

The influence of silicon anode morphology on energy storage performance in lithium-ion batteries

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Abstract:

In the context of the global energy transition and the extreme need for high - performance energy storage systems, lithium - ion batteries (LIBs) have become a core technology. However, the limited capacity of traditional graphite anodes restricts the further development of LIBs. Silicon anodes, which owns ultra - high theoretical capacity, have emerged as a promising solution, yet their practical application is still hindered by severe volume expansion during lithiation. This research holistically examined the relationship between the morphology of silicon anodes and their energy storage performance in LIBs, systematically analyzed four typical morphologies: silicon nanoparticles, nanotubes, bulk silicon, and thin-film silicon, and scientifically explored how morphological features - such as particle size, hollow structures, and film thickness - affect lithium ion diffusion, volume expansion mitigation, and cycle stability. The results revealed that different silicon anode morphologies exhibit distinct advantages and challenges. Silicon nanoparticles show excellent rate performance but suffer from agglomeration - induced capacity decay. Silicon nanotubes can effectively buffer volume expansion but are constrained by complex fabrication processes. Bulk silicon, when modified by nano structuring, balances performance and cost to some extent, while thin - film silicon demonstrates good flexibility but low areal capacity. The study offered strategies to address the key issues in silicon anode commercialization, contributing to high energy densities of electric vehicles and their energy storage.

Keywords: lithium-ion battery; silicon anode; energy storage performance.

1. Introduction

Nowadays, in the context of the global energy crisis and the environmental pollution, the development of electric vehicles and renewable energy storage technologies is promoted as solutions. Lithium-ion batteries, with their high energy density and long cycle life, have become the core of the new energy development. However, the tradition graphite anode struggles to maintain the high requirement of high energy density. In this case, silicon has become the next promising anode material due to its super high theoretical capacity and abundant reserves. However, a significant challenge remains: during the process of Lithium intercalation, there are about 300% volume will be expanded. This expansion will lead to the broken electrode structure, electrolyte permeation and unstable interface. With these effects, the battery life is severely influenced.

In recent years, researchers have mitigated the volume expansion problem of silicon anodes by regulating their microstructure [1]. For example, nanoparticles can shorten the diffusion path of lithium ions, but their high specific surface area enhances electrolyte consumption [2]. The hollow structure of nanotubes provides a buffer space for volume expansion, but complex preparation processes limit mass production. Although the composite of thin-film silicon and flexible substrates improves structural stability, it faces the issue of increased interfacial impedance. Additionally, nanostructured modification of bulk silicon shows potential in balancing capacity and cycle stability, but finding out that how to balance cost and performance remains needed, waiting for scientific breakthroughs.

Research on the regulation strategy of silicon anode morphology and its energy storage performance optimization. Silicon anodes high-capacity advantage is restricted by volume expansion, and morphology control fundamentally balances lithium storage demand and material stability through structural design. Current studies have shown that strategies such as analogization, porosity, and dimension manipulation can increase the cycle life of silicon anodes by 2-3 times.

This research will investigate regulation methods of typical morphologies, and systematically analyze the correlation mechanism between regulations and energy storage performance. This research will focus on regulating typical silicon anode morphologies and systematically investigates the underlying mechanisms between these regulations and energy storage performance.

2. Lithium Storage Mechanism, Core Challenges and Performance Analysis of Typical Morphologies of Silicon Anodes

2.1 Lithium Storage Mechanism and Core Challenges

The lithium storage capacity of silicon anodes stems from the electrochemical alloying reaction of lithium with silicon. When the battery charges, lithium ions migrate from the cathode through the electrolyte, penetrate the solid electrolyte interphase film, and insert into the silicon lattice, forming various lithium-silicon alloys such as $\text{Li}_{12}\text{Si}_7$, $\text{Li}_{13}\text{Si}_4$, and $\text{Li}_{22}\text{Si}_5$. This reaction grants silicon an ultra-high theoretical capacity of 4200 mAh/g, which is 10 times more than the traditional graphite anodes. However, this advantage is accompanied by a critical drawback: during the alloying process, a volume expansion of up to 300% [3].

This extreme volume change triggers a series of chain reactions that degrade battery performance. The SEI film on the electrode surface, which is crucial for stabilizing battery performance, repeatedly ruptures and reforms. Unlike the stable condition, each rupture exposes fresh and highly reactive silicon surfaces to the electrolyte, triggering continuous side reactions that consume lithium ions and electrolyte, lowering the efficiency. Third, the repeated formation of new SEI films further increases impedance, significantly shortening the battery's cycle life and accelerating capacity decay. Consequently, as noted in recent studies [4], to mitigate the battery's decay problem, regulating the morphology of silicon anodes has emerged as a key strategy researchers investigated. By optimizing the structure of silicon, researchers aim to balance ion transport efficiency and mechanical stability, thereby enhancing the overall performance of silicon-based lithium-ion batteries.

2.2 Performance Analysis of Typical Morphologies

2.2.1 Silicon Nanoparticles

Silicon nanoparticles are defined as silicon materials with a particle size typically less than 100 nm. Their small size offers distinct advantages for lithium storage. The reduced particle dimension shortens the diffusion path of lithium ions, allowing for faster ion transport. This advantage significantly improves the battery's rate performance—

tests have shown that silicon nanoparticles can maintain over 80% of their capacity at a high current density of 10 C. Additionally, their large specific surface area (ranging from 50 to 100 m²/g) facilitate effective surface modifications, such as carbon coating. These coatings act as a protective layer, reducing direct contact between silicon and the electrolyte, thereby mitigating side reactions and improving stability.

However, despite their benefits for storage and stability, silicon nanoparticles also have notable drawbacks. First, their high specific surface area, while beneficial for surface modification, increases the contact area with the electrolyte, accelerating electrolyte consumption and side reactions. This results in a low first-cycle Coulombic efficiency, typically only between 70% and 85%. Furthermore, during cycling, the volume expansion causes the nanoparticles to agglomerate, forming larger clusters that hinder ion and electron transport. This agglomeration leads to rapid capacity decay, demonstrated by the fact that after 100 charge-discharge cycles, the capacity retention rate often drops below 50% [5].

Despite these challenges, silicon nanoparticles remain a key research focus due to their excellent rate performance and the significant potential for further optimization through surface engineering.

2.2.2 Silicon Nanotubes

Silicon nanotubes are tubular silicon structures with a hollow core, typically featuring an inner diameter of 50–200 nm and a wall thickness of 10–30 nm [6]. The most significant advantage of this morphology is its ability to accommodate volume expansion. During lithiation, the hollow cavity provides a buffer space for the silicon to expand, which can reduce the mechanical stress on the electrode, and eventually protect the battery. Studies have shown that this structure can reduce the volume expansion rate from 300% to approximately 120%, significantly improving the battery's cycle stability.

Moreover, the porous structure of the nanotube walls enhances electrolyte infiltration, facilitating faster ion transport. Compared to silicon nanoparticles, silicon nanotubes exhibit a 30% higher ion diffusion rate, which contributes to better rate performance. However, the fabrication of silicon nanotubes presents challenges. Most synthesis method (e.g, template-assisted chemical vapor deposition, involve multiple complex steps and expensive equipment, hindering scalable production and resulting in costs approximately three times higher than silicon nanoparticles. Additionally, controlling the uniformity of wall thickness and structure during synthesis is challenging, leading to

inconsistencies in performance. Critically, under cyclic mechanical stress, the nanotube walls are prone to collapse, ultimately limiting long-term cycling stability.

2.2.3 Bulk Silicon

Bulk silicon refers to silicon materials with a macroscopic structure, typically in the form of wafers or blocks. One of the primary advantages of bulk silicon is its relatively simple preparation process and low raw material cost, which makes it suitable for large-scale applications. Additionally, its macroscopic structure provides a certain degree of mechanical integrity, maintaining electrode stability under specific conditions.

However, severe volume expansion during lithiation can cause catastrophic electrode failure. To address this issue, researchers have developed nano structuring modifications for bulk silicon, such as creating porous arrays or three-dimensional networks [7]. These modifications introduce voids and channels within the bulk structure, allowing space for volume expansion and reducing internal stress. For example, researches demonstrated that bulk silicon modified with a three-dimensional hierarchical porous structure exhibits a 60% reduction in stress concentration and improved cycle stability, retaining over 70% capacity after 200 cycles [8].

Despite these improvements, challenges remain. The nano structuring process, which often involves electrochemical etching or laser machining, increases production costs by more than 200%, compared to unmodified bulk silicon. Additionally, it's difficult to achieve uniform nano structuring across large bulk samples, leading to inconsistent performance. Even with modifications, bulk silicon experiences greater volume expansion than nanostructured counterparts. Furthermore, microcracks form over time. In sum, greater volume expansion and timing microcracks formation can lead to gradual capacity loss.

2.2.4 Thin-Film Silicon

Thin-film silicon is a form of silicon deposited as a thin layer, typically with a thickness ranging from 50 to 500 nm, onto a substrate such as copper foil or flexible polymer films. The thin structure of this morphology significantly reduces the absolute volume change during lithiation, which helps alleviate the stress caused by expansion and improves electrode stability. This characteristic makes thin-film silicon particularly suitable for applications requiring flexibility, such as wearable devices and flexible batteries.

Studies have shown that confirmed stabilized efficiencies is about 9.6% [9], demonstrating excellent mechanical

and electrochemical stability. Additionally, the close contact between the thin film and the substrate enhances electron transport, improving the battery's rate performance. However, thin-film silicon has limitations. Its thin thickness results in low areal capacity, which restricts its applications scenarios and requires high energy density. Another limitation is the high interfacial resistance between the thin film and the substrate, which can reach up to $100 \Omega \cdot \text{cm}^2$. To reduce this resistance, researchers have explored the use of intermediate layers, such as graphene. However, the intermediate layers is complex and costly for the fabrication process, couple with other difficulties such as achieving uniform deposition of thin-film silicon over large areas, which can lead to inconsistencies in battery performance.

3. Recommendations and Outlook for Silicon Anodes

3.1 Technological Innovation

To overcome the limitations of current silicon anode morphologies, several technological innovations are proposed. First, it's promising to refine the design of heterostructures, such as silicon-carbon nanotube composites. These composites integrate silicon's high capacity with carbon nanotubes' superior conductivity and mechanical flexibility, enhancing electron transport and structural stability. The second innovative technology is 3D printing, which allows for the precise fabrication of complex silicon anode structures [10]. For example, using digital light processing (DLP) 3D printing to create honeycomb-structured silicon anodes can provide sufficient space for volume expansion and enable a volume expansion rate of less than 80%. This technology enables the customization of anode structures to balance performance and stability, opening new avenues for silicon anode design.

3.2 Cost Reduction

Reducing the cost of silicon anodes is crucial for their commercialization. One strategy is the development of calculable synthesis methods. For example, using fluidized bed chemical vapor deposition to produce silicon nanoparticles on a large scale can effectively reduce production costs to one-third of traditional methods. Additionally, utilizing low-cost raw but abundant materials in silicon, such as rice husk ash, can significantly lower material costs. Researches demonstrated that silicon derived from rice husk ash has comparable performance to com-

mercially available silicon, while reducing raw material costs by more than 40%.

Another key aspect is to optimizing the manufacturing process [11]. For example, simplifying synthesis steps, improving yield, and reducing energy consumption can all contribute to lower production costs. To be specific, developing template-free methods for synthesizing silicon nanotubes could eliminate the need for expensive templates and reduce the production time, hence enhancing economic viability.

3.3 Development Trends

The future development of silicon anodes will focus on the integration of multiple strategies to balance performance, cost, and scalability. One important trend is the synergistic optimization of morphology, electrolyte, and substrate. For example, matching thin-film silicon with solid electrolytes could eliminate the side reactions associated with liquid electrolytes, significantly improving cycle stability.

Another trend is the combination of Artificial Intelligence (AI) and machine learning to accelerate the development of silicon anodes. AI and machine learning can predict the performance of different morphologies based on structural parameters, such as particle size, porosity, and wall thickness, reducing the concern for time-consuming and costly experiments. Machine learning designed hierarchical silicon nanostructures show a 20% improvement in capacity retention compared to traditionally designed structures. Furthermore, the application of silicon anodes in specialized fields, such as electric vehicles and grid energy storage, will drive the development of tailored morphologies. For electric vehicles, high energy density and long cycle life are critical, requiring silicon anodes with optimized nanostructures. For grid storage, cost and safety are prioritized, favoring modified bulk silicon or low-cost thin-film silicon options.

4. Conclusion

In the context of global energy transition and energy storage technology upgrading, silicon anode has become a key direction for lithium-ion battery performance breakthroughs due to its high theoretical specific capacity. But owing to its volume expansive which leads to a kind of difference of circulating long-term constraints the commercial application. Focusing on silicon anode morphology and energy storage performance, research can analyze structural properties and electrochemical properties of

typical morphologies, such as nanotubes, bulk silicon, and thin-film silicon. Therefore, morphological control is established as the core role of silicon anode optimization, validating structural design as the driver of performance gains. They provided theoretical support for the engineering development of silicon anode with high stability and high energy density.

The different morphology of silicon anode has various impact on volume expansion buffer, ion transport efficiency and structural stability. Although nanoparticles have high-rate potential, they are susceptible to capacity decay due to agglomeration. Nanotubes alleviate swelling by their hollow structure, but they are constrained by the high cost of preparation. Nano-modified bulk silicon can balance performance and cost, but the bottleneck of uniformity remains undiscovered. Thin-film silicon is suitable for flexible materials, but it faces challenges in capacity and interface resistance. These findings clarified morphology fixation is intrinsically linked to silicon anode's better performance. This reaffirms the logical relation between structural design and performance improvement from another standpoint.

The main focus is the analysis of the typical morphology of silicon anode and its energy storage performance, enabling battery engineers to accurately select and optimize the silicon anode morphology to accelerate high-performance lithium-ion battery product development. It further enables researchers to broaden the design paradigms of silicon anode structure and pursue targeted innovative research, while providing critical reference for new investigators to this industry.

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