

Structural Regulation and Electrochemical Performance of High-Capacity Silicon-Carbon Composite Anode Materials

Yucheng Jiang^{1*}, and Zhixuan Zhu²

¹School of Chemistry and Environmental Engineering, Liaoning University of Technology, Jinzhou, 121000, China

²School of Energy and Chemical Engineering, Xiamen University Malaysia, Sepang, 43900, Malaysia

Abstract. With the rapid development of new energy vehicles and energy storage industries, enhancing the energy density and cycle life of lithium-ion batteries has become a critical technological bottleneck. Silicon-carbon composite anode materials, leveraging silicon's high theoretical specific capacity and carbon's excellent conductivity, demonstrate significant potential in overcoming the performance limitations of traditional graphite anodes. This paper systematically elucidates the lithium storage mechanism of silicon-based materials and their inherent defects. It analyzes the role of carbon materials in composite systems, including structural support, enhanced conductivity, and interfacial stabilization. Performance optimization strategies are summarized from perspectives including interfacial engineering, structural regulation, surface modification, and heteroatom doping. Research results indicate that the first-cycle coulombic efficiency of the comprehensively optimized Si/C composite anode exceeds 90%, with a capacity retention rate surpassing 80% after 100 cycles, maintaining excellent stability under high-rate conditions. However, its industrialization still faces challenges such as precise structural control, development of low-cost carbon sources, high areal loading stability, and insufficient understanding of interfacial mechanisms. This paper proposes a synergistic approach integrating “material design—process development—mechanism exploration” to achieve a controllable, green, and low-energy-consumption fabrication pathway. This provides a theoretical foundation and technical reference for developing high-energy-density, long-life lithium-ion batteries.

1 Introduction

As new energy vehicles rapidly evolve toward longer ranges and faster charging capabilities, the performance of power batteries has become the core bottleneck constraining industrial upgrading. Lithium-ion batteries have established themselves as the mainstream energy storage technology in the current power battery sector due to their high energy density, long cycle stability, and excellent energy conversion efficiency. However, faced with the urgent

* Corresponding author: 231810072@stu.lnut.edu.cn

demand for electric vehicles to achieve a range exceeding 1,000 kilometers and fast-charging rates capable of reaching 80% capacity within 15 minutes, existing lithium-ion batteries have approached their technological limits in balancing energy density improvements with safety performance. Among these, the anode material serves as the core carrier for charge storage and transfer in batteries. Its performance directly determines the battery's energy density, cycle life, and rate capability. Therefore, developing high-capacity, highly stable anode materials has become a key direction for overcoming the performance bottlenecks of lithium-ion batteries.

Graphite-based anodes have long dominated the commercial anode market due to their excellent cycling stability, low volumetric expansion rate, and mature industrial manufacturing processes. However, their theoretical specific capacity of only 372 mAh/g is insufficient to meet the demands of developing high-energy-density batteries exceeding 400 Wh/kg [1]. In contrast, silicon-based materials exhibit a theoretical specific capacity as high as 3579 mAh/g, a value derived from the $\text{Li}_{4.4}\text{Si}$ alloying reaction. Simultaneously, silicon-based materials have advantages such as abundant resource reserves, low cost, and excellent environmental compatibility. They are widely recognized as the core candidate system for next-generation high-capacity anode materials [1]. However, silicon-based materials exhibit a volumetric expansion rate as high as 300% during lithium insertion and extraction, readily causing electrode structural pulverization and active material shedding. This simultaneously leads to repeated rupture and regeneration of the SEI film at the solid-liquid interface, resulting in continuous electrolyte consumption. Ultimately, this manifests as rapid degradation with first-cycle coulombic efficiency often below 80% and deteriorated cycling stability [2]; furthermore, silicon itself exhibits extremely low electrical conductivity. These inherent limitations severely hinder the commercialization of silicon-based materials.

To address the above issues, silicon-carbon (Si/C) composite modification strategies have become a mainstream research direction within the field and have been extensively validated. Carbon materials possess excellent electronic conductivity, structural stability, and chemical inertness. On one hand, they serve as rigid support frameworks that provide efficient volumetric expansion buffer space for silicon-based active materials, alleviating structural stress in electrodes. On the other hand, they can block direct contact between silicon and electrolyte through surface coating or interfacial bonding structures, suppressing side reactions and promoting the formation of stable SEI films [2]. Previous studies have demonstrated that distinct carbon structures can enhance the cycling stability of silicon-based anodes by regulating electron transport pathways, ion diffusion channels, and interfacial stability within composite systems. This approach elevates the capacity retention rate after 100 cycles to over 80% while simultaneously optimizing the initial coulombic efficiency to exceed 90%. However, the current Si/C composite system still faces three core challenges. First, insufficient precision in composite structure design hinders the uniform dispersion of silicon particles and the synergistic interaction between carbon phases. Second, limitations in selecting high-performance carbon sources result in a lack of carbon precursors that combine low cost with high structural compatibility. Third, under high areal loading conditions exceeding 3 mAh/cm^2 , controlling cycle stability proves difficult, failing to meet the industrialization demands of practical batteries.

This study aims to conduct systematic research on the precise control of composite structures and the synergistic optimization of electrochemical performance in Si/C composite anode materials. It seeks to provide new theoretical foundations and technical references for overcoming practical application bottlenecks in silicon-based anode materials.

2 Fundamental theory and research status of silicon-carbon composite anode materials

2.1 Electrochemical properties of silicon-based materials

The core mechanism for lithium storage in silicon involves reversible alloying reactions, forming multiple alloy phases such as Li_2Si , $\text{Li}_{15}\text{Si}_4$, Li_7Si_3 , and $\text{Li}_{4.4}\text{Si}$. Using a lithium ion/metallic lithium electrode (Li^+/Li) as the reference electrode, the entire reaction process can be divided into three stages. The initial lithium insertion stage corresponds to a voltage range of 0.5–0.2 V. During this stage, lithium ions insert into the silicon lattice, forming an amorphous lithium-silicon alloy ($\alpha\text{-Li}_x\text{Si}$). The volume expansion is relatively gradual, not exceeding 50%. Upon entering the deep lithiation stage, the voltage drops below 0.2 V. The amorphous alloy gradually transforms into crystalline $\text{Li}_{4.4}\text{Si}$, causing a sharp volume expansion reaching 3 to 4 times its initial state. During lithium extraction, the voltage recovers to 0.2–1.0 V, causing crystalline $\text{Li}_{4.4}\text{Si}$ to reversibly decompose into silicon and lithium, accompanied by volume contraction. However, this process is prone to structural cracking due to residual stress.

Research indicates that the phase transition behavior of lithium-containing products is closely related to temperature. At higher temperatures, crystalline phases with high lithium content, such as $\text{Li}_{4.4}\text{Si}$, are more readily formed. At low temperatures, the amorphous phase predominates. Furthermore, when the discharge voltage falls below 50 mV, the amorphous lithium-containing products undergo in-situ crystallization to transform into stable crystalline phases, a process that further intensifies the concentration of volumetric stress [3].

2.2 Inherent defects of silicon-based materials

2.2.1 Poor electronic conductivity and increased polarization

The intrinsic electronic conductivity of silicon is extremely low, ranging from 10^{-6} – 10^{-4} S/cm at room temperature. This characteristic directly results in high electrode interface resistance and low electron conduction rates. During charging and discharging, this defect manifests as: increased interface polarization voltage, especially at high rates where polarization can exceed 200 mV; the formation of a “surface-core” reaction gradient within silicon particles, where the surface undergoes excessive lithiation while the core remains unreacted, generating significant internal stress; Electron stacking induces excessive electrolyte decomposition, forming thick and unstable SEI films. These films contain substantial organic components, further increasing electrical impedance.

2.2.2 Structural failure caused by volume expansion

The volumetric expansion of silicon exhibits anisotropic characteristics, with expansion rates differing by up to 20%–30% across different crystal orientations. This leads to structural deformation occurring preferentially along stress concentration directions. Using in-situ transmission electron microscopy (TEM) and X-ray computed tomography (CT) techniques, scientists have made observations. During lithiation, silicon nanocolumns exhibit dome-shaped expansion, with the expansion rate at their apex exceeding that of the lateral wall regions. Conversely, during delithiation, volume contraction leads to powdering at the edges of the nanocolumns, ultimately forming fractured bowl-shaped structures [3]. After multiple cycles, pulverized silicon particles detach from the conductive network to become isolated particles. These particles cannot participate in subsequent electrochemical reactions and may

clog electrolyte channels, ultimately causing rapid battery capacity degradation. Typically, the capacity retention rate after 100 cycles falls below 40%.

2.2.3 High-magnification kinetic limitations

Under high-rate charging and discharging conditions, the kinetic limitations of silicon-based materials become more pronounced. During charging, interfacial resistance causes the voltage to rapidly reach the cutoff value, yet lithium ions have not fully intercalated within the silicon particles, preventing the capacity from being fully released. During discharge, the lag in electron transport traps a significant amount of lithium within the silicon lattice, resulting in a “cliff-like capacity decay.” For instance, at a 2C discharge rate, the capacity retention rate often falls below 30%.

2.3 The mechanism of carbon materials in silicon-carbon composite systems

2.3.1 Nano-carbon composite materials

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are widely used in constructing electronic transport networks due to their high aspect ratio and excellent conductivity. Research indicates that CNTs not only effectively suppress silicon particle agglomeration but also enhance electrode structural stability [4]. For example, carbon nanotube paper (CNTs paper) prepared via vacuum filtration can form SiOC/CNTs composite paper electrodes after surface impregnation and pyrolysis of a polysiloxane precursor. The reversible capacity of this composite electrode reaches 1168 mAh/g, and it exhibits excellent ion diffusion capability due to the open pores provided by its porous network structure [4]. This structure significantly reduces electrode weight by eliminating the need for binders and current collectors.

Another study employed an electrodeposition method to deposit SiOC onto a copper substrate, introducing a CNTs anchoring layer between the SiOC and the substrate [4]. This method significantly enhances the bonding strength between SiOC and the copper substrate, preventing electrode material detachment. After 100 cycles at 0.1C, the capacity remained at 1078 mAh/g, and at 1C, the capacity retention rate approached 70%, demonstrating excellent cycle stability and rate capability [4].

2.3.2 Graphene composite materials

Graphene, with its high specific surface area, excellent electrical conductivity, and flexibility, is considered a key building block for silicon-carbon composite systems. To overcome graphene's tendency to agglomerate, researchers fabricated a three-dimensional graphene nanosheet (3D-GNS) framework and combined it with SiOC [4]. Electrochemical test results indicate that the composite material retains a reversible capacity of 701 mAh/g after 100 cycles, achieving a capacity retention rate of 84.8% [4]. Its three-dimensional conductive network effectively shortens the lithium-ion diffusion path and enhances the utilization rate of active sites.

Additionally, a SiOC fiber/rGO composite material (3D-GNS/SiOCf) can be obtained by combining electrospinning with graphene oxide coating [4]. This material not only possesses a hierarchical porous structure conducive to lithium-ion insertion and extraction but also exhibits enhanced mechanical stability due to the flexible coating of rGO. After 500 cycles at 0.5 A/g, the capacity remains at 686 mAh/g, and even at a high rate of 2.0 A/g, it retains a capacity of 330 mAh/g [4].

2.4 Research progress on silicon-carbon composite anodes

The current methods for preparing silicon-carbon composites primarily include ball milling, high-temperature decomposition, magnesium thermoreduction, and chemical vapor deposition (CVD). Among these, the ball-milling method offers a simple process but exhibits limited electrochemical performance; particles synthesized via high-temperature decomposition exhibit a narrower size distribution and more stable properties; materials produced by thermite reduction achieve capacities exceeding 2000 mAh/g and demonstrate outstanding performance at high rates, though they demand stringent experimental conditions; CVD can mitigate silicon's volume effect to some extent, but its production capacity remains limited [5]. In summary, different preparation methods each have their advantages and limitations, and the appropriate process and raw materials should be selected based on application requirements.

3 Research and optimization of electrochemical performance

3.1 Interface engineering

The core objective of interface engineering is to construct low-impedance, highly stable solid-liquid interfaces, primarily achieved through two approaches.

One approach involves regulating electrolyte composition. By optimizing the ratio of electrolyte solvents and additives, the formation of a stable SEI film dominated by inorganic components can be guided. Fluorinated additives such as fluorinated ethylene carbonate (FEC) and lithium bis(fluorosulfonyl)imide (LiFSI) preferentially decompose during charging to generate LiF, a key inorganic component of the SEI. LiF possesses high mechanical strength and chemical stability, effectively suppressing repeated SEI breakdown. Studies indicate that electrolytes containing 10–15% FEC can elevate the first-cycle coulombic efficiency of Si/C anodes to over 90% and improve 100-cycle capacity retention by 20–30 percentage points [6]. Furthermore, employing a high-concentration electrolyte composed of 3–5 mol/L LiFSI and dimethyl carbonate (DMC) reduces solvent molecule participation in SEI formation and lowers the organic component ratio. This enhances the ionic conductivity of the SEI film from 10^{-6} S/cm to 10^{-5} S/cm [6].

Second is the construction of artificial SEI films. By pre-forming artificial SEI films on Si/C surfaces through physical or chemical methods, direct reactions between the electrolyte and silicon can be avoided at the source. Al_2O_3 or Li_3PO_4 coatings prepared using atomic layer deposition (ALD) technology typically have a thickness of 5–10 nm. These coatings feature a dense structure that effectively blocks electrolyte penetration while maintaining sufficient flexibility to buffer volume expansion of the electrode during cycling, thereby significantly enhancing interface stability [7].

3.2 Structural regulation

By designing multi-level structures and composite morphologies, it is possible to simultaneously achieve the dual objectives of controlled-release volume effects and optimized electron and ion transport [8].

One key aspect is the nanoscale regulation of silicon particles. Controlling silicon particles to a nanoscale of 50–100 nm significantly reduces local volumetric stress and ion diffusion distances. The volumetric expansion rate of nanoscale silicon decreases from approximately 300% to below 200%, with interparticle voids effectively buffering expansion-induced stresses. Furthermore, grafting carbon chains onto the silicon surface can

further suppress agglomeration of nanoscale silicon particles, thereby enhancing their dispersion and structural stability [8].

Second is the design of a multi-level pore structure. By constructing a multi-level pore structure composed of micropores, mesopores, and macropores with a pore size distribution ranging from 2 to 200 nm, synergistic effects among multiple structural functions can be achieved. Macropores (50–200 nm) provide buffer space for silicon volume expansion during charge/discharge cycles, preventing electrode structural compression. Mesopores (2–50 nm) facilitate electrolyte permeation and efficient lithium-ion transport. Micropores (<2 nm) increase the specific surface area of carbon phase materials and enhance bonding strength between carbon and silicon particles, collectively improving the composite material's structural integrity and electrochemical performance [9].

3.3 Surface modification and doping regulation

Surface carbon coating modification is one of the key methods to enhance the stability of Si/C composite anodes. By coating the Si/C material surface with different types of carbon layers through processes such as pyrolysis or chemical vapor deposition (CVD), the interfacial contact characteristics and electrical conductivity can be effectively improved. For instance, using graphene or amorphous carbon as the coating layer enables the formation of a continuous conductive network during charge-discharge cycles. This reduces direct contact between active silicon particles and the electrolyte, thereby mitigating stress concentration caused by volume expansion. Research indicates that carbon coatings not only enhance electron transport rates but also maintain electrode structural integrity during cycling, significantly improving capacity retention and cycling stability [9].

Heterogeneous atom doping involves introducing heteroatoms such as nitrogen (N), phosphorus (P), and sulfur (S) into the carbon phase to regulate its electronic structure and interfacial chemical properties. Nitrogen doping creates active sites like pyridine N and pyrrole N within the carbon framework, boosting electronic conductivity by approximately 3–5 times compared to undoped carbon while enhancing lithium ion adsorption. Phosphorus doping forms P–C bonds, expanding the interlayer spacing of carbon layers to facilitate lithium ion insertion and diffusion, thereby improving overall ionic transport efficiency. Sulfur doping introduces additional polar sites, further enhancing the chemical bonding strength between carbon materials and silicon interfaces, providing structural support for achieving efficient and stable lithium ion transport [10].

3.4 High-magnification performance optimization

The key to enhancing high-rate performance lies in optimizing electron and ion transport efficiency. Beyond the aforementioned structural and interfacial control strategies, comprehensive improvements can be achieved through methods such as constructing continuous conductive networks, modifying current collectors, and optimizing electrode thickness. Introducing carbon nanotubes (CNTs) and graphene into Si/C composite systems forms a three-dimensional continuous conductive network composed of silicon particles, CNTs, and graphene. This transforms the electron transport pathway from the traditional “point-to-point contact” to a “surface-to-surface penetration” structure, thereby increasing electron conduction rates by 1–2 orders of magnitude [11]. Furthermore, employing porous copper foil with a porosity of 40–60% as the current collector significantly enhances the bonding strength between the electrode and collector. This approach also provides additional pathways for electrolyte permeation, reducing interfacial impedance and improving overall reaction kinetics [12]. Regarding electrode design, optimizing electrode thickness from conventional 150–200 μm to 50–100 μm not only shortens lithium-ion diffusion paths but

also increases capacity retention by 15–25 percentage points under high-rate (2C) conditions, achieving synergistic acceleration of electron and ion transport [12].

4 Challenge

Despite demonstrating outstanding electrochemical performance in theoretical research and experimental exploration, silicon-carbon composite anode materials still face multiple challenges in practical application and large-scale production. First, insufficient precision in structural design remains a core bottleneck. The uniformity of silicon and carbon distribution at the microscopic scale directly impacts volume expansion buffering effects and electron/ion transport efficiency. Current fabrication techniques struggle to achieve atomic- or nanoscale-level precise control over composite structures, leading to structural instability and performance degradation during long-cycle operation. Second, the development of efficient, low-cost carbon sources and the economic viability of preparation processes remain urgent issues. Although high-performance carbon materials like graphene and carbon nanotubes can significantly enhance electrochemical performance, their complex and costly preparation processes hinder industrial-scale application. Therefore, identifying low-cost, environmentally friendly carbon precursors that ensure structural compatibility and performance stability has become a key research focus. Additionally, cycling stability under high areal loading conditions remains in the exploratory phase. While silicon-carbon composite anodes typically exhibit good performance at low areal loadings under laboratory conditions, approaching industrial-scale high-capacity requirements often leads to stress concentration and intensified interfacial side reactions, resulting in rapid capacity decay. Simultaneously, the complexity of interfacial chemistry and insufficient understanding of its mechanisms hinder the refinement of performance optimization strategies. The composition, evolution, and stability of the SEI film exhibit significant variations across different electrolyte systems and composite structures, with no unified theoretical model currently available for systematic explanation. Future research urgently requires leveraging in-situ characterization and multiscale simulation techniques to deeply elucidate the mechanisms of interfacial evolution, thereby providing theoretical foundations for precise engineering of the interface.

5 Conclusion

The future development of silicon-carbon composite anode materials should be advanced through multidimensional synergistic efforts to achieve a balance between performance, cost, and sustainability. At the material design level, multi-level structures and multi-phase synergistic systems should be further developed to achieve dual objectives: controlled release of volume effects and optimized electron and ion transport. Regarding process innovation, the implementation of green, low-energy-consumption, and scalable preparation technologies should be promoted to enhance industrial conversion feasibility. At the application level, synergistic design pathways between electrodes and electrolytes should be explored through holistic optimization of the entire battery system to meet the distinct demands of high-energy-density power batteries and long-life energy storage batteries. By integrating efforts in material innovation, process optimization, and system integration, silicon-carbon composite anodes hold promise to transcend laboratory limitations, achieving a genuine leap from theoretical research to commercial application. This advancement will provide robust support for the development of next-generation high-performance lithium-ion batteries.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

References

1. M.Y. Luo, Z.G. Jiang, High-performance anode material for lithium-ion batteries comprising carbon-coated silicon-graphite with a specified structure. *Advances in Analytical Chemistry* **15**, 108-122 (2025)
2. W. Zhang, X.P. Qi, S. Fang, J.H. Zhang, B.M. Shi, J.Y. Yang, Effects of carbon on silicon-carbon composites in lithium-ion batteries. *Progress in Chemistry* **32**, 454–466 (2020)
3. L. Zhang, X.B. Zhao, Research progress in surface and interface control of silicon-based anode materials for lithium-ion batteries. *Journal of Liaoning Shihua University* **40**, 49–58 (2020)
4. J.Z. Zhang, Q. Han, H.X. Chen, Z.M. Shi, Y.S. Liu, W.Y. Lei, J. Wei, Y. Zhang, Research progress of carbon materials modified SiOC anodes in lithium-ion batteries. *Journal of the Chinese Ceramic Society* **52**, 3327–3337 (2024)
5. Y.M. Xie, J. Guo, X.H. Dong, Research and development status and trend of silicon carbon anode materials for lithium ion batteries. *Material Sciences* **10**, 248–252 (2020)
6. H. Wu, Y. Cui, Designing nanostructured Si anodes for high energy lithium ion batteries. *Nano Today* **7**, 414–429 (2012)
7. Y. Yao, M.T. McDowell, I. Ryu, et al., Interconnected silicon hollow nanospheres for lithium-ion battery anodes with long cycle life. *Nano Letters* **11**, 2949–2954 (2011)
8. Y. Li, K. Yan, H.W. Lee, et al., Growth of conformal graphene cages on micrometre-sized silicon particles as stable battery anodes. *Nature Energy* **1**, 15029 (2016)
9. H. Kim, B. Han, J. Choo, J. Cho, Three-dimensional porous silicon particles for use in high-performance lithium secondary batteries. *Angewandte Chemie International Edition* **47**, 10151–10154 (2008)
10. M.H. Park, M.G. Kim, J. Joo, et al., Silicon nanotube battery anodes. *Nano Letters* **9**, 3844–3847 (2009)
11. A. Magasinski, P. Dixon, B. Hertzberg, et al., High-performance lithium-ion anodes using a hierarchical bottom-up approach. *Nature Materials* **9**, 353–358 (2010)
12. C.K. Chan, H. Peng, G. Liu, et al., High-performance lithium battery anodes using silicon nanowires. *Nature Nanotechnology* **3**, 31–35 (2008)