

Innovative Structural Engineering of Silicon-Based Anodes for Lithium-Ion Batteries

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Abstract: The transition towards renewable energy sources has led to an increasing reliance on lithium-ion batteries (LIBs) for applications in electric vehicles and portable electronics. Among the various components of LIBs, silicon-based anode materials are gaining attention due to their high theoretical capacity and the abundant availability of silicon. Despite their potential, silicon anodes encounter significant obstacles during charge-discharge cycles, including substantial volume expansion and poor electrical conductivity. To address these challenges, a range of structural optimization strategies has been investigated. This review highlights recent developments in the structural engineering of silicon-based anodes, particularly focusing on innovations in nanostructure design and composite materials. Nanostructuring silicon helps reduce particle size and optimize microstructures, which mitigates volume expansion, improves cycling stability, and promotes enhanced lithium-ion diffusion. Composite approaches, integrating silicon with carbon and metal oxide materials, further enhance conductivity and mechanical integrity. However, despite substantial advancements, issues such as production cost, long-term durability, and scalability remain significant barriers to the widespread adoption of silicon anodes. Future research should focus on integrating material design with interface engineering and exploring novel synthesis techniques to enable the large-scale implementation of silicon-based anodes in high-energy-density storage systems.

Keywords: Lithium-ion battery(LIB), Silicon-based, Structural design, Review

1. Introduction

As the global energy landscape evolves, there is an increasing demand for advanced energy storage systems. Among various options, lithium-ion batteries (LIBs) have emerged as a leading focus due to their efficiency and widespread use across different industries. Performance metrics such as energy density and longevity are critical in assessing the effectiveness of these batteries, particularly in sectors like electric vehicles and portable electronics, where high performance and prolonged endurance are essential [1]. Traditional anode materials are increasingly inadequate in meeting the growing requirements, prompting the need for new anode materials that offer higher specific capacity, better cycling stability, and longer operational life, all of which are vital for advancing LIB technology [2].

Silicon-based materials stand out due to their theoretical specific capacity of 4200 mAh/g, a figure that significantly surpasses that of conventional graphite (372 mAh/g), making them promising candidates for use in lithium-ion batteries [3]. However, these materials face challenges such as

significant volume expansion (up to 400%) during the charge-discharge cycles, which leads to structural degradation and capacity loss [4]. Additionally, silicon's low electrical conductivity ($6.7 \times 10^{-4} \text{ cm}^{-1}$) further restricts its practical application. Over the past several decades, numerous research efforts have focused on addressing these challenges, exploring strategies such as structural optimization, surface modifications, and improvements in binder and electrolyte formulations, all of which aim to enhance the cycling stability and conductivity of silicon-based anodes [5].

While there have been considerable advancements, significant challenges remain in meeting the varied demands of real-world applications. Nevertheless, the progress made in material design and surface engineering continues to highlight the potential of silicon-based anode materials for future lithium-ion battery applications. This paper examines two primary approaches for structural optimization—nanostructural engineering and composite material development—to offer valuable insights and guide future research in this field.

2. Challenges of silicon-based anodes

Silicon-based anode materials have drawn significant attention for use in lithium-ion batteries (LIBs) due to their high theoretical specific capacity of 4200 mAh/g, a value that far exceeds that of traditional graphite anodes, which offer only 372 mAh/g. This remarkable capacity arises from silicon's ability to form bonds with up to 4.4 Li⁺ per atom. Additionally, silicon is abundant and cost-effective, providing an economic advantage for large-scale applications. However, the deployment of pure Si anodes faces several substantial challenges. A primary concern is the extensive volumetric expansion—up to 400%—that occurs during lithiation. This dramatic increase in volume generates significant internal stress, which can disrupt the structural integrity of the anode and lead to material failure. Furthermore, the continuous expansion and contraction of silicon throughout the charge and discharge cycles induces frequent formation and breakdown of the SEI layer. This ongoing cycle accelerates the degradation of active materials, resulting in diminished capacity retention. Another critical limitation is silicon's low intrinsic electrical conductivity ($6.7 \times 10^{-4} \text{ cm}^{-1}$) [6], which restricts the efficiency of ion transport and limits the overall performance of the anode. These combined factors contribute to the reduced cycling stability and hinder the long-term viability of silicon-based anodes in practical applications.

3. Nanostructure design of silicon-based materials

The design and application of nanomaterials play a crucial role in energetic storage devices such as LIBS. Nanostructure design enhances the contact area between particles by reducing their size [7]. In nanostructured silicon materials, the reduced particle size and the available space around them allow for greater expansion without breakage, which helps mitigate the volume changes issue of silicon-based materials and thus improves the long-term cycling stability of the battery. Nanomaterials are known for their exceptional specific capacity and cycling stability. Furthermore, the microstructure of these materials can be fine-tuned to further improve the energy density and lifespan of the LIBS. Nanostructures can be classified into various types: zero-dimensional particle structures, one-dimensional nanowire and nanotube structures, two-dimensional thin film and sheet structures, three-dimensional spherical and porous structures

3.1. Zero-dimensional silicon nanostructures

Zero-dimensional silicon nanoparticles, owing to their nanostructure size effect, can withstand substantial stress changes, effectively addressing the structural pulverization issue caused by volume expansion [8]. The particle size of silicon nanoparticles significantly influences battery performance. Research indicates that when the size of silicon particles is less than 150 nm, their cycling

performance improves, as smaller particles can prevent fracture during charge and discharge cycles [9]. However, when silicon particle sizes exceed 150 nm, larger particles tend to fracture during cycling, which negatively impacts cycling stability, as shown in Figure 1. This threshold of 150 nm is considered critical for silicon particles used in LIBS. Despite the promising potential of silicon nanoparticles in LIBS, challenges remain. Due to their large specific surface area, more electrolyte is consumed when forming the SEI layer. Additionally, smaller nanoparticles tend to agglomerate, which further complicates the application, and the high cost of producing silicon nanoparticles limits their large-scale implementation.

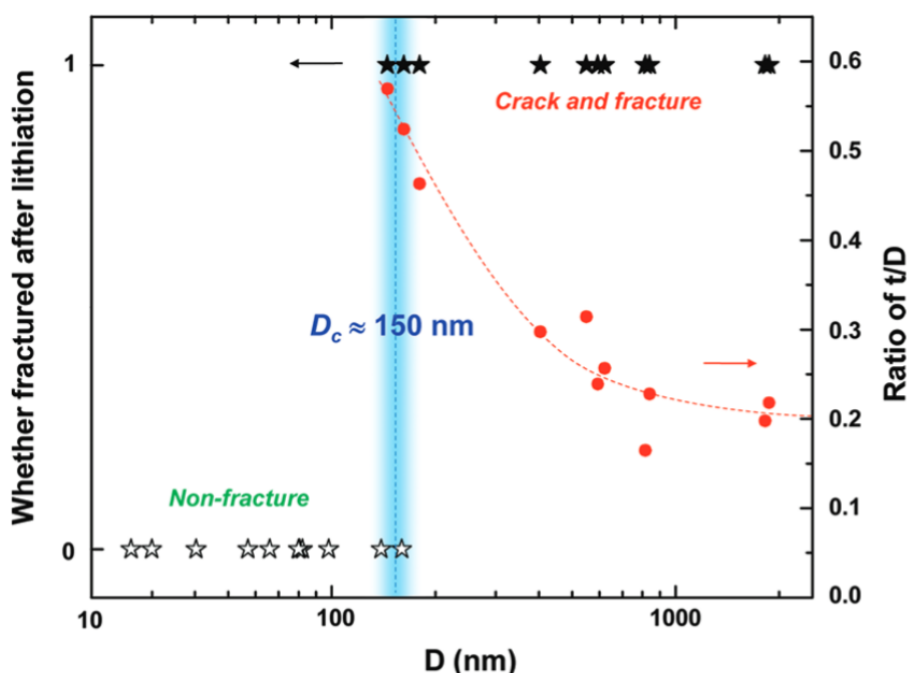


Figure 1: Particle size dependence on fracture behavior of silicon nanoparticles during lithiation

The figure presents statistical data showing that the critical size (D_c) of silicon nanoparticles is approximately 150 nm. In the non-fracture region ($D < D_c$), silicon nanoparticles undergo cracking and fracture during the first lithiation process, as indicated by hollow star marks. However, when the particle size (D) exceeds D_c , SiNPs consistently undergo cracking and fracture, as shown by solid star marks. As the particle size decreases, the ratio of t/D increases monotonically from about 0.2 to 0.6, represented by red dots. This trend suggests that smaller SiNPs delay the onset of cracking, aligning with the observed transition into the non-fracture region [9].

3.2. One-dimensional silicon nanostructures

One-dimensional silicon (Si) nanostructures, including nanotube and nanowire structures, offer distinct advantages over other nanostructures. These structures provide continuous Li^+ transport channels, which are crucial for improving battery performance. The pores and voids in Si nanotubes create enough space for volume change during the lithiation and delithiation process, reducing volume fluctuations during cycling and effectively preventing structural pulverization [10]. At the same time, the thin walls of Si nanotubes shorten the diffusion path for electrons and Li^+ , enhancing performance. Park et al. synthesized Si nanotubes using a reduction decomposition method with an alumina template, treated by an etching process, as shown in Figure 2. These nanotubes demonstrated remarkable electrochemical properties, achieving a reversible charge capacity of 3247 mAh/g and a coulombic efficiency of 89%. After 200 cycles, the original structure of the nanotubes was maintained.

However, compared to Si nanoparticles, the production of Si nanotubes is more expensive and complex, limiting their widespread application in LIB anodes. Si nanowires, on the other hand, are capable of accommodating lateral expansion during the lithiation process, reducing cracking caused by volume expansions [11]. Chen developed a silicon nanowires electrode that effectively withstand large strains with silicon anode materials. These electrodes can effectively withstand large strains, maintain good electronic contact, and significantly shorten the Li^+ insertion distance. With this design, Si nanowires not only achieve theoretical charge capacity but also maintain approximately 75% of discharge capacity during cycling, showing minimal degradation. Although Si nanowire electrodes hold promise for improving capacity and energy density, further research is required to address issues related to radial volume changes and enhance Li^+ transport along the axis, ultimately improving cycling stability and performance for practical use in LIBs.

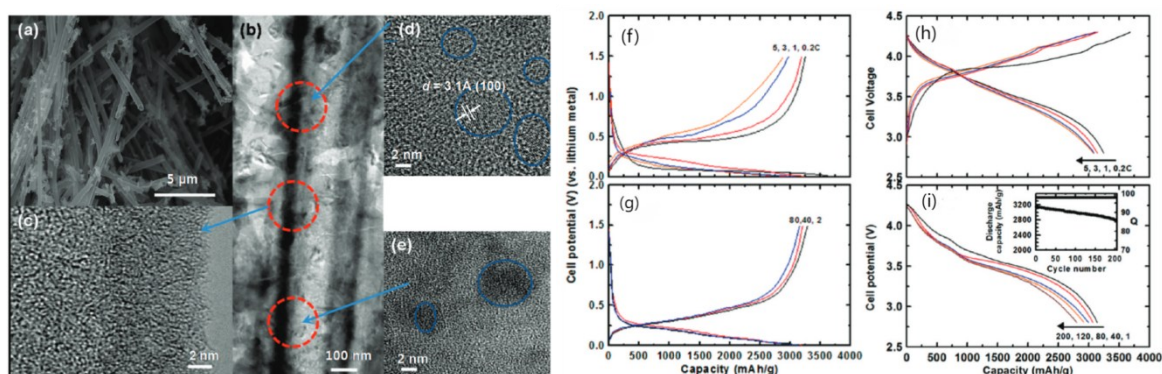


Figure 2: Characterization and performance of cycled silicon nanotubes

Figure 2 displays several images and performance metrics of cycled silicon nanotubes. Panel (a) shows the SEM image of Si nanotubes extracted from LIBs after 200 charge-discharge cycles. Panel (b) presents the corresponding TEM image. High-resolution electron microscopy (HREM) images in panels (c), (d), and (e) are from the red dashed circles in (b). The rate capability and voltage profiles of the Si nanotubes, tested in a button-type half-cell, are compared with those of lithium metal. These samples were cycled between 0 and 1.5V (a and b). The battery was tested at a fixed 1C rate for all discharge cycles, shown in panel (f), with the charge rate varying from 0.2C to 5C (15A/g). Panel (g) illustrates the voltage curves after the 2nd, 40th, and 80th cycles, with cycling between 0 and 1.5V at 1C. Panels (h) and (i) show the rate capability and cycling performance of Si nanotubes in a soft-pack lithium-ion battery (cathode: LiCoO_2), cycled between 2.75V and 4.3V over 200 cycles. The C-rate was incremented from 0.2C to 5C for both charge and discharge (1C = 3A/g), with cycling tests conducted at 1C in panel (i) [10,11].

3.3. Two-dimensional silicon nanostructures

Two-dimensional silicon (Si) nanostructures primarily include Si thin films and Si nanosheets. The large surface area relative to volume enables faster lithiation and delithiation, minimizes polarization, and enhances the kinetics of electrode reactions [12]. Ette et al. produced hydrogenated silicon nanocrystals within Si thin films using plasma-enhanced chemical vapor deposition (PECVD). At a 0.2C rate, the material exhibited an initial discharge capacity of 3090 mAh/g, which reduced to approximately 2250 mAh/g after 50 cycles. When tested at a 1C rate, the initial discharge capacity was 1832 mAh/g, with 70% capacity retention after 125 cycles. Phosphorus doping was employed to reduce lithium reactivity and phase changes, which enhanced material conductivity and minimized volume changes. The performance of Si thin films is closely related to their thickness [13]. Ohara et al. deposited Si thin films of varying thicknesses (50, 100, and 150 nm) on Ni foil and observed that

thinner films exhibited better cycling performance. The 50 nm Si thin films retained over 3500 mAh/g of charge capacity after 200 cycles at 2C, while the 150 nm films maintained around 2200 mAh/g at 1C after 200 cycles [14]. However, Si thin films still face limitations for commercial LIB applications, especially due to the instability of the SEI layer, which consumes extra lithium during cycling. Si nanosheets, with their vertical nanoscale structure, experience reduced volume changes during cycling, facilitating rapid electron and Li⁺ transfer while maintaining a stable SEI layer [15]. Ryu et al. developed high-quality Si nanosheets from natural clays through a one-step molten salt exfoliation and chemical reduction technique, as shown in Figure 3. This process yields high-purity mesoporous Si nanosheets with a significant output. The carbon-coated Si nanosheet anodes demonstrated a reversible capacity of 865 mAh/g and outstanding cycling stability. After 200 cycles at 0.2C, the capacity retention rate was 93.1%, with retention rates of 92.3% and 91.7% after 500 and 700 cycles at 0.5C and 1C, respectively. Additionally, the volume expansion was significantly suppressed, with a 42% expansion after 200 cycles at 0.2C [16].

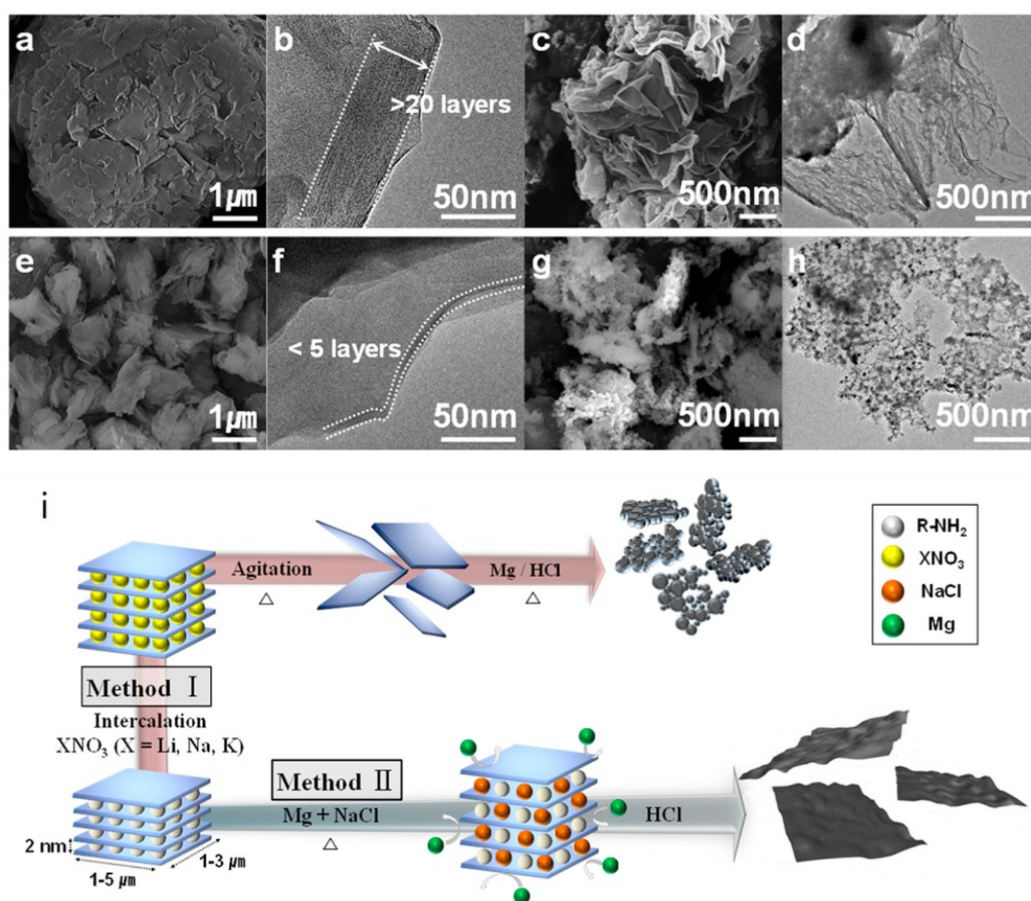


Figure 3: Preparation and characterization of silicon nanosheets

Figure 3 displays a series of images of Si nanosheets and raw clay minerals. Panels (a) and (b) show the SEM and TEM images of the raw clay minerals. Panels (c) and (d) present SEM and TEM images of ultrathin Si nanosheets synthesized via molten salt-induced exfoliation combined with chemical reduction (Method II). Panels (e) and (f) feature the SEM and TEM images of pre-exfoliated clay minerals. Panels (g) and (h) depict SEM and TEM images of Si nanosheets that collapsed during continuous chemical reduction (Method I). Panel (i) illustrates a schematic of the synthesis process for ultrathin Si nanosheets, comparing the two different methods used for production [16].

3.4. Three-dimensional silicon nanostructures

Three-dimensional silicon (Si) nanospheres possess uniform sizes and spherical shapes, which are essential for ensuring consistent electrochemical performance across the anode material, resulting in improved battery stability. The spherical structure offers several advantages, including higher structural stability, larger surface area, lower density, and shorter charge transfer distances [17]. Tang et al. used 50 nm polystyrene microspheres as templates to fabricate hollow Si nanospheres with identical inner diameters, as shown in Figure 4. At various current densities (0.05, 0.1, 0.2, 0.5, and 1.0 A/g), the average discharge capacities of the hollow Si material were from 938 to 407 mAh/g, respectively [18]. Yao et al. employed solid silica nanospheres as templates to synthesize interconnected Si hollow nanosphere electrodes. The initial discharge capacity was 2725 mAh/g, with a capacity loss rate of less than 8% per 100 cycles. After 700 cycles, the Si hollow nanosphere electrode maintained a capacity of 1420 mAh/g [19].

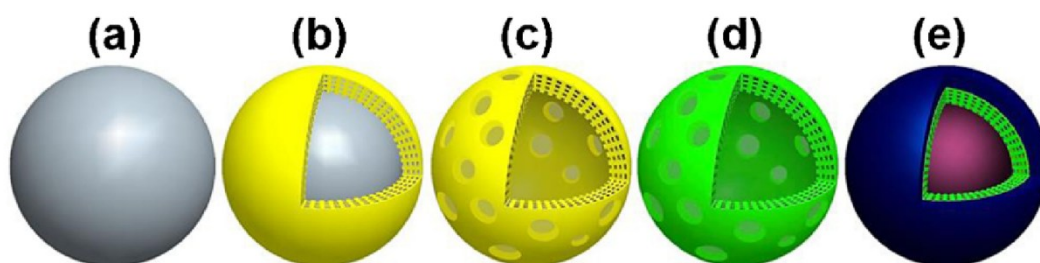


Figure 4: Schematic outlining the synthesis stages: (a) PS nanoparticles, (b) PS@SiO₂, (c) HSiO₂, (d) HS, and (e) HSi@C [19]

3.5. Silicon nanoporous structures

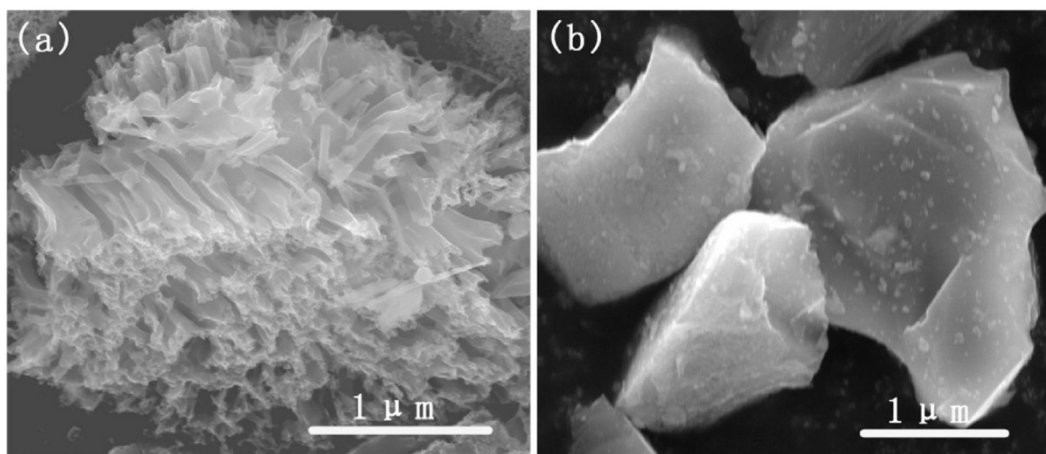


Figure 5: (a) SEM image of 1 μm etched nanoporous Si particles and (b) SEM image of 1 μm original Si particles [20]

The preparation of nanoporous structures is an effective way to enhancing the cycling stability of silicon (Si) electrodes. The porous structure provides additional space for Si in the lithiation and delithiation processes. It also increases the contact area between the electrode material and the electrolyte, shortens the diffusion paths for electrons and Li⁺, and enhances the rate performance. Zhang et al. prepared nanoporous Si by etching polycrystalline Si nanoparticles, as shown in Figure 5. The formation of a nanoporous framework within micron-sized particles significantly reduced Si particle agglomeration at the nanoscale, contributing to improved cycling performance. After 220

cycles, the electrochemical performance showed considerable improvement, with a Coulombic efficiency greater than 99.5%. An initial discharge capacity of 3652 mAh/g and a charge capacity of 3067 mAh/g were achieved at a current density of 0.3 A/g under constant current conditions. The initial Coulombic efficiency was 84%, rising to 97.2% after the second cycle. Even after 100 cycles, the charge capacity remained at 2043 mAh/g, with the Coulombic efficiency surpassing 99% [20].

4. Composite material structure design of silicon-based materials

In addition to the micro-nano structure design of Si, researchers often use composite material design to optimize the performance of Si. By rationally designing the structure, composites combine different forms of silicon with other materials, integrating the advantages of different materials and structures to overcome the limitations of single Si electrodes. The most common composite material structures currently include core-shell structures and interlayer structures.

4.1. Core-shell silicon structures

Core-shell structures typically use silicon as the core material, with a shell layer formed on its surface. During charge and discharge cycles, the shell layer effectively limits the changes of silicon, thereby reducing the pulverization of silicon particles. The shell layer not only blocks the direct contact between the silicon particles and the electrolyte but also reduces interface reactions, enhancing the stability of cycling and capacity retention of LIBS. Common shell materials include carbon materials, metal oxides, and conductive polymers [21].

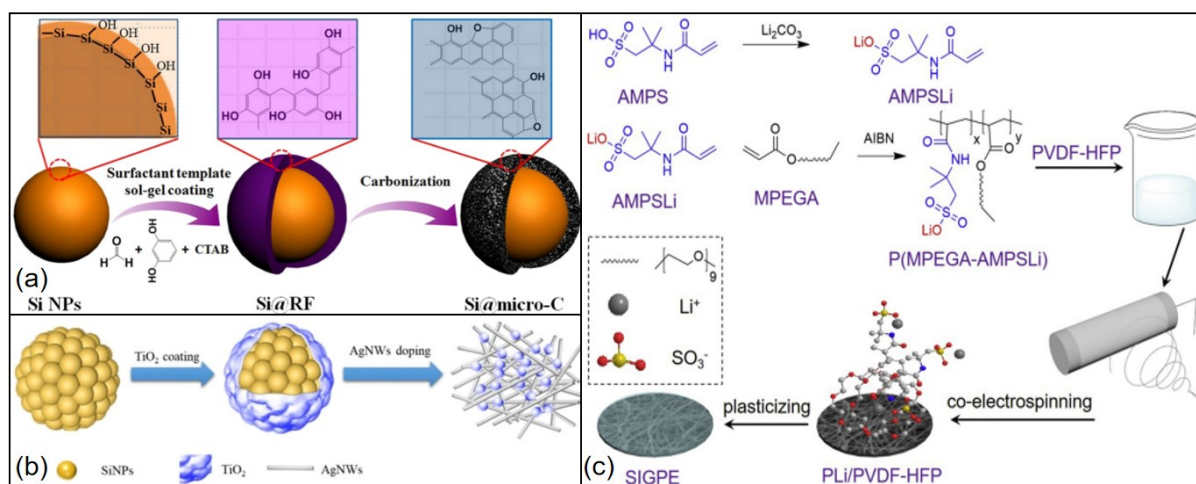


Figure 6: Synthesis routes: (a) schematic of the interfacial layer coating on silicon nanoparticle via the surfactant-template sol-gel method (b) synthesis route of SiNPs@TiO₂/AgNWs (c) synthesis route of PLi/PVDF-HFP membrane and SIGPE [24]

Luo et al. employed a microporous carbon coating approach on silicon nanoparticle, creating uniform coaxial core-shell structure, as depicted in Figure 6(a). This sol-gel synthesis technique is straightforward, scalable, and enables the direct growth of phenolic resin on the surface with controlled uniform thickness. The carbon layer forms a microporous structure and a phenolic resin framework, facilitating rapid Li⁺ transport and the formation of a stable SEI layer. By precisely controlling the phenolic resin-based carbon thickness to 10 nm, excellent protection and high electrochemical performance were achieved for silicon nanoparticles. After 500 cycles at 500 mA/g, the material achieved a high capacity of 1006 mAh/g, with a Coulombic efficiency exceeding 99.5% [22]. Li et al. used SiNPs as the core and TiO₂ as the shell to form a core-shell structure that

accommodates the volume changes of silicon-based materials, improving the interface stability of the electrode. Additionally, AgNW doping created a conductive network, enhancing the material's conductivity, as shown in Figure 6(b). In comparison to pure SiNPs electrode, the SiNPs@TiO₂/AgNWs electrode demonstrated superior electrochemical performance, achieving an initial discharge capacity of 3524 mAh/g at a current density of 400 mA/g [23]. Shen developed a novel bifunctional core-shell composite material with a thermally stable polyimide core and a composite single-ion conducting polymer, as shown in Figure 6(c). The composite membrane exhibited remarkable thermal dimensional stability at temperatures as high as 190°C. When the half-cell was stored at 150°C after charging, the core-shell structure SIGPE battery maintained excellent potential stability, while conventional batteries rapidly short-circuited, significantly enhancing the safety of LIBS. The ion conductivity of the plasticized gel electrolyte reached $1.7 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$, with a Li⁺ transference number of 0.77. The assembled LiFePO₄ battery exhibited excellent cycling stability, retaining 85% of its initial capacity after 100 cycles, demonstrating its long-term reliability and durability [24].

4.2. Yolk-shell silicon structures

In traditional core-shell structure, the shell typically wraps around the surface of silicon particles. During the lithiation and delithiation cycles, silicon undergoes volume changes, subjecting the shell to significant mechanical stress. Prolonged volume deformation can cause the shell to rupture, negatively affecting the battery's capacity and performance. While core-shell structures can partially limit silicon expansion, the stability of the shell remains a challenge over long cycling periods. To address this, researchers have proposed a unique core-shell structure called the yolk-shell structure. The key feature of the yolk-shell structure, compared to traditional core-shell designs, is the gap between the Si particles and the wrapped shell, which provides a free space for the volume changes of Si particles in cycles. This design allows silicon to freely expand and contract during the cycling processes, preventing shell rupture due to excessive expansion. The shell stability is maintained, while also facilitating the formation of a stable SEI layer. Liu et al. improved a method in room temperature solution, where silicon nanoparticles were coated with a silica wrapped shell, followed by a polydopamine shell for carbonization, resulting in a N-doped carbon coating. The SiO₂ sacrificial shell was selectively removed with hydrofluoric acid treatment, yielding a "yolk-shell" structured Si@void@C material, as shown in Figure 7(a). The engineered void space enables silicon to expand freely during cycling without causing any damage to the outer carbon shell, thereby preserving its structural integrity and maintaining an impressive specific capacity of 2800 mAh/g. After 1000 cycles at a rate of 0.1C, 74% of the capacity was retained, with a Coulombic efficiency of 99.84%.[25] Wu et al. compared the advantages and disadvantages of traditional core-shell structures and yolk-shell structures, as shown in Figure 7(b). The yolk-shell structure offers several advantages: (1) It creates a void to accommodate silicon's volume changes, maintaining structural stability; (2) It prevents direct contact between silicon and the electrolyte, which helps to stabilize the SEI layer and minimize active material loss. However, during the early stages of lithiation, the contact area between the silicon core and shell is restricted to a single point, limiting the efficiency of electron and ion transport. While core-shell structures do not offer the same stability as yolk-shell structures, the core and shell remain in close contact throughout the cycle, ensuring efficient lithium-ion transport. Selecting the appropriate shell material can effectively withstand silicon's expansion without rupture, allowing core-shell structures to still exhibit superior performance [26].

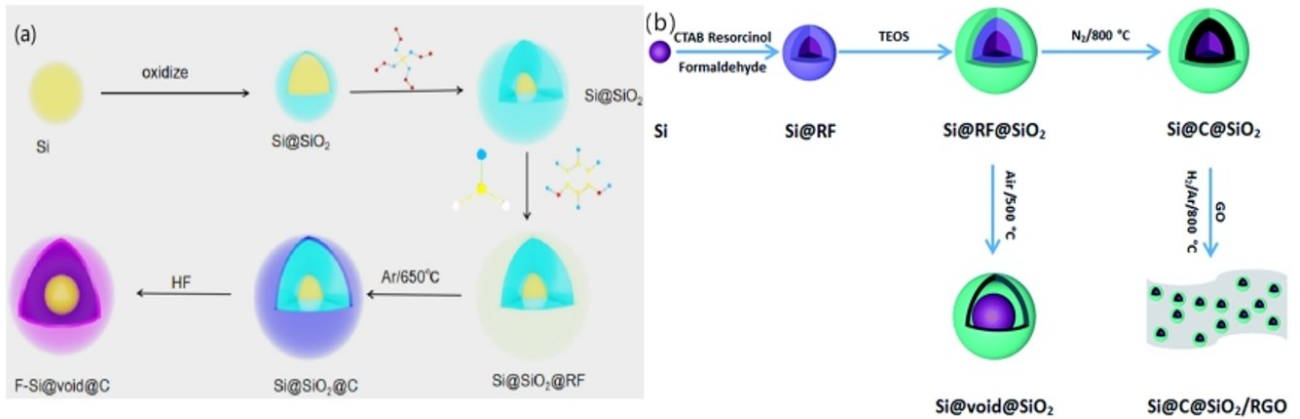


Figure 7: Schematic of the process: (a) yolk-shell structure F-Si@Void@C [25] (b) schematic of the fabrication process of the yolk-shell structures Si@void@SiO, Si@C@SiO₂, and Si@C@SiO₂/RGO [26]

4.3. Interlayer silicon structures

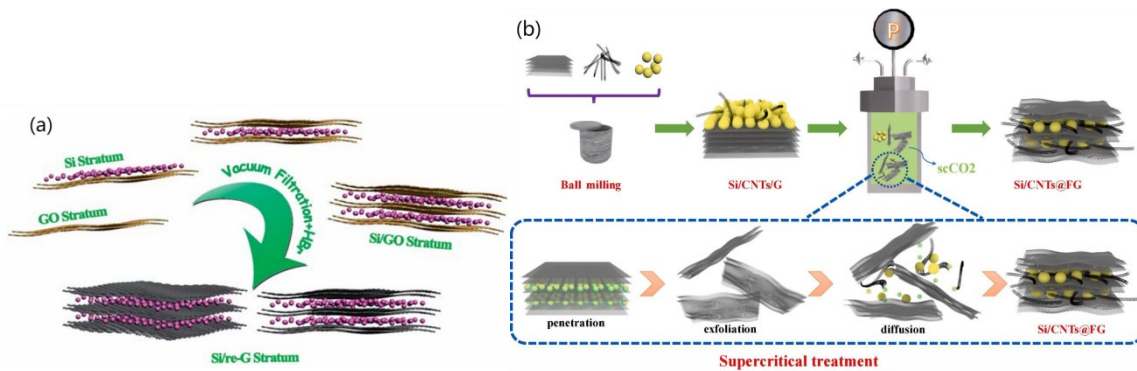


Figure 8: (a) Alternating interlayer structure of Si nanoparticles and graphene [27] (b) schematic of the synthesis process of Si/CNTs@FG composites [27]

Interlayer structures sandwich active materials between different layers, forming a multilayer system. Compared to traditional blended composite materials, interlayers provide enhanced stress and strain toughness, as well as improved electrical contact in the lithiation/delithiation cycles. These interlayer materials not only offer mechanical support to prevent the pulverization or detachment of active materials during charge and discharge but also enhance electrode conductivity, facilitating rapid ion conduction. Sun et al. successfully developed a silicon-reduced graphene alternating layer structure by liquid-phase exfoliation of graphene and uniform dispersion of a silicon solution, as shown in Figure 8(a). This structure demonstrated a large reversible capacity and improved cycling performance. By combining silicon nanoparticles with reduced graphene oxide layers via a vacuum filtration technique, the structure effectively alleviated silicon's volume changes and improved both conductivity and mechanical stability. After 100 cycles, the half-cell of this novel structure maintained a capacity of 1500 mAh/g, exhibiting significant stability in cycling at a current density of 1.35 A/g [28]. Wang et al. used supercritical CO₂ technology to exfoliate graphite into folded graphite (FG) sheets, preparing Si/CNTs@FG composites, where SiNPs and CNTs were evenly dispersed in the material, as shown in Figure 8(b). This layered structure effectively mitigated silicon's expansion stress during charge and discharge. The Si/CNTs@FG composite exhibited remarkable electrochemical performance, achieving an impressive specific capacity of 1203 mAh/g at a current density of 0.2 A/g. Additionally, it demonstrated outstanding capacity retention,

maintaining 970 mAh/g after 100 cycles, which highlights its excellent stability over extended cycling. Moreover, the material showcased impressive rate capability, delivering 635.2 mAh/g even at a high current density of 2 A/g. These results not only underline the high performance of Si/CNTs@FG as an anode material but also present a scalable and effective strategy for developing advanced silicon-based anodes with superior electrochemical properties [28].

5. Conclusion and outlook

Silicon-based materials, recognized for their high capacity and low cost, are considered some of the most promising options for anode materials in lithium-ion battery (LIB). This paper reviews the advancements in the structural design of silicon-based anodes and the challenges encountered. With a theoretical specific capacity of 4200 mAh/g, these materials are highly valued, especially for use in electric vehicles and portable electronics. However, pure silicon materials suffer from issues such as significant volume expansion and low conductivity, which limit their long-term stability and cycling efficiency. To address these challenges, researchers have proposed various solutions, including nanostructure design and composite material design. These approaches, which involve reducing the size of silicon particles and optimizing material structures, have shown promising results. Recent advancements in nanostructural design, such as nanoparticles, nanotubes, and nanowires, have significantly improved the volume expansion problem and enhanced electrochemical performance. Furthermore, innovations in composite material structures, such as core-shell and interlayer designs, have greatly improved the stability and conductivity of silicon-based anodes.

Looking ahead, silicon-based anode materials hold broad application potential in lithium-ion batteries, especially in high-performance fields like electric vehicles and wearable devices. Despite the progress made, however, practical applications still face significant challenges. The production cost of nanomaterials remains high, and large-scale manufacturing processes need significant improvements to reduce costs and increase production capacity. Additionally, more advanced structural designs and synthesis methods need to be discovered [29]. To further promote the application of silicon-based anode materials, future research must make breakthroughs in material design, interface engineering, and manufacturing processes. The diversified development of silicon-based materials, particularly when combined with other novel materials, will provide new momentum for high-performance energy storage systems. Interdisciplinary research is crucial to solve the complex problems silicon-based anode materials face. While no single solution can address all these challenges [30], persistent collaboration and in-depth research are expected to make silicon-based anode materials a key component of next-generation energy storage systems.

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