78] 2020    |
| C/Si@MPC-G                      | 9.72% Si                     | –                               | 90.9%  | 665 at 0.5 C                                        | 3.6                              | 50           | 95.6%, at 0.5 C | 1st cycle: 0.01–1.5 V after 1st cycle: 0.01–1.0 V | 0.005–1.0 V   | [79] 2020    |
| Si: macropore-exploited graphite: pitch carbon (EGS) | 17:73:10 | 1.7                             | 92.9%  | 914 at 0.1 C                                        | 3.4                              | 50           | 789 mAh g\(^{-1}\), 86%, at 0.5 C | 0.005–1.0 V | [80] 2019 |
| Si: graphite (MGS)              | 6.3:93.7                     | 6.9                             | 93.0%  | 527 at 0.1 C                                        | 3.5                              | 50           | 516 mA g\(^{-1}\), >97% at 0.5 C | 0.005–1.0 V | [81] 2019 |
| B-Si/CNT@Graphite               | 90% graphite                 | 11.2                            | –      | –                                                   | –                                | 5.2          | 83.4%, at 1.12 mA/cm\(^2\) | 1.5 V | [82] 2019 |
| Si/graphite/Graphite            | ~10% Si                      | 687.7 at 0.5 C, 650 at 1 C      | 90.6%  | –                                                   | –                                | 50           | 96.7%, at 1 C | 0.001–1.5 V, 1 C = 1000 mAh g\(^{-1}\) | 0.01–1.5 V | [83] 2018 |
| Si/graphite/pyrolytic carbon (SiGC) | 12.8% Si                      | 818 at 0.1 A/g                  | >80%   | –                                                   | –                                | 300          | 610 mAh g\(^{-1}\), 83.6%, at 0.5 A/g | 0.14–1.5 V | [84] 2018 |
| Porous Si/C (Watermelon)        | Si/C:graphite                | 65%                             | 650 at 1/6 C | 2.52                  | 450          | 516 mA g\(^{-1}\), >97% at 0.5 C | 0.005–1.0 V, 1 C = 2.4 mA cm\(^{-2}\) | 1st cycle: 0.005–1.0 V after 1st cycle: 1.5 V | [85] 2017 |
| Porous Si/C (SEAG)              | Si:graphite                  | ~6.3% Si, 2.8% Ni               | 93.8%  | 525 at 0.1 C                                        | ≥3.4                             | 50           | 533 mAh g\(^{-1}\), 82%, at 1/6 C | 0.005–1.0 V, 1 C = 2.4 mA cm\(^{-2}\) | [85] 2017 |
| Si/C (Watermelon)               | 12.5:87.5                    | 4.1                             | 89.2%  | 620 at 0.1 C                                        | 2.54                              | 50           | 1.91 mAh cm\(^{-2}\), 75%, at 0.5 C | 0.005–1.0 V, 1 C = 600 mAh g\(^{-1}\) | [87] 2017    |
and an optimum porosity should be searched for a different electrode.

For the Si electrode, very few methods have been found to maintain the electrode with excellent cycling performance by compressing electrode coatings to high densities. One reason is that Si is fracturing into smaller particles after calendaring [4, 91]. The other reason is that the calendaring can break the carboxymethyl cellulose (CMC) molecular bridges formed between the silicon particles and conductive additive particles as well as at the interface with the current collector [91]. As a result, it is leading to a poor conductivity network and also reducing the electrode resiliency to endure the electrode volume change during cycling [91]. Karkar et al have tested the calendered nanosilicon/carbon nanoplatelets/CMC electrodes, and they have found that the calendaring caused a significant decrease in the electrode cycling stability. However, the ICE and cycling performance of the calendered electrode were improved by a post-calendering treatment (called maturation). The maturation includes the electrode storage in a humid atmosphere for two days before drying. They believed that this maturation induces the restoration of cohesive bonds between Si particle and binder as well as the interface with the current collector, which resulted in a significant improvement of mechanical strength [91].

The Si/graphite composite electrode coating can be calendered due to the deformable and slippery properties of graphite, thus leading to a high volumetric energy density for batteries [75]. Li et al have prepared a Si/C-graphite electrode by blending a porous Si/C (34 wt% carbon) composite and graphite (Si/C: graphite, 1:2 by weight) and investigated the effect of calendering on the electrode performance. They found that after calendering, the mesoporous Si/C composite retained its original morphology; after the prelithiation, the Si/C-graphite electrode showed excellent retention of >84% after 300 cycles when paired with a Li(Ni1/3Mn1/3Co1/3)O2 cathode in a full cell [85]. This result indicates the commercial feasibility of nano Si/graphite electrodes. Very recently, Son et al have prepared ultrathin Si/coated macroporous carbon/graphite composite with the outermost carbon covering (C/Si@MPC-G) via simple mechanical agitation and CVD. They found that this novel structure allows the macroporous architecture to endure high mechanical pressure without fracturing of both the pores and Si particles during electrode calendering. The C/Si@MPC-G electrode in a half cell delivered a volumetric capacity of 1064 mAh cm−3 with an ICE of 90.9% and very stable cycling. The electrode in a full cell showed a volumetric energy density of 932 Wh/L and specific energy of 333 Wh kg−1. This work indicates that appropriate composite design can enable calendering-compatible Si/graphite to achieve high energy LIBs [79].

4.9. Advanced binders

Binder is playing a critical role in terms of mechanical stability and cycling performance of Si electrodes. Theoretically, an advanced binder should reversibly buffer the electrode volume change and maintain strong adhesion with other electrode components and the current collector. Many binders have been investigated in the literature to obtain stable cycling performance for Si-based electrodes. Choi et al have reviewed polymeric binders for the silicon electrode, including linear type binders, branched type binders, cross-linked binders, self-healing binders, and conductive binders [92]. The present review focuses on the commercial or readily producible binders.

Poly(carboxylic acid)s and their alkali metal salts, such as NaCMC, PAA, and LiPAA or NaPAA, are typical linear homopolymeric binders, and alginate is a typical linear copolymeric binder [93]. These binders can bond to native silicon oxide (Si-O-Si) and silanol (Si-OH) groups on silicon surfaces with either strong ester-like covalent bonds or weaker hydrogen bonds [4, 92]. Generally, LiPAA binder can bring a higher ICE in the Si electrode compared to the PAA binder because PAA can absorb some lithium to form LiPAA during lithiation. All these polymeric binders are commercially available or easy to prepare.

Polymerized β-cyclodextrin is a typical binder with a hyperbranched network structure. This structure makes β-cyclodextrin interacted with Si particles by multidimensional hydrogen-bonding, leading to solid contacts between the different electrode components. Jeong et al have introduced this binder for Si electrodes [93]. The Si electrode slurry was made by mixing 60 wt% Si (120–200 nm), 20 wt% conductive agent, and 20 wt% β-cyclodextrin binder. The electrode showed capacity retention of 50.6% after 150 cycles at a cycling rate of 4200 mA g−1. In comparison, the capacity retention of the Si electrode with an alginate binder was only 27.1% [93]. They found that the Si nanoparticles, with the polymerized β-cyclodextrin binder, lost the contacts initially but recovered during the following cycling due to the multidimensional network, which was considered a self-healing effect [93].

Some other self-healing binders have also been reported. Bao et al have developed a self-healing polymer binder with a double hydrogen bonding for the Si electrode and improved the electrode capacity and cycling significantly [94]. Zhang et al have used a linear modified PAA cross-linked with a quadruplet hydrogen-bonded unit (ureido-pyrimidinone) to prepare a self-healable binder, which improved the Si cyclability due to its excellent endurability to huge volume change [42]. Although these self-healing binders are very effective in keeping the mechanical integrity of the Si electrodes during cycling, only a few binders possess good electrical conductivity. Very recently, Hu et al have reported a novel binder (ESVCA) with both excellent conductivity and self-healing property. With this binder, the Si electrode delivered a reversible capacity of 1786 mAh g−1 at a cycling rate of 500 mA h g−1, and after 200 cycles, the capacity retention was 71.3% at room temperature. At elevated temperature, the electrode showed a reversible capacity of 1743 mAh g−1 at a cycling rate of 2000 mA h g−1, and the capacity retention was 74.1% after 200 cycles [95].

Conductive binders can keep the electrode components in a better electrical conductive network compared to the conventional binders, which often lose electrical contact with Si particle during cycling. Some conductive binders have been reported including polyaniline hydrogels.
[96], poly (phenanthrenequinone) [97], poly (1-pyrenemethyl methacrylate-co-triethylene oxide methyl ether methacrylate) [97], and poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT: PSS) [98], PEDOT: PSS is a commercial product and has high conductivity (1000 S cm$^{-1}$). However, these conductive binders are failed to hold solid interaction with Si and cannot provide a stable mechanical network [95].

PAA-CMC is a typical cross-linked binder developed by Koo et al [99]. They prepared Si electrode slurry by mixing 60 wt% Si (100 nm), 20 wt% conductive carbon, and 20 wt% binder (10 wt% PAA + 10 wt% CMC). The ester linkages were formed during the electrode drying process (150 °C in a vacuum) by the condensation reaction between carboxylic acid moieties of PAA and hydroxyl groups of CMC. The prepared Si electrode delivered a capacity of about 2140 mAh g$^{-1}$, and the capacity retention was 75% at 300 mA g$^{-1}$ after 100 cycles [99].

Choi et al have developed a new molecular pulley binder strategy inspired by the working principle of moving pulleys (figure 7). In this design, the PAA is attached to the polyrotaxane ring, and the topological crosslinking between them combines the covalent and noncovalent crosslinking. Therefore, the stress is significantly reduced by ring sliding, just like the tension of the rope in a moving pulley is reduced by distributing and equalizing the localized force. In the electrode, the Si microparticles are surrounded by a highly elastic binder layer, thus maintaining the conductive pathways to the Si particles, resulting in the pulverized Si particles connected during the cycling process [100]. They have made the polyrotaxane-PAA-Si electrode coating consisting of 80 wt% Si microparticles, 10 wt% conductive carbon, and 10 wt% binder. When cycled at 0.64 mA cm$^{-2}$ (0.2 C), the polyrotaxane-PAA-Si showed an initial areal capacity of 2.67 mAh cm$^{-2}$ and preserved 2.43 mAh cm$^{-2}$ (91% retention) after 150 cycles. When cycled at a higher current density of 1.25 mAh cm$^{-2}$ (0.4 C), the polyrotaxane-PAA-Si anode showed an 85% retention of the initial capacity after 370 cycles [100].

In practical applications, Si is typically mixed with some form of carbon (mostly graphite) to construct a composite electrode for the LIB. In this regard, the future research of binders should focus on the compatibility of hydrophilic silicon and hydrophobic graphite in the composite electrodes.

4.10. Advanced electrolyte additives

Electrolyte additives are crucial to the Si electrode cycling performance. A small amount of functional additive is considered one of the most viable, economic, and practical strategies for overcoming the issues related to huge volume change and initial capacity loss of Si electrodes. Eshetu et al have reviewed the electrolyte additives used for Si electrodes [101]. They classified these additives into organic type additives (FEC, VC, alkoxysilanes, isocyanate, CO$_2$), ionic (salt-type) additives (LiBOB), and other additives (Succinic Anhydride (SA), Tris (Pentafluorophenyl) borane (TPFPP)) [101]. Kim et al have listed more than 20 electrolyte additives used for Si anode that had been reported in the past 10 years [102]. All these additives can bring the performance improvement of Si electrodes in terms of capacity retention and Coulombic efficiency. Among them, however, FEC and VC are still the most widely used additives in electrolyte solutions for Si electrodes.

FEC is generally recognized as the most effective electrolyte additive in forming a passivating SEI on the silicon surface. The main products of FEC decomposition on the electrode are known to be ROCO$_2$Li, LiF, and polymerized FEC [101]. These decomposition products can contribute to the formation of a uniform and stable SEI layer on the silicon surface, thus preventing further decomposition of LiPF$_6$ salts and FEC at lower potentials [103]. Despite the beneficial features, the addition of FEC can cause serious gassing at elevated temperatures and rapid consumption of FEC with cycling, thus leading to an immediate failure after the FEC reservoir is used up [101]. It has been reported that insufficient FEC caused sharp deterioration during cycling [104]. However, it has also been reported that excessive FEC caused worse performance at elevated temperatures. As a result, in a Si composite electrode, the FEC content should be carefully adjusted according to the Si content in the composite material. On the other hand, Shin et al have found that in an LMO/graphite full cell, the FEC remaining after forming the SEI layer on the anode side is harmful to the cathode side, especially at elevated temperature [105]. Therefore, the FEC amount in a full cell with a Si anode should also be optimized to minimize the unfavorable effects of FEC on the cathode.

The prior reports on graphite anodes inspired the exploitation of VC, and VC was also identified as an effective additive for Si thin-film anode. Chen et al have reported that with 1 wt% VC in EC: DMC (1:1 in volume) containing 1 M LiPF$_6$, the ICE was promoted from 67.9% to 72.5%. The reversible capacity in VC-containing electrolyte was stable at 2000 mAh g$^{-1}$ even up to 200 cycles, and gradually decayed to more than 500 mAh g$^{-1}$ after 500 cycles [106]. Leiveau et al [107] and Dalavi et al [108] have observed slightly enhanced performances with VC on silicon nanowires and nano silicon film, respectively. However, VC can cause high impedance and significant internal resistance. Jaumann et al have found that the VC additive outperformed the additive FEC for nano-silicon anodes in terms of lifetime and efficiency [109]. The reason was that the formation of a very flexible surface film could survive the massive volume changes of silicon without surficial crack propagation. However, the SEI film surface showed high resistance for Li$^+$ migration due to the absence of the defect in the film structure. As a result, it makes VC not suitable for high power applications. In contrast, the FEC-derived SEI showed less flexibility and reversibility compared to VC but exhibited excellent conductivity for Li$^+$ ions, which are the first requirements for high power applications [109].

Very recently, DMAA was selected by Zhu et al as a novel electrolyte additive used for the nano silicon electrode in a half cell. They have found that a stable SEI layer was formed on the silicon electrode surface at a high potential due to the presence of DMAA, thus suppressing the electrolyte decomposition. Also, the DMAA additive can further improve the electrochemical properties of silicon anode in an FEC containing electrolyte. With 2.5 wt % DMAA in the 1 M LiPF$_6$/EC: DMC: DEC: FEC (3: 3: 3: 1) electrolyte, the silicon anode
Figure 7. Proposed stress dissipation mechanism of Polyrotaxane-PAA binder for Si microparticle anodes. (A) The pulley principle to lower the force in lifting an object. (B) Graphical representation of the operation of Polyrotaxane-PAA binder to dissipate the stress during repeated volume changes of Si microparticles, together with chemical structures of polyrotaxane and PAA. (C) Schematic illustration of the pulverization of the PAA-Si microparticle electrode during cycling and its consequent SEI layer growth [100]. Copyright: The American Association for the Advancement of Science, 2017.

showed an ICE of 80.16% and the capacity retention was over 80% after 500 cycles [110].

It is challenging to develop electrolytes containing only one additive to obtain satisfactory overall electrochemical performance. Besides, the development of electrolyte systems should consider the whole high-energy-density of LIB instead of the Si electrode. For example, for a full cell compatible with nickel-rich cathodes and silicon-based anodes, the electrolyte and additive designers should consider stabilizing the high-voltage cathode electrolyte interface (CEI) and modifying the unstable SEI film. Therefore, a tailored system with a blend of several additives might be one of the options to enhance the overall performance. Some co-additives have been tried to minimize the shortcomings of
Figure 8. (a) Schematic representation revealing the role of the FEC + LiFMDFB-derived SEI toward the morphological stability of Si/graphite composite (SGC) anodes. Cross-sectional SEM images of cycled SGC anodes (b) without and (f) with LiFMDFB. Elemental mapping images (O, Si, and F) of cycled SGC anodes (c)–(e) without and (g)–(i) with LiFMDFB [112]. Copyright: Royal Society of Chemistry, 2019.

FEC (low thermal stability) in Si-based batteries. Jo et al have tested a binary additive of FEC/di(2,2,2-trifluoroethyl) carbonate (DFDEC) (10 wt% and 1 wt% in EC/EMC electrolyte) for the Si/graphite composite electrode in a half cell, and they have found the electrode capacity was significantly improved during cycling compared to that with FEC alone [111]. Han et al have used a dual-function additive, lithium fluoromalonato-(difluoro)borate (LiFMDFB), to stabilize both Li-rich cathode and Si-graphite anode in a full cell. They have found that LiFMDFB can protect the Li-rich cathode by generating a stable CEI while simultaneously tuning FEC-oriented SEI on the Si/graphite anode. Figure 8 shows the role of the FEC + LiFMDFB-derived SEI toward the morphological stability of Si/graphite anodes. With LiFMDFB, the Si/graphite particles are covered by the uniform SEI even after 200 cycles. They think the stress-tolerant SEI was caused by the coordination between the FMDFB anion and FEC molecules. As a result, the full cell delivered capacity retention of 85%, a Coulombic efficiency of 99.5%, and an energy density of 400 Wh kg$^{-1}$ after 100 cycles. This dual-function additive approach (generating stable SEI and CEI simultaneously) provides an effective way to develop electrolyte additives for high-performance batteries [112].

5. Summary and outlook

Even though lively discussions and debates are going on about post-lithium battery technologies, it is still the fact that LIB technology is here for many years to come [113]. LIB is the present approach viable for mobile and transport applications, but it is still not optimal even for these applications—there is much room to improve its performance. It should also be kept in mind that the existing production lines limit the fast adoption of new technologies and materials demanding uncommon handling procedures. The most accessible approach to obtain better batteries, the criteria depending on the applications, is to generate gradual improvements in the LIB chemicals (electrodes and electrolytes). The easiest way is to replace graphite with silicon gradually and add more additives with specific functionalities in the electrolyte. However, the simpler is the composition of the anode and electrolyte, the more affordable is the battery pack.

New production methods and particle structures have been actively developed, but often the commercialization aspects have been forgotten. An attractive solution to circumvent the material-based challenges of silicon is to reduce the particle size into the nanoscale. However, nanosizing may raise another problem related to the general safety concerning the production and use of nanomaterials of any kind. One option to circumvent the problem associated with the unstable SEI is to use solid electrolytes, which would also address the safety issue related to liquid electrolytes. Full silicon anode is not able to be realized with the present structures of the electrodes using slurries, but more advanced structures need to be developed. The development takes years and its commercialization even more. For the next ten years, the technology of choice for rechargeable batteries is LIB, but there are emerging technologies coming—especially for niche fields. However, their performance is not dramatically exceeding the optimized LIB performance, and also they have their specific disadvantages.
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