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Development of Silicon-Based Anode for Lithium-ion Batteries and Its Application in Solid-State Electrolytes

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Abstract

Lithium-ion batteries (LiBs) have been widely used in all aspects of people's daily lives because of their high energy density, wide operating temperature range, high operating voltage, and good safety and cycling stability. The anode is an important part of Li-ion battery, which can store and release Li-ion. Therefore, the choice of anode has a key influence on improving battery performance. The silicon-based anode is expected to be the anode material for next-generation high-performance lithium-ion batteries due to its high theoretical specific capacity and other advantages. However, the volume change of silicon during lithiation and the induced instability of SEI pose a considerable challenge to the development of silicon anode. This paper reviews the development of silicon anodes in lithium-ion batteries, systematically introduces the challenges and improvement methods posed by silicon-based materials as anodes, and investigates the application of silicon anodes in solid-state electrolytes. Finally, some views are presented on the future development of silicon-based cathodes for lithium batteries.

Keywords: Lithium-ion battery; Silicon-based anode; Solid-state electrolyte; Carbon cover; Nanomaterials.
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1. Introduction

With the continuous development of science and technology, energy shortage has become a major challenge for the global society. As a new type of energy storage device, lithium-ion batteries have had a profound impact on human society, science and technology. Lithium-ion batteries have the advantages of high energy density, good cycle stability, green environment protection, and wide operating temperature range, and their electrode materials and performance have been continuously improved in the past decades.[1] Today, commercial lithium-ion batteries are widely used in consumer electronics (*e.g.*, cell phones, Bluetooth headsets, tablet PCs, and laptops), in electric transportation (*e.g.*, small logistics vehicles, electric cars), and in energy storage systems (small homes and large power plants).[2]

The anode in a lithium-ion battery plays an important role in the size of its energy density and rate performance, and research on negative electrode materials is constantly being explored.[3] Among them, silicon-based anodes are expected to be more promising anode materials for lithium-ion batteries due to the following characteristics.[4] First, silicon (Si), a group IV element, has a theoretical specific capacity of 3580 mAh g^{-1}(silicon forms $Li_{15}Si_4$ with lithium at room temperature), about ten times higher than that of graphite (372 mAh g^{-1}), a traditional anode material.[5] Secondly, the embedded lithium potential of silicon is about 0.5V, slightly higher than graphite, which can effectively mitigate the formation of lithium dendrites during the charge/discharge cycle of the battery.[6] In addition, the abundance of silicon in the earth's crust is 25.8%, and the application of silicon can greatly reduce its production cost.[7] However, there are still many challenges in the practical application of silicon anode electrodes. Silicon undergoes huge volume expansion (~400%) during lithiation, which can lead to cracking and crushing of the electrode sheet, making the electrode gradually fail, thus leading to a decrease in the electrochemical cycling performance of the battery (Fig. 1).[8]

In order to solve the problem of volume expansion of silicon-based anode materials, one can design the nanostructure of silicon anode. Nanosilicon can provide a relatively short transport pathway for lithium ions and electrons, which can effectively improve the rate performance.

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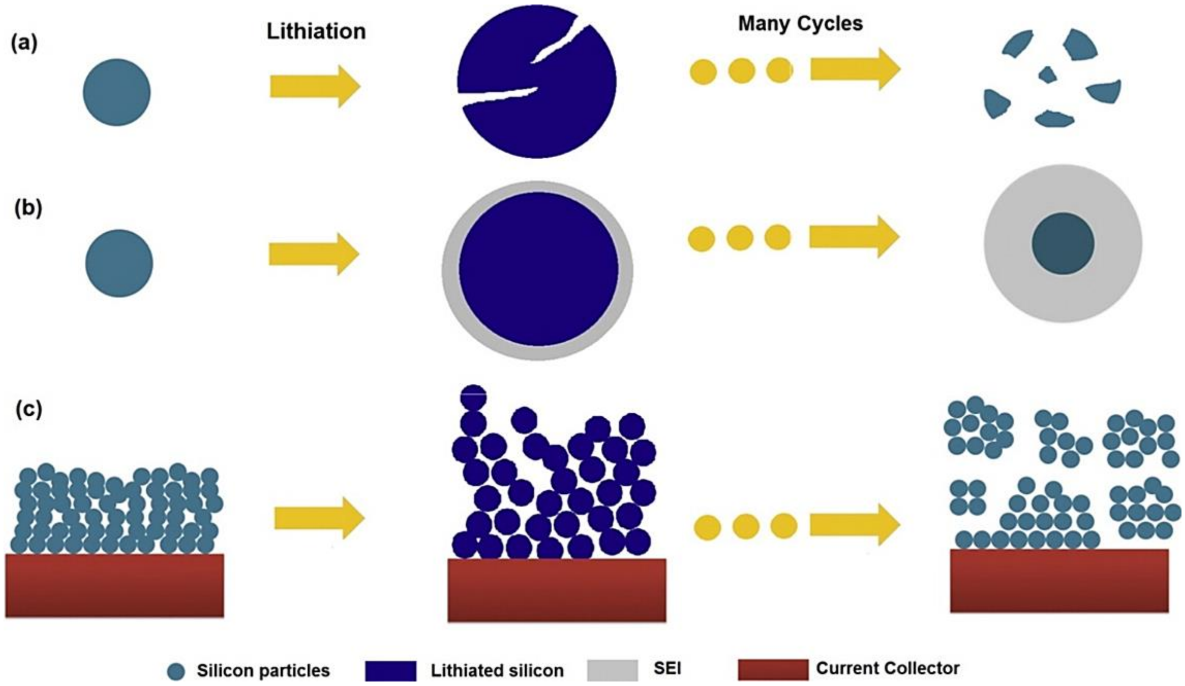

Fig. 1 Failure mechanism of silicon electrode. Reproduced with the permission from [8], Reproduced with the permission from Copyright 2012 Elsevier.

In addition, the nanostructure generates less stress during lithium ion embedding and detachment, which can mitigate the volume expansion.[9] The structural design for silicon nanoparticles includes silicon nanoparticles,[10] Silicon nanotubes,[11] Silicon Nanowires,[12] Porous silicon,[13] Silicon nanofilms,[14] and silicon nanosheets,[15] *etc*. However, silicon nanoparticles are highly prone to agglomeration, which can gradually reduce the battery capacity. In addition, silicon nanoparticles increase the contact area with the electrolyte, leading to a continuous consumption of lithium ions, resulting in an irreversible increase in capacity and a decrease in coulombic efficiency.[16]

Compared with nano-silicon materials, micron-sized silicon materials offer certain advantages. Microsized Si has a higher tap density, which enables higher volumetric capacity under the same mass loading; at the same time, micronsized silicon electrodes can also achieve higher area capacity with the same electrode thickness.[17] In addition, the microsized silicon particles have a lower specific surface area, which can reduce the generation of harmful byproducts, thereby realizing a higher Coulombic efficiency.[18] However, the volume expansion problem of micro-sized silicon particles is not well solved, and thus the structure is prone to be damaged during the cycling process, which leads to a drastic decrease in capacity . Silicon composite structures constructed from a combination of nanoscale units and micrometer-sized silicon can solve this problem.[19,20]

Therefore, in addition to the nanosized structural modification of silicon, silicon-based composites become another way to improve the electrochemical performance of silicon-based anodes. When silicon is compounded with an active or inactive material with better electrical conductivity and less bulk effect, the bulk expansion of silicon can be effectively mitigated while improving electrical conductivity.[21] In addition, the core-shell, egg-yolk core-shell, as well as layer and sheet structures formed by the composites can significantly improve the cycling stability of the silicon anode. Common silicon composites include silicon-carbon composites, silicon alloy materials, silicon and metal oxide composites, *etc*..[22] Based on the above two approaches, the combination of nanosizing and composite structure can better enhance the mechanical strength as well as electrochemical properties of silicon-based materials, which has become the research development direction of silicon anode in recent years.

In addition, the volume of the silicon anode tends to expand during cycling, leading to the crushing and cracking of the active material, which leads to the instability of the solid electrolyte interface (SEI) formed during the first charge and discharge and hinders the ion transport in the electrode. Compared with the liquid electrolyte used in conventional Li-ion batteries, the application of solid electrolyte can greatly improve the cycling stability of the SEI layer.[23] In addition, the solid-state electrolyte is more sufficient in terms of safety compared with the liquid electrolyte. Therefore, the application of silicon-based anode in solid-state lithium-ion batteries has a good development trend and prospect.

This paper reviews the application and development of silicon-based anode in lithium-ion batteries. Given the defects of silicon material, this paper details different methods of improving silicon-based anodes in terms of nanostructures, composite structures, and a combination of the two. Subsequently, the application of silicon-based anode in the solid-state development of lithium-ion batteries is investigated.

Finally, the paper expresses the views on the future development of silicon-based anode.

2. Silicon-based anode

Since silicon has a high theoretical specific capacity of about 3578 mAh g^{-1} at room temperature,[24] In the pursuit of high-capacity, high-performance lithium-ion batteries, a number of solutions have been explored for the energy storage application of silicon-based anode materials. The core challenge is to solve the problem of electrochemical performance degradation caused by the volume expansion of silicon material during battery cycling.[25]

In addition, the instability of the SEI is a key factor affecting electrochemical performance. During the initial lithiation (charging and discharging) of a silicon electrode, solvents and some salts in the electrolyte solution in contact with the silicon surface are reduced, resulting in the formation of a passivation film known as the solid electrolyte interphase (SEI).[26] This is evidenced by a significant decrease in the capacity of lithium-ion batteries after the first cycle.[27] In general, the SEI layer plays a benign role. The layer has some electrical conductivity and ion exchange properties. It can improve the cycling performance of the battery by passivating the reactivity of the anode and preventing additional electrolyte degradation.[28] The presence of SEI allows lithium ions to be freely embedded and dislodged in the electrode material, while serving to protect the electrode material. However, the huge volume expansion caused by the silicon leads to a gradual cracking of the silicon particle surface, as well as causing mechanical deformation of the SEI layer, resulting in a new silicon surface being exposed. At this point the electrolyte again comes into contact with the silicon and continuously degrades and re-forms the SEI.[29] This continuous reorganization process results in the unrestricted growth of the SEI layer, which causes it to become increasingly inhomogeneous and unstable. At the same time, this process will continuously consume Li ions and electrons reextracted from the anode, which will lead to the degradation of the battery's recyclable capacity, resulting in poor cycling stability.[30] Reducing the particles to nanoscale size can reduce their mechanical stress; building composite electrodes can improve their mechanical properties and reduce volume expansion.[31-33]

2.1 Silicon nanomaterials

In recent years, the application of nanomaterials in lithium-ion batteries has become increasingly widespread. It has become a trend to improve electrochemical performance as well as to study new lithium-ion storage mechanisms. For electrode materials, the decrease in the size of the active material particles leads to an increase in the overall surface area of the electrode, which greatly increases the opportunity for lithium ions to be embedded in the electrode area and can significantly enhance the surface effect, thus improving the storage performance of lithium-ion batteries.[34] As for silicon anode materials, the nano-size can increase the material's specific surface area, effectively reduce the surface stress, and further solve the crushing and cracking problems caused by volume expansion.[35] At the same time, the nanostructure allows the transport path of lithium ions to be further shortened, enabling lithium ions to be rapidly embedded and dislodged during charging and discharging, thus enhancing the multiplier performance of the battery.

However, the nanosizing of silicon has certain drawbacks. Synthesizing nanostructured silicon is more complex, and the nanoparticle size is difficult to control. The increase in specific surface area exposes more of the active material to the electrolyte, leading to the instability of SEIs.[36] Therefore, based on the experience of previous research on nanomaterials, different structures of nanosilicon have been designed and synthesized, including zero-dimensional, one-dimensional, two-dimensional, and three-dimensional nanosilicon materials, *etc*., and they have been improved and innovated.[37,38]

Zero-dimensional nanosilica materials are mainly silicon nanoparticles. With the advantages of a larger specific surface area and higher surface activity, they are widely used in anode materials for lithium-ion batteries. In order to better improve the electrochemical performance and stability of lithium-ion batteries, structural improvements have been made to the nanosilica particles.[39] Gao *et al.* introduced a continuous ultrathin carbon layer on top of silica nanorods to stabilize the structure. They successfully reduced the carbon-coated hollow silica particle structure in $AlCl_3$-NaCl molten salt at high temperatures using metallic aluminum powder.[40] The specific reaction (1) process is as follows:

$$4Al + 3SiO_2 + 3AlCl_3 + NaCl \rightarrow 3Si + 6AlOCl + NaAlCl_4 \quad (1)$$

Its synthesis process is mainly by etch-reduce/nucleation-growth (Fig. 2). The results show that the whole shell layer is formed by a Si/C/Si sandwich-like interlayer, in which silicon dominates, while the carbon layer, as a skeleton, plays an important role in stabilizing the core-shell structure.

When used as anode materials for lithium-ion batteries, the silicon nanohollow structure has high battery capacity, long cycle life, and excellent rate performance. The specific capacities of the material were 2179, 1988, 1798, 1505, 1240, and 974 mAh g^{-1} at 0.5, 1, 2, 4, 6, and 8 A g^{-1}, respectively. They possessed a specific capacity of 1774 mAh g^{-1} after 200 cycles at a current density of 1 A g^{-1}. After pre-lithiation treatment, 80% of the initial capacity was maintained after 1100 cycles at a current density of 8 A g^{-1}.

One-dimensional silicon nanomaterials, such as silicon nanotubes, have attracted much attention among the many silicon nanostructures. Silicon nanotubes have a good volume of internal cavities and a large hollow structure, which can effectively shorten the transport path of lithium ions and, at the same time, accommodate the volume expansion of silicon.[41] Silicon nanotubes are generally categorized into ordinary hollow structures and complex hollow structures. Ordinary hollow structures have only a single layer of core-shell structure, while complex hollow structures have multiple

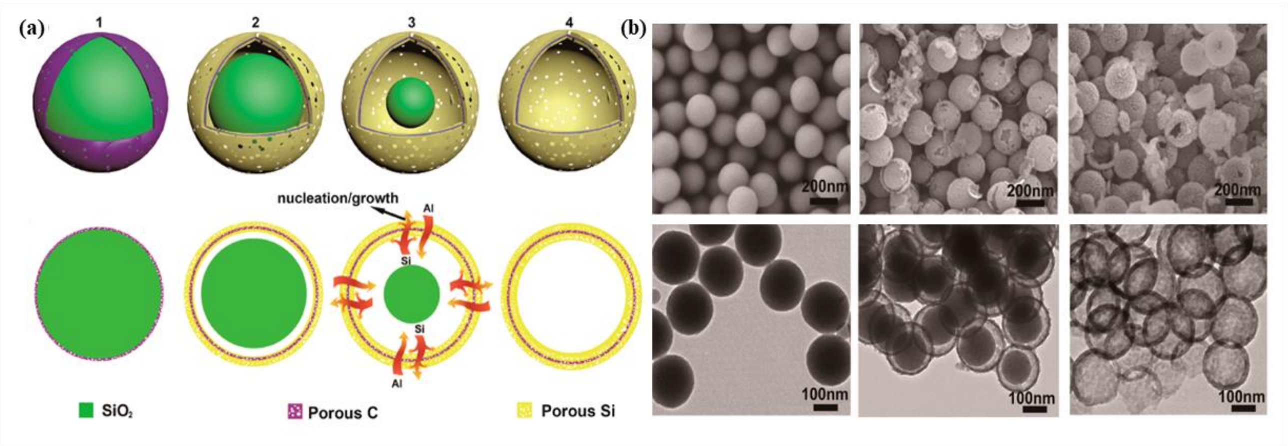

Fig. 2 Schematic synthesis of silicon hollow nanostructures along with SEM and TEM. Reproduced with the permission from [40], Copyright 2018 American Chemical Society.

layers of core-shell structure and multiple internal cavities.[42] It has been shown that silicon nanotube materials with a multilayered core-shell structure can solve the problem of dramatic volume expansion of silicon anode.[43] Song *et al.* designed and synthesized a nanotube-like geometric array sealed by silicon nanotubes.[44] This particular structure exhibits strong mechanical anisotropy, and the internal space of these nanotubes provides the additional free surface to accommodate volume expansion during lithiation. This electrode was shown through testing to exhibit high initial Coulombic efficiency (>85%) and stable Coulombic efficiency (>80% after 50 cycles). The capacity can reach 2000 mAh g^{-1} after 50 cycles at a current density of 200 mA g^{-1}.

Also, as one-dimensional nanomaterials, silicon nanowires were extensively studied in the early years. As electrodes, silicon nanowires can provide a good active surface. They can provide efficient electron and ion transport channels along the linear direction, effectively improving the battery's stability. Ge *et al*. synthesized porous doped silicon nanowires by directly etching boron-doped silicon wafers.[45] The structure has high porosity and good electron transport properties, providing good structural stability for the electrode. The material showed better electrochemical properties and long cycle life with alginate as a binder. After 250 cycles at current densities of 2, 4, and 18 A g^{-1}, its capacity remained stable above 2000, 1600, and 1100 mAh g^{-1}, respectively. However, silicon nanowires are difficult and more expensive to prepare compared to bulk-phase silicon.

Two-dimensional silicon nanomaterials include silicon nanosheets, silicon nanofilms and other materials. Among them, two-dimensional silicon nanosheets have the advantages of easy access to lithium ions, easy compatibility with other materials, and small volume expansion due to the ultrathin sheet structure, which is considered a candidate for anode materials for lithium-ion batteries. However, most of the experimentally synthesized silicon nanosheets do not exhibit high cycling performance, and the structured material is worthy of further research. Ryu *et al*. prepared 5-nm-thick porous silicon nanosheets in a one-step process using inexpensive natural clays.[46] The silicon nanosheets, after carbon capping, exhibited excellent electrochemical performance as well as cycling stability when used as anode electrodes in lithium batteries. It possessed a high reversible capacity of 865 mAh g^{-1} at a current density of 1.0 A g^{-1} and a capacity retention of 92.3% after 500 cycles. It also exhibits high multiplicative performance with 60% capacity retention at 20 A g^{-1} compared to 2.0 A g^{-1}. In addition, the silicon nanosheet electrode expanded only 42% in volume after 200 cycles. However, the insufficient cycle life of silicon nanosheets at high current densities and their weak mechanical strength have hindered their practical application. Wang *et al*. employed a facile synthesis to design a sandwich-like h/s/h-Si NS.[47]

The sandwich-like honeycomb SiO_2 NS/solid SiO_2 NS/honeycomb SiO_2 NS templates were prepared by self-assembly, followed by the synthesis of h/s/h-Si@C NS by magnesium thermal reduction at 650 °C, as well as carbon layer coating (Fig. 3). This unique structure effectively improves the overall mechanical strength of the material while retaining enough space to accommodate the volume expansion of the Si anode electrode. The coating of the conductive carbon layer facilitates the formation of a stable electrode/electrolyte interface. h/s/h-Si@C NS showed a high initial coulombic efficiency (86%), high reversible capacity (1624 mAh g^{-1} after 100 cycles at 1000 mA g^{-1}), good rate capability (over 1000 mAh g^{-1} at 4000 mA g^{-1}), and long cycling life even at 4000 mA g^{-1} (93% retained capacity after 1000 cycles).

Three-dimensional silicon nanomaterials have a complete overall structure compared to zero-dimensional, one-dimensional, and two-dimensional materials, and at the same time, have a large surface area and a high surface-area-to-volume ratio, which can make up for some of the shortcomings of zero-dimensional to two-dimensional materials and inherit their advantages. Porous silicon is a three-dimensional nanomaterial.[48,49] The porous structure can provide enough space to buffer the volume expansion of lithium batteries

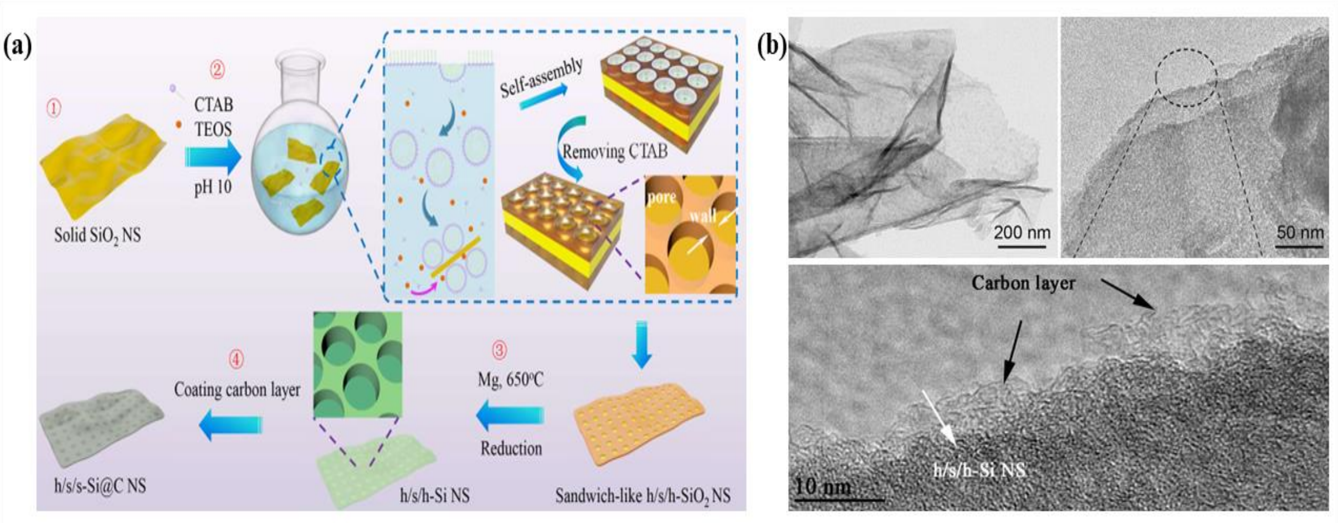

Fig. 3 Schematic of the preparation process of h/s/h-Si@C NS and its TEM images. Reproduced with the permission from [47], Copyright 2023 American Chemical Society.

during lithiation for good stability.[50] Jia *et al.* utilized low-cost microemulsions of silica nanoparticles and obtained spherical micron-sized silica with a porous structure by magnesium thermal reduction.[51] The material can simultaneously enhance the electrode's structural stability and electrochemical performance (Fig. 4). Using silica nanoparticles as the base material can effectively reduce the cost. In addition, by removing the magnesium oxide phase and retaining sufficient cavity space, the volume change of silicon can be effectively mitigated, thus preventing the rupture of the SEI layer and enhancing its cycling stability. The conductivity and structural stability of the electrode are further improved by covering the porous silicon (p-Si) particles with a carbon coating. Tests show that the p-Si/C electrode possesses a capacity of about 1467 mAh g^{-1} at a current rate of 2.6 A g^{-1}; its capacity can still be maintained at about 83% after passing 370 cycles. When the rate is increased to 11 A g^{-1}, the capacity can be maintained at about 650 mAh g^{-1}.

2.2 Silicon composite materials

In addition to designing nanostructures for silicon, many have investigated the application of silicon-based composites for lithium-ion batteries by designing rational composite structures to limit silicon's volume expansion and improve electrode materials' electrochemical properties.[52] Composite materials retain the advantages of each component material and achieve better performance and a more stable structure through the coordinated action of the components.[53] Silicon composites include silicon-carbon composites, silicon alloys, and silicon-metal oxide composites.

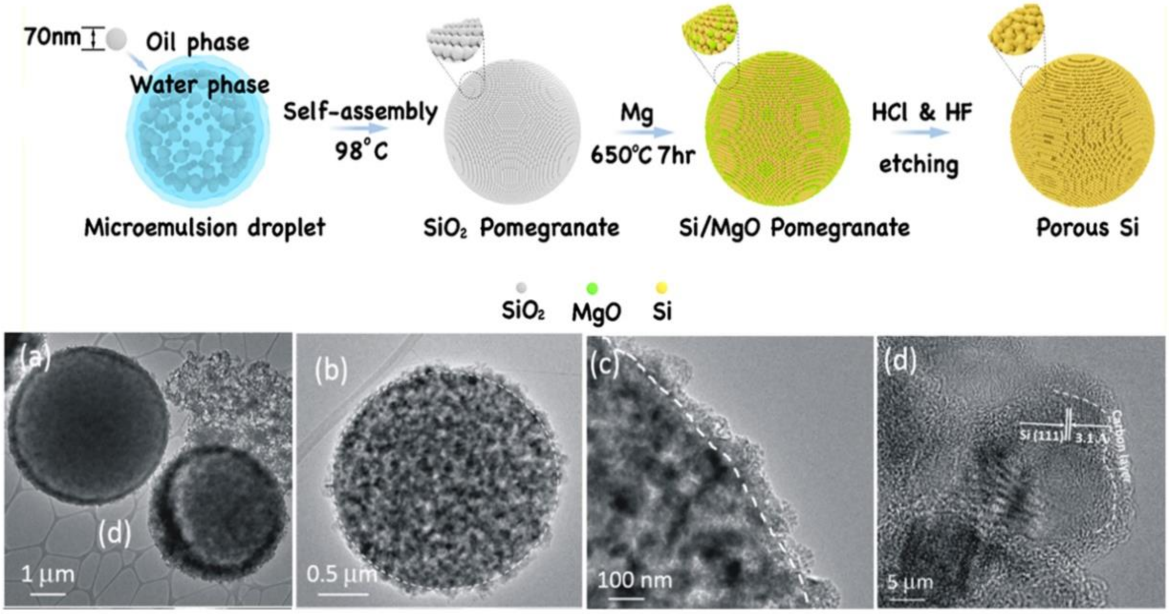

Fig. 4 Schematic of the porous silicon preparation process and its TEM and HR-TEM images. Reproduced with the permission from [51], Copyright 2018 Elsevier.

Silicon-carbon composites are considered the most promising anode materials for lithium-ion batteries. Carbon is considered the most suitable material to work with silicon due to its low volume change and excellent electrical conductivity and mechanical properties.[54,55] Due to their high mechanical strength, carbon materials are often present in composites in the form of carbon coatings to reduce the volume expansion of silicon.[56] The carbon layer can effectively reduce the direct contact between the active material and the electrolyte, thus preventing the continuous formation and breakage of the SEI film.[57] Silicon-carbon composites will be very important in improving lithium-ion batteries' cycle stability and cycle life. Previously, synthesizing Si/C composites required a cumbersome and complex coating process. Li *et al.* successfully embedded ultra-small silicon particles in a carbon matrix using a simple silicon and carbon integration strategy.[58] The method is based on octaphenyl polyhedral oligomeric silsesquioxane (Ph-POSS), and since Ph-POSS has both an inorganic -Si_8O_{12} core ($SiO_{1.5}$) and an organic phenyl shell, polymer nanospheres encapsulating the -Si_8O_{12} core were prepared by Friedel-Crafts crosslinking of the phenyl shell. After high-temperature heat treatment and magnesium thermal reduction, the polymer nanospheres were transformed into a carbon matrix, while the -Si_8O_{12} core was reduced and grown in situ to produce ultra-small Si particles. This unique structure has the following characteristics: first, the ultra-low size silicon particles can effectively reduce the damage caused by silicon volume changes during cycling. Second, the carbon matrix helps to improve the conductivity of the composite electrode, and the carbon phase can also act as a barrier to protect the silicon particles from agglomeration. In addition, the porous structure can provide an effective channel for Li+, while the spherical structure facilitates the shortening of the diffusion path. This electrode structure with ultra-small silicon size, effective carbon barrier and permeable nanopore space, exhibits excellent electrochemical performance in lithium-ion batteries.The Si/C anode can achieve an initial discharge capacity of 2139 mAh g^{-1}. A capacity of 738 mAh g^{-1} was retained after 120 cycles at a current density of 0.4 A g^{-1}.

Graphite, a traditional carbon material, is the most commonly used anode-active material due to its low potential, abundant reserves, and good stability. However, its limited theoretical capacity (372 mAh g^{-1}) can no longer meet the energy density required by the growing demand. Therefore, studies have been initiated to investigate the improvement of graphite-silicon composite for electrode performance. Typical graphite (carbon) materials include carbon nanotubes,[59] carbon nanofiber.[60,61] graphene,[62,63] *etc*.

Carbon nanotubes are one-dimensional structured graphitic materials with flexible mechanical properties, high electrical conductivity, and high specific surface area. Since carbon nanotubes have unique structural features that enable the construction of an electron conduction network, they can not only provide enough space to mitigate the huge volume expansion of silicon but also provide a fast ion transport path during cycling, which further improves the multiplicity performance as well as the cycling stability.[64] Li *et al.* designed and synthesized a boron-doped silicon and carbon nanotube composite (B-Si/CNTs) using a solid-state approach.[65] It has been shown that this enhanced graphite material has excellent structural stability and can be used as a tough electrode structural framework to accommodate volume changes in silicon.It has been tested to have a good reversible capacity (2426 mAh g^{-1}) and cycling stability (88.2% retention after 200 cycles); Graphite can be used as a stable framework for high-load applications. The B-Si/CNT@G material compounded with graphite exhibits ultra-high capacity and cycling stability. It has a high average capacity of 5.2 mAh cm^{-2} at an ultra-high load of 11.2 mg cm^{-2} and a retention rate of 83.4% after 100 cycles（Fig. 5). This fully demonstrates the good compatibility between silicon and graphite during cycling.

Graphene, a graphitic material with a two-dimensional structure, is characterized by both high mechanical flexibility and electronic conductivity and is therefore widely used to synthesize silicon-graphene (Si/G) anodes to improve the electrochemical performance of Si anode materials by increasing the conductivity.[67] Li *et al.* synthesized Si-C/VGSs/graphite composites as anode for lithium-ion batteries by uniformly depositing amorphous Si-C nanolayers on graphite doped with N-doped porous flexible vertical graphene sheets (VGSs).[68] This Si/G composite, consisting of Si-C nanolayers and graphite wrapped with porous flexible VGSs, was prepared by thermal CVD to realize the cycle stability, fast charging capability, and high energy density of lithium batteries. The uniformly dispersed sub-nanometer silicon particles in the silicon-carbon nanolayers and the directional ion transport channels of the VGSs ensure rapid delivery of lithium ions. Meanwhile, the VGS with a porous structure provides enough space for high loading and volume expansion of silicon, which effectively accommodates the volume change of silicon. In the half-cell test, the electrodes showed high specific capacity (683.6 mAh g^{-1}), superior rate performance (481.6 mAh g^{-1} at 5C), high initial CE (93.1%), and high-capacity retention (91.3% after 1000 cycles at 1C). It also demonstrated superior fast charge capability (180.8 Wh kg^{-1}, 8.2 min charge at 5C) and long cycle life (80.0% capacity retention after 800 cycles at 1C) in the full battery test.

Heteroatom doping is a common strategy for modifying carbon materials to improve electrode materials' conductivity and lithium storage capacity. Zhang *et al.* prepared Si@C/P nanoparticles with excellent electrochemical properties by sol-gel method and carbonization process.[66] In this experiment, a phosphorus-doped carbon skeleton was successfully synthesized for the first time by using phosphate-doped phenol formaldehyde resin as both carbon and phosphorus source. The synergistic effect of carbon coating and phosphorus doping limits the volume expansion of silicon and improves the diffusion rate of Li ions. The core-shell structure in the material improves the conductivity and structural stability,

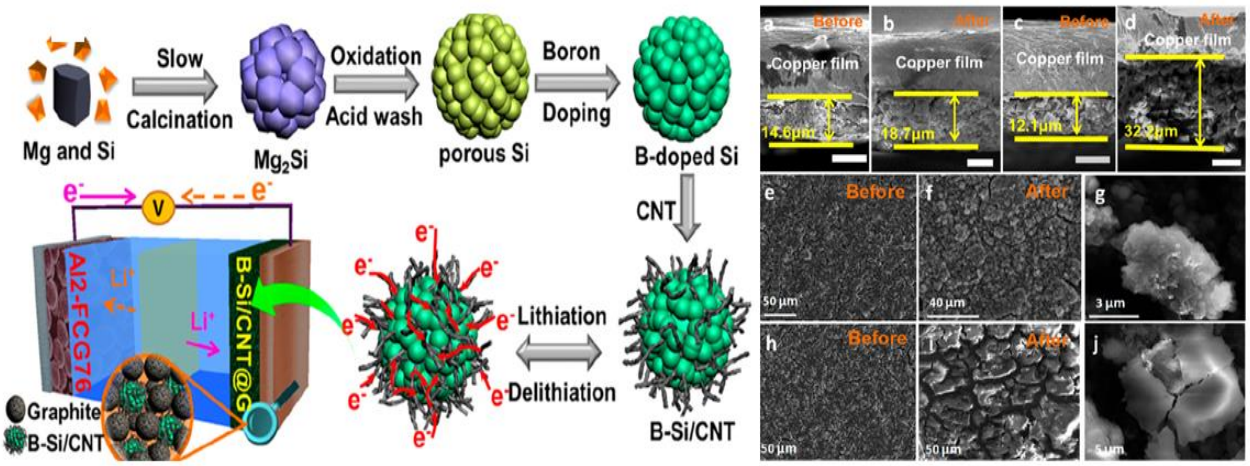

Fig. 5 Schematic of B-Si/CNT synthesis and SEM comparison before and after cycling. Reproduced with the permission from [65], Copyright 2019 American Chemical Society.

while the doping of phosphorus in the carbon skeleton further enhances the active sites and conductivity of the material. The Si@C/P electrode exhibits excellent electrochemical performance, with a specific capacity of 1873 mAh g^{-1} after 100 cycles at a current density of 1 A g^{-1} and a high initial coulombic efficiency of 84.4%. Even at a high current density of 4.0 A g^{-1}, an average specific capacity of 1422.3 mAh g^{-1} was achieved.

In recent years, flexible and self-supporting silicon-carbon composite electrode materials have attracted more and more attention. In the conventional electrode preparation process, active ingredient particles and conductive carbon additives are coated to form a layered structure on a metal foil collector by forming a slurry of certain viscosity through a non-conductive polymer binder. However, during the drying process, the electrode slurry has a large shrinkage stress. The adhesion between the active material layer and the collector is poor, which may lead to delamination of the active material and increase the charge transfer resistance. Compared to the conventional slurry method, flexible self-supporting electrodes can be obtained without other added components, such as non-conductive polymer binders, conductive additives, and metal collectors. The elimination of conventional additives significantly reduces the interfacial resistance and total weight of the battery component, thereby increasing the flexible electronic device's specific weight and volumetric energy density.[69]

Electrostatic spinning is an easy-to-use and scalable technique for producing continuous mesh structures with high specific surface area and mechanical flexibility at the micro- and nanoscale.[70] It is commonly used to prepare nanofiber materials. And carbon nanofibers are a common flexible material that can be used to design and synthesize free-standing, self-supporting films. Xie *et al*. fabricated a free-standing Si@void@C/CNFs anode electrode without conductive additives, binders, and collectors using a simple template removal method and electrostatic spinning technique.[71] The material is composed of silicon nanoparticles with the structure of yolk-shell and carbon nanofibers (Fig. 6).

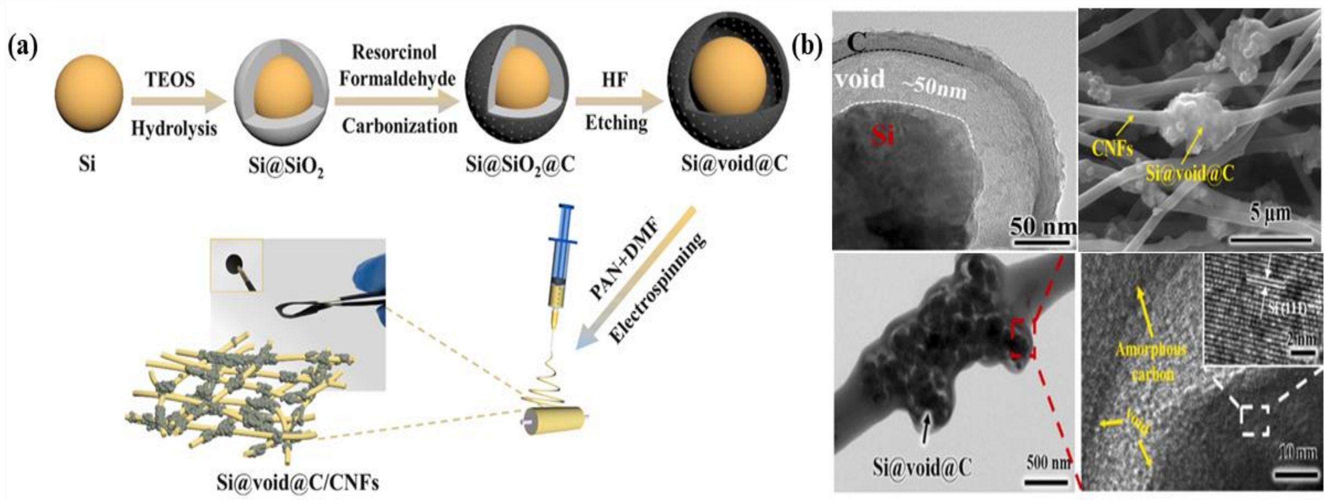

Fig. 6 Schematic preparation of Si@void@C/CNFs composites and TEM and SEM images. Reproduced with the permission from [71], Copyright 2022 Elsevier.

Among them, the yolk-shell structure helps to buffer the volume expansion of silicon during discharge/electrical cycling, and to improve its structural stability. while the N-doped carbon fiber forms a 3D interconnection network, which provides sufficient additional active sites for Li+ storage and ensures fast electron transfer. Electrochemical tests showed high reversible capacity and good cycling performance, with a discharge capacity of 627.5 mAh g^{-1} and a capacity retention of 69.3% after 100 cycles at 0.1 A g^{-1}, superior to 196.0 mAh g^{-1} of Si@C/CNFs and 116.2 mAh g^{-1} of Si/CNFs. Even at the current density of 1000 mA g^{-1}, Si@void@C/CNFs still maintain a high discharge capacity of 317.1 mAh g^{-1}.

In addition to silicon-carbon composites, silicon composites also include silicon alloy materials, silicon-metal oxide composites, and so on. Fe, Cu, Ni, Al, Ti, Mg, Sn, and other metals are commonly used to form Si/M alloy materials, which can not only improve the electrical conductivity of silicon-based electrodes but also increase the proportion of active materials in the electrodes, which can effectively enhance the charging and discharging capacity of lithium-ion batteries.[72] At the same time, the composite material with added metal has high-strength mechanical properties, which can well alleviate the volume expansion of the silicon anode electrode. Umirov's group worked on the design of high-performance silicon alloys. They annealed melt-spun amorphous alloy ribbons at a certain temperature and synthesized a silicon nano-alloy with uniform grain distribution.[73] This new approach is a good solution to the problem of microstructural homogeneity of melt-spun nanosilicon in inactive matrix alloys. The results show that the silicon alloy electrode has an initial discharge capacity of 900 mAh g^{-1}, exhibits a high coulombic efficiency of more than 99% from the second cycle, and retains a capacity of about 98% after 100 cycles.

The composites formed by silicon and metal oxides can improve the conductivity and stability of the anode electrode very well. Zhu *et al*. designed and synthesized a silicon nanoparticle with a zinc oxide coating.[74] In this study, diethyl zinc [Zn (C2H5)2, DEZ] and water were used as the precursor and oxygen reactant source of zinc, and the electrodes were coated with ZnO by atomic layer deposition (ALD). The coating improved the mechanical structural integrity and interfacial stability. The reversible capacity of Si/ZnO was shown to be 1500 mAh g^{-1} at 260 cycles; by protecting the interface with ZnO, the electrode could achieve high-quality charging up to 1.4 mg cm^{-2}, which exhibited excellent cycling stability.

Based on the research on silicon-carbon composites and silicon-metal oxide composites, attempts have been made to design new bilayer-structured silicon composites. Zhang *et al*. prepared bilayer-structured Si@Al_2O_3@C nanoparticles using solvent evaporation, sol-gel and annealing methods.[75] (Fig. 7). The alumina layer, as an artificial SEI film, was able to improve the cycling stability of the material, while the carbon coating increased the electrical conductivity of the composite and mitigated the volume expansion of silicon. The protection of the dual-coating structure led to a significant improvement in the electrochemical performance of Si. The specific capacity of Si@Al_2O_3@C nanoparticles was 1316.1 mAh g^{-1} after 100 cycles at a current density of 1 A g^{-1}, and the average discharge capacity was still 781.6 mAh g^{-1} at 4 A g^{-1}. In addition, the material has an initial coulombic efficiency (ICE) of 82.9%. This novel structure opens new avenues for the study of silicon anodes.

3. Silicon-based anodes in solid-state electrolytes

Research on traditional liquid lithium-ion batteries has been saturated, and liquid lithium batteries have been commercialized on a large scale. However, with the increasing demand for battery safety, the flammability and volatility of liquid electrolytes have become a concern. At the same time,

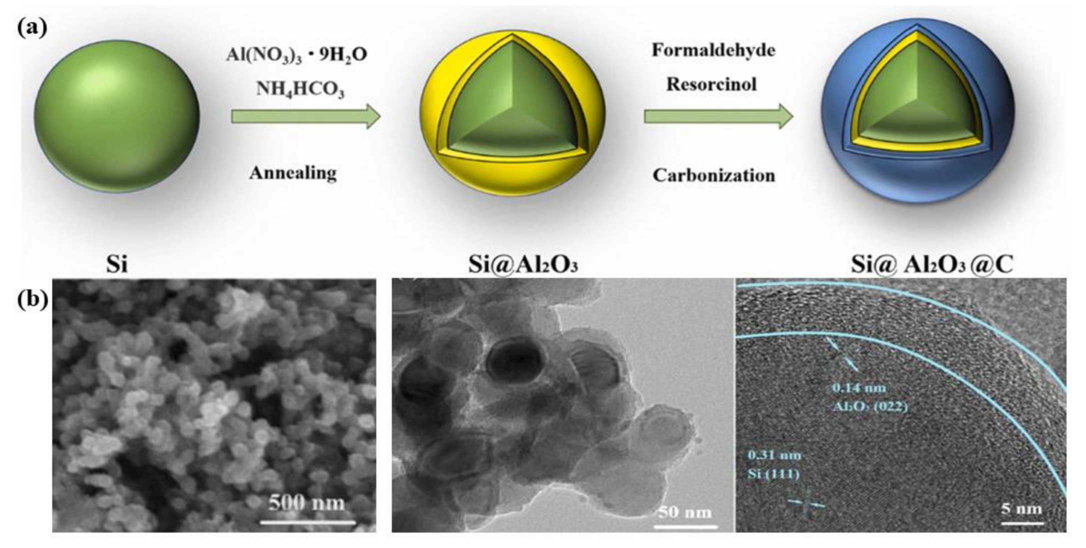

Fig. 7 Preparation of Si@Al_2O_3@C along with SEM, TEM and HRTEM. Reproduced with the permission from [75], Copyright 2021 Elsevier.

the prolonged use of most mobile portable devices will lead to the deterioration of the service life of liquid lithium batteries. Therefore, more and more researchers and scientists have begun to turn to the direction of solid-state electrolyte research. Compared to liquid electrolytes, solid electrolytes have the advantages of low flammability, high thermal stability, low explosion risk, and low leakage.[76] At the same time, solid-state lithium-ion batteries can have a longer cycle life, and compared to liquid lithium-ion batteries, solid-state lithium-ion batteries consist of fewer components and materials, which can greatly reduce the quality and size of the battery and improve the use of battery space.[77] Because solid-state electrolytes can be used in a wider range of electrochemical windows.[78] silicon, an electrode material with high theoretical specific capacity and low working potential, has been gradually applied to solid-state electrolytes.

In addition, the gradual decomposition of the electrolyte during the cycling process and the easy expansion of the silicon anode electrode during the cycling process will lead to the instability of the solid electrolyte interface (SEI) and hinder the ion transport in the electrodes, thus reducing the cycle life of the battery. The application of solid electrolytes can effectively avoid all the disadvantages of electrolytes, thus improving the cycling stability of silicon anode. Common solid electrolytes that can be used with silicon are oxide, sulfide, and polymer electrolytes.

3.1 Silicon-based anode in oxide electrolytes

Solid oxide electrolytes have received extensive attention in recent years with the advantages of higher ionic conductivity at room temperature, wider electrochemical windows, lower preparation cost, and more stable electrochemical performance. Common oxide electrolytes include garnet-type $Li_7La_3Zr_2O_{12}$(LLZO), $Li_{3x}La_{2/3-x}TiO_3$(LLTO), as well as heteroatom-doped substitution (*e.g.*, Ta-element doped LLZTO and Ta-element-substituted LLZTa) and LISICON-type $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ lithium-ion fast conductors. These oxide electrolytes have high ionic conductivity and better contact with the electrodes, which can improve lithium-ion transport efficiency.[79]

Elemental doping (substitution) modification strategies have been widely applied to the design of composite solid-state electrolytes. Chen *et al*. prepared an elementally Ta-doped LLZO solid-state electrolyte (LLZTO) and deposited a silicon layer on a dense LLZTO ceramic plate to prepare a silicon/garnet interface.[80] The LLZTO electrolyte has ultra-high ionic conductivity when working at high temperatures, which can realize the battery charging and discharge under high current density and can inhibit the self-discharge phenomenon of the battery as well as the occurrence of other side reactions so as to improve the Coulombic efficiency; the doping of Ta element can effectively inhibit the generation of interfacial by-products between the active substance and the electrolyte, avoiding the higher interfacial resistance. The tested nano-silica layer was more compatible with the garnet electrolyte, with good cycling and multiplicity performance. The results show that the anode of the silicon layer below 180 nm can maintain good electrochemical contact with the LLZTO electrolyte, and the capacity retention is more than 85% after 100 cycles, which shows a good cycling stability performance. When a 45 nm silicon layer was used, the reversible capacity reached 1978 mAh g^{-1} after 100 cycles at a current density of 0.1 C (Fig. 8). In a full cell test with a $LiFePO_4$ cathode added, the capacity retention was 72% after 100 cycles.

The interfacial contact between the electrode and the oxide electrolyte can produce some undesirable reactants with high resistance, which limits the application of silicon-based anode in solid-state lithium batteries. To enhance the silicon/electrolyte interfacial effect and improve the compatibility of the interface between the silicon anode and the solid-state electrolyte, Ferraresi *et al*. treated the surface of the LLZTa (Ta instead of LLZO) electrolyte with argon plasma etching, which effectively removes the resistive substances such as Li_2CO_3, and then deposited 50 nm thick silicon thin-film electrodes on the surface of this smooth solid-state electrolyte, and developed the Si/Garnet-type LLZTa solid-state lithium-ion batteries.[81] The design improves the contact environment between silicon and electrolyte, enhances the ionic transport of the electrolyte, and further improves the

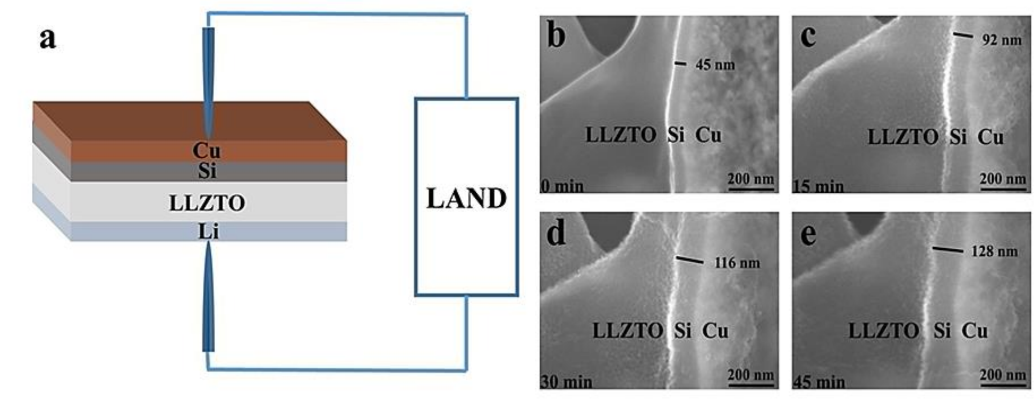

Fig. 8 In-situ SEM study during polarization of Cu/ Si/LLZTO/Li cell with silicon layer thickness of 45 nm. Reproduced with the permission from [80], Copyright 2018 American Chemical Society.

cycling performance of the cell. The results show that the Si film/LLZTa/Li has an initial capacity of 2700 mAh g^{-1} and maintains 1200 mAh g^{-1} after 100 cycles.Oxide electrolytes have some defects inherent in the oxide itself. For the electrode/electrolyte interface, the oxide electrolyte has poor interfacial contact ability and poor interfacial stability during cycling, resulting in a rapid increase in interfacial impedance after cycling, making the effective capacity of the anode insufficient and greatly reducing the cycle life of solid-state batteries.[82] Also, oxide solid electrolytes are difficult to achieve thin layer thicknesses.[83] Therefore, based on the current research status, less research has been reported on single-component oxide electrolytes, and more silicon-based Li-ion batteries are being prepared with composite electrolytes by using oxides as the main component and adding other electrolyte materials to improve the interfacial contact. In addition, it is also possible to add some polymer components to the oxide solid electrolyte and mix it with a trace amount of ionic liquid/high performance lithium salt electrolyte to maintain the safety advantages of the solid electrolyte and achieve better electrochemical performance.

3.2 Silicon-based anode in sulfide electrolytes

Compared with oxide electrolytes, sulfide electrolytes contain substances with smaller electronegativity and ionic radius, the weaker binding force for lithium ions, and wider transport channels for ions, resulting in higher ionic conductivity, which promotes the ionic diffusion ability of silicon anodes.[84] Common sulfide electrolytes are based on Li_2S-SiS_2 and Li_2S-P_2S_5. Due to their excellent mechanical ductility, sulfides are able to accommodate the volume expansion of the silicon-based anode and provide stable contact between the electrolyte and the active material, thus increasing the energy density of the battery while maintaining good electrochemical performance.[85] Silicon anode electrodes have been widely developed for use in sulfide electrolytes.

Incorporation of sulfide electrolytes in Si-based anodes is beneficial to enhance their mechanical structural stability. Cao *et al*. systematically investigated the electrochemical and mechanical evolution of Si nanocomposite anodes in sulfide SE-based ASLBs by operando synchrotron XANES, ex situ SEM and ex situ synchrotron XnT.[86] By ex situ SEM studies, it was observed that the sulfide electrolyte SE showed a mud-like morphology when a high external stress was applied, and it was hypothesized that the flexibility of SE made the close contact with Si nanoparticles possible. And during the lithiation process, Li is gradually alloyed with Si to form Li_xSi, which is accompanied by volume expansion and generates certain internal mechanical stress. Under external pressure and internal stress, the Si electrode was observed to consist of large aggregates with small pores or interstices. In contrast, the Si-SE composite electrodes had fewer pores or interstices between the multiphase aggregates, indicating that the addition of SE could alleviate the aggregation of Li_xSi and improve its structural stability. A chemo-elasto-plastic model was further developed, and the results demonstrated the smaller plastic deformation and von Mises stress evolution of the Si-SE anode composites relative to the Si anode. Since SE is more flexible than Si, it acts as a mechanical buffer and helps to reduce the stresses generated by the volume expansion of Si, thus contributing to the mechanical stability.

Okuno *et al*. prepared nanoporous Si particles by reduction of mesoporous SiO_2 spheres with Mg_2Si as anode active material for lithium-ion batteries with Li_3PS_4 as solid electrolyte.[87] Through electrochemical impedance analysis and field emission scanning electron microscopy, it is demonstrated that the elastic deformation of Li_3PS_4 sulfide electrolyte can effectively relieve the structural stress caused by the volume change of silicon anode material during lithiation and desulfurization, thus improving the cycling stability of lithium batteries. Test results show that the battery has 90% capacity retention after 50 cycles. In the stacked cell at 0.30 mA cm^{-2}, the area capacity reached 2.0-4.4 mAh cm^{-2} after the 47th cycle.

Most of the current solid-state lithium-ion batteries with silicon anodes are in the form of dry mixed electrodes with silicon nanoparticles, which have a low mass loading of the particle structure. Kim *et al*. prepared a lamellar Si composite electrode by infiltrating a conventional LIB electrode with a solid electrolyte using a well-mixed Li_6PS_5Cl-ethanol solution.[88] The liquid LPSCl electrolyte could be compatible with Si and solidified on the surface of Si, providing close ionic contact as well as a favorable ionic transport path. The LPSCl-infiltrated Si electrode exhibited an ultra-high reversible capacity of more than 3000 mA hg^{-1} at 0.25 mA cm^{-2} and 30°C compared with the conventional dry hybrid electrode. And the all-solid-state LCO/Si cell with LPSCl-infiltrated LCO and m-Si electrodes exhibited a high energy density of 338 Wh kg_{LCO+Si}^{-1} at 0.14 mA cm^{-2} and 30 °C.

Yamamoto *et al.* used a slurry mixing method to prepare composite electrode sheets with uniformly distributed micrometer-size silicon particles.[89] The team centrifuged a slurry mixture containing silicon particles and a solid sulfide electrolyte (LPS) in centrifuge tubes containing ZrO_2 spheres of various sizes to increase the contact area between the silicon material and the sulfide electrolyte. The volatile binder was then removed from the laminated cells to reduce the internal resistance of the cells. The cracks perpendicular to the silicon composite layer during cycling buffered the internal strain due to the change in silicon volume, and the cells exhibited excellent cycling stability. After testing, a high initial coulombic efficiency (95%) was demonstrated. After 47 cycles at 0.30 mA cm^{-2}, the actual area capacity was 2.0-4.4 mAh cm^{-2}. After 100 cycles, the remaining cell capacity was 2300 mAh g^{-1}; after 375 cycles, it still had a capacity of 1700 mAh g^{-1}.

As a solid electrolyte with excellent performance, sulfide electrolyte has been widely studied recently. Although it has many obvious advantages, sulfide produces strong, irritating, and toxic gases during the preparation process, which can have a considerable impact on the human body and the surrounding environment. Therefore, the synthesis environment of sulfide is quite demanding. In order to solve the problem of sulfide solid electrolyte is easy to water reaction to generate H_2S gas, some oxides (Li_2O, P_2O_5, Fe_2O_3, ZnO, *etc.*) as well as halides on the sulfide system can be doped or replaced, to further improve the air stability of the material, reduce the generation of H_2S.[90,91] In addition, sulfides themselves have poor electrochemical stability, resulting in a narrow electrochemical window. It can usually be compounded with some other sulfides, as well as high-performance lithium salt electrolytes, to improve its electrochemical performance and structural stability.

3.3 Silicon-based anodes in polymer electrolytes

Polymer solid-state electrolyte has many obvious advantages, such as lightweight, good ductility, good flexibility, good interfacial compatibility, *etc*., and has become a solid-state electrolyte in lithium-ion solid-state battery with faster development.[92] Polyethylene oxide (PEO), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), and others are currently used as polymer electrolytes.[93] At the same time, in order to further improve the ionic conductivity of the polymer electrolyte, the composite polymer electrolyte membrane, which is synthesized by mixing the polymer electrolyte with some other polymer materials and additives, has also become an important development direction.

Other solid electrolyte materials (*e.g.*, oxide electrolyte) can be introduced on top of the polymer material to form a composite solid electrolyte for even better performance. Huo *et al*. developed a flexible interface between a silicon anode and a composite electrolyte consisting of polypropylene carbonates (PPCs) and garnet powder.[94] The composite polymer electrolytes (SPEs) had smooth surfaces and high ionic conductivity. The introduction of garnet powder (LLZTO) into the SPEs promoted the complete dissociation of lithium salts and enhanced the migration of Li ions. The solid polymer electrolytes (SPEs) of this PPC/garnet/LiTFSi were shown to have high conductivity (of 4.2×10^{-4} S cm^{-1}) at room temperature. When combined with the silicon layer anode, the internal stresses resulting from volume changes during lithiation and delithiation of the silicon anode can be greatly reduced. After conducting electrochemical tests, the capacity of the cell was shown to be 2520 mAh g^{-1}, 2260 mAh g^{-1}, 1902 mAh $g^{-1,}$ and 1342 mAh g^{-1} at 0.1 C, 0.2 C, 0.5 C, and 1 C, respectively. In addition, the all-solid-state battery composed with $LiFePO_4$ as the cathode exhibited a specific capacity of 2296 mAh g^{-1} and had a capacity retention rate of 82.6% after 100 cycles at 0.1 C at room temperature.

However, the low ionic conductivity of polymer electrolytes makes it difficult to penetrate into the electrodes; in addition, the surface of the electrodes and the polymer electrolytes can suffer from poor contact, resulting in high interfacial resistance, which affects the rapid transfer of ions and electrons.[95] Gel-type Polymer Electrolytes (GPEs) have gained much attention due to their high ionic conductivity, ease of handling, impressive low-temperature performance, and excellent interfacial adhesion.[96] Pandey *et al.* succeeded in completely infiltrating gel polymers into silicon-coated vertically aligned carbon nanofibers (Si-VACNFs).[97] This study used PVdf-HFP as the polymer material and LiTFSI was added to obtain flexible solid gel electrolyte membranes by solution casting method. Si-VACNFs are a kind of high-capacity three-dimensional nanostructured anode, which can allow the electrolyte to penetrate better and form a stable electrode-electrolyte interface with the combination of GPEs. And the flexible gel polymer electrolyte can effectively relieve the structural stress caused by the change of silicon volume during charging and discharging. The GPEs have a high electrical conductivity of 2.2×10^{-3} S cm^{-1}, a high ion transfer efficiency at room temperature, and good thermal and mechanical stability. Si-VACNFs/GPEs solid-state batteries have high specific capacity, good multiplicity performance, and long cycle stability. They have high specific capacities of 3450 mAh g^{-1} and 1732 mAh g^{-1} at 0.36 A g^{-1} and 3.8 A g^{-1}, respectively. It retains a capacity of 1070 mAh g^{-1} after 100 cycles at 2.6 A g^{-1}.

In situ polymerization is usually a reasonable solution for designing gel polymer electrolytes. This method typically converts a mixed solution of polymer precursors into GPEs in situ within the cell, and enhances the interfacial contact between the solid electrolyte and the electrode through the wettability of the solution.[98] Zhao *et al.* designed a gel solid electrolyte with 1,3,5-trioxane (TXE) as the polymer monomer and lithium bistrifluoromethanesulfonimide (LiTFSI) and lithium difluoro(oxalato) borate (LiDFOB) as the lithium salts for in situ polymerization.[99] The lithium salt LiDFOB was able to induce the cationic polymerization of TXE, promote the formation of the polymer backbone, and thus effectively protect the anode structure (Fig. 9). The gel quasi-solid electrolyte has a high ionic conductivity of 2.16 mS cm^{-1} at room temperature and a favorable Li^+ transfer number (of 0.61).

In addition, the modified interface of this electrolyte with the anode in a half-cell containing a silicon-graphite (Si-Gr) anode effectively improves the cell's rate performance and cycle life. The in situ generated polymer skeleton and modified SEI interface effectively suppressed the volume expansion of the silicon graphite (Si-Gr) anode, which reduced the expansion rate to 26.7% after 300 cycles, which was significantly lower than that of 60.7% for the conventional liquid electrolyte. The tests of the NCM622 || Si-Gr full cell showed that the polymer electrolyte could inhibit the dissolution and corrosion of the cathode active material, which also protected the cathode structure. After 200 cycles at 25 °C, the capacity retention of the full cell was as high as 86.0%, while the average coulombic efficiency was as high as 99.79%. In addition, the electrolyte further improves the cycling stability of the battery at a high temperature (of 60 °C).

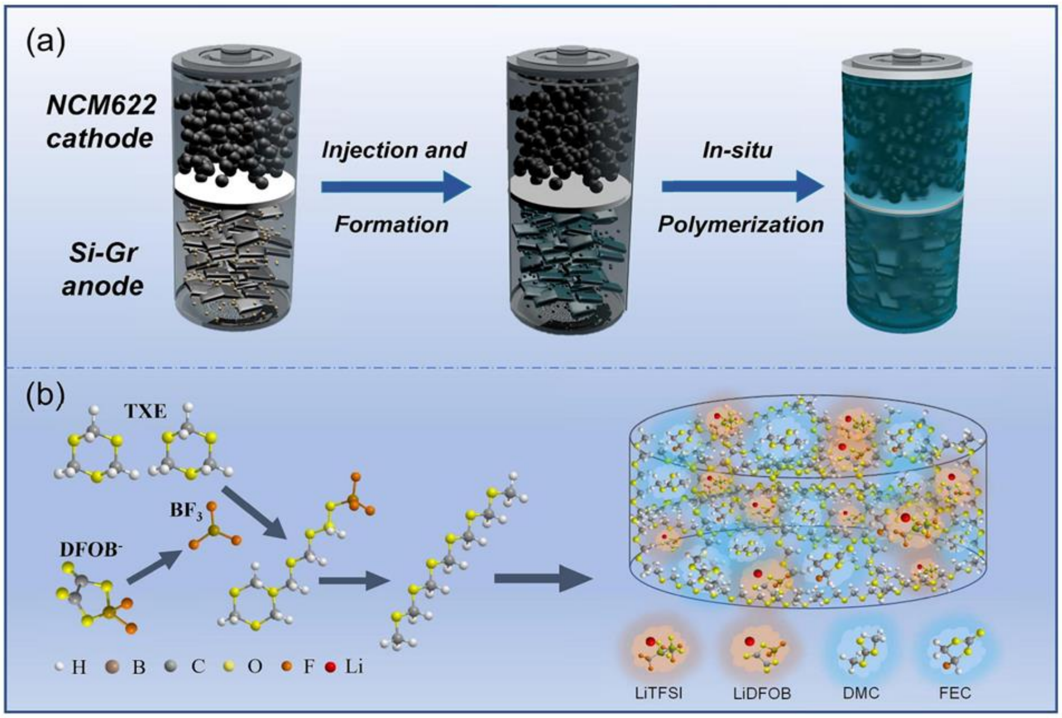

Fig. 9 Schematic illustration of preparing the full cell and mechanism of the polymerization from TXE to polymer skeleton. Reproduced with the permission from [99], Copyright 2023 Elsevier.

Solid polymer electrolytes have problems such as low ionic conductivity at room temperature and poor interfacial stability, which can be improved by adding some additives to the polymer electrolyte or adding other electrolytes to form a composite electrolyte to improve its electrochemical performance. In addition, the polymer electrolyte also has poor thermal stability, which often leads to degradation and melting deformation problems at high temperatures, reducing battery life and safety performance. Adding thermal stabilizers can effectively improve the safety at high temperatures, but may affect the electrochemical performance; how to prepare additives with both thermal stability and other properties has also become a key issue.[100]

Based on the current state of research, all three of the above solid-state electrolyte types have been shown to be compatible with silicon-based anodes. Each of them has different advantages, but all of them also have some disadvantages. It is noteworthy that the huge volume expansion problem of silicon-based materials is still one of the major factors hindering the development of silicon-based solid-state lithium-ion batteries. Therefore, solid-state electrolytes must have excellent mechanical properties to accommodate the volume change of silicon materials. Although oxide electrolytes have high ionic conductivity at room temperature, their mechanical properties and interfacial impedance with electrodes are not very favorable. In contrast, polymer and sulfide electrolytes have good mechanical properties and provide a flexible and stable electrode-electrolyte interface. However, the low ionic conductivity of polymer electrolytes at room temperature limits the high specific capacity of silicon-based anodes. Sulfide electrolytes, on the other hand, have attracted the interest of most researchers due to their extremely high ionic conductivity at room temperature. Despite their poor air stability, sulfide electrolytes will have an increasing advantage in the future path of silicon-based solid-state battery applications as more targeted modification strategies are proposed and optimized.

4. Conclusions and Outlook

With the advantages of high theoretical specific capacity, low embedded lithium delithiation potential, abundant resource reserves, and environmentally friendly, green and safe, silicon-based anode materials are considered to be the most promising lithium-ion battery anode materials that can replace the traditional graphite anode and achieve large-scale commercialization in the future. However, the main obstacle plaguing the practical application of silicon-based anode is the volume expansion of the silicon material during the embedded lithium delithiation cycling process, which will bring a series of negative effects, such as crushing of the active material and damage to the overall structure of the material, which will reduce the coulombic efficiency and cycle life of the battery. The first half of this paper summarizes the development and improvement of silicon-based anode materials in Li-ion batteries. In response to the aforementioned problems, this paper focuses on the structural modification strategies of silicon-based anode materials, including the design of nanosized structures of silicon materials (zero-dimensional, one-dimensional, two-dimensional, and three-dimensional silicon nanomaterials) as well as composite structures (silicon-carbon composites, silicon-alloyed materials, and silicon-oxide materials, *etc*.). These designs further enhance the electrochemical performance of silicon-based anodes in Li-ion batteries.

However, the nanosized design of silicon also has certain disadvantages, such as the small size of the nanostructures and the high specific surface area, which result in low first-round Coulomb efficiency, and the high cost of nanomaterial preparation, which limits its large-scale industrialization. At the same time, the silicon composite structure also places certain requirements on the particle size of silicon, and the compatibility between silicon and composite materials is also not a small challenge. Therefore, in the future, silicon nanomaterials will be more frequently combined with composite structure modification strategies to further structurally optimize the performance of silicon-based anode materials, overcome their own defects, and make them perfectly suitable for the structural system of lithium-ion batteries.

In addition, the application of silicon-based anode materials in solid-state lithium-ion batteries is reviewed in the second part of this paper. With the development of large-scale electrode materials, the research on traditional liquid lithium-ion batteries has been saturated. With the further improvement of the practical performance and safety requirements for commercial lithium batteries, lithium-ion batteries are inevitably developing in the direction of solid-state. As a high-performance electrode material for lithium-ion batteries, silicon-based anode materials will have great potential to be matched and combined with solid-state electrolytes. This paper focuses on the research progress of silicon-based anode applied to solid-state electrolytes (oxide electrolytes, sulfide electrolytes, and polymer electrolytes). Compared with liquid electrolytes, the application of silicon in solid-state electrolytes is still in the experimental stage, but it also has a large space for development.

There are significant challenges to the future development of silicon-based anodes and their application in solid-state electrolytes. One of the main problems is the poor stability of the interface formed between the silicon-based anode electrode and the solid-state electrolyte, resulting in batteries that often exhibit significant capacity degradation during cycling. Therefore, improving the structural design of the solid-state electrolyte and regulating the interfacial compatibility between the electrolyte and the electrode is a key idea for the solid-state of silicon-based anode lithium-ion batteries.

With the continuous innovation of design ideas, the research on the application of silicon-based anode in lithium-ion batteries is constantly breaking through, and its performance is constantly improving. The silicon anode material has a bright future and a better commercialization prospect. It is believed that with the continuous improvement of the silicon material preparation process and the gradual maturing of the industrial scale, the above problems will be gradually solved, and high-capacity, high-performance silicon anode lithium-ion batteries can be produced in the future.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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