Application of Nano-Silicon Based Materials in Anode of Lithium Ion Battery

Nanxiang Ma *

School of Material science and engineering, Beijing University of Technology, Beijing, 100000, China

* Corresponding Author Email: xmgh204716@emails.bjut.edu.cn

Abstract. As a fundamental element in advanced energy storage systems, the characteristics of lithium-ion battery anode materials critically determine overall cell performance. While conventional graphite anodes with limited theoretical capacity (372 mAh/g) struggle to meet high energy density requirements, silicon-based materials boasting an exceptional theoretical capacity of 4200 mAh/g have emerged as promising alternatives. Nevertheless, practical implementation faces significant challenges due to structural degradation and interface instability induced by over 300% volumetric expansion during lithiation/delithiation processes. This review comprehensively examines nano-engineered silicon materials for anode applications, with particular emphasis on three principal configurations: silicon nanoparticles (Si-NPs), silicon nanowires (Si-NWs), and porous/networked silicon structures-analyzing their defining characteristics, fundamental properties, and recent technological advancements. Comparative studies of silicon nanomaterials with distinct microstructures reveal their respective merits and limitations. Experimental evidence demonstrates that nanostructuring effectively enhances electrochemical performance. Although current research remains confined to laboratory-scale exploration, these findings establish valuable technical foundations for future commercial-scale production.

Keywords: lithium-ion battery, anode, nanotechnology, Si-NPs, Si-NWs, porous/networked silicon.

1. Introduction

With the global energy structure transformation and environmental protection requirements, the rapid development of new energy vehicles (NEVs) and energy storage systems has put forward higher requirements for lithium-ion batteries (LIBs). The range, charging speed, and safety of new energy vehicles have become the core indicators of market competition, and battery energy density is the key factor determining these performances. At present, the capacity improvement space of mainstream commercial lithium-ion battery positive electrode materials, such as lithium iron phosphate and ternary materials, is limited due to their physic properties, and anode materials have become the core direction to break through the energy density bottleneck. The theoretical capacity of traditional graphite anodes is only 372 mAh/g, while silicon-based materials are considered an ideal choice for the next generation of anode materials due to their theoretical capacity of up to 4200 mAh/g [1]. In addition, silicon has abundant reserves (accounting for 28% of crustal elements), low cost, and slightly higher lithium insertion potential than graphite (about 0.4 V vs. Li/Li $^+$), which can effectively suppress lithium deposition and improve battery safety.

However, the practical application of silicon-based materials faces significant challenges. NEVs require fast charging (e.g., 15-minute charging to 80%), long cycle life (>1000 cycles), and low-temperature performance, demanding anode materials with not only high capacity but also structural stability and conductivity. The mainstream "lithium iron phosphate + graphite" technology, while cost-effective, has reached its energy density limitation (~240 Wh/kg), failing to meet future ultra-fast charging and long-range requirements. Thus, developing novel anode materials that combine high energy density with cycling stability is imperative.

Although silicon-based materials outperform graphite in theoretical performance, their large-scale applications are still limited by the following core issues: Firstly, Silicon undergoes >300% volumetric expansion during lithiation, causing electrode pulverization, active material detachment, and current collector failure, severely degrading cycle life [2]. Secondly, repeated volume changes lead to continuous fracture and regeneration of the solid electrolyte interphase (SEI), accelerating electrolyte depletion and reducing Coulombic efficiency (initial efficiency typically <80%). Finally, Silicon semiconductor properties possess in high internal resistance, limiting rate capability and hindering high-power applications [3].

To address these challenges, strategies such as nanostructuring, composite design, surface coating, and prelitigation have been proposed. Among these, nano-silicon-based materials have emerged as a research hotspot due to their size effects (shortening lithium-ion diffusion paths) and structural tunability (e.g., porous, core-shell, or alloyed architectures). By reducing particle size to the nanoscale, the specific surface area of Silicon-based electrodes increases dramatically, facilitating faster lithium-ion diffusion and mitigating mechanical stress. The core advantage of nano-Silicon-based materials lies in balancing capacity and stability through microstructural engineering. For example, three-dimensional porous structures fabricated via sole-gel methods provide expansion buffer zones, increasing specific surface area to >200 m^2/g and suppressing crack propagation [4]. TiO_2-coated Si nanoparticles (SiNPs@TiO_2) combined with silver nanowires (AgNWs) form conductive buffer layers, achieving an initial discharge capacity of 3524 mAh/g while reducing interfacial impedance [5]. Kim.et. al has proved amorphous silicon nanolayer-coated graphite anodes (α-Si/graphite) via Ni-catalyzed hydrogenation and chemical vapor deposition (CVD), achieved Initial coulombic efficiency of 93.8%, energy density exceeding 1060 Wh L^{-1} at 10 mA cm^{-2} current density, with fast-charging performance 1.5 times higher than commercial graphite anodes [6]. Du.et.Al has designed of yolk@multishell structure, encapsulating silicon particles in hollow carbon tubes, with layered assembly of porous carbon and SnS_2 nanosheets, achieved Delivers 1513.6 mAh g^{-1} after 100 cycles at 1 A g^{-1}, and 331.4 mAh g^{-1} after 100 cycles in full-cells at 0.2 A g^{-1}[7]. Additionally, nanomaterials enable shorter diffusion pathways, enhancing rate performance and making them suitable for fast-charging scenarios. However, the synthesis of nano-silicon anodes remains challenging due to complex surface chemistries, low tap densities, and high production costs.

This article discusses the implementation schemes of various nano-silicon-based materials in the anode materials of new energy vehicle batteries, compares and analyzes the advantages and disadvantages of various materials and synthesis methods, and puts forward its own suggestions, providing theoretical guidance and practical reference for the development of new energy vehicle batteries.

This review is divided into five parts:

1) Introduction: Overview of NEV battery requirements, limitations of conventional anodes, and the advantages for nano-Silicon materials.

2) Case: Three fundamental types of silicon-based nanomaterials, specifically nanoparticles, nanowires, and porous/network, including their essential definitions and fundamental characteristics.

3) Analysis & challenge: Provide specific examples and explanations for each type of nano-silicon material

4) Summary: Conduct a comparative analysis of the advantages and disadvantages of the three materials and provide proposals.

5) Conclusion: Summarize the core findings, propose material selection suggestions, and look forward to the future prospects of nano-Si anodes.

2. Case description

2.1. Silicon Nanoparticles (SiNPs)

Silicon nanoparticles (SiNPs) are high-purity crystalline silicon materials with particle sizes ranging from 1 to 200 nanometers, featuring an extremely large specific surface area (90-95 m^2/g) and unique surface reactivity. They possess stable physical and chemical properties, low bulk density (improvable via surface modification), and are non-toxic and biocompatible. In battery technology, their core advantage stems from nanoscale size effects: smaller particles shorten lithium-ion diffusion pathways and partially mitigate volume expansion during lithiation/delithiation (single-particle expansion rate <150 %). But challenges still remain in addressing more volume expansion and SEI film stability.

2.2. Silicon Nanowires (SiNWs)

A nanowire is a one-dimensional nanomaterial with a diameter ranging from a few to several hundred nanometers and a high aspect ratio, often extending to micrometers or millimeters in length. Depending on their composition, nanowires can be categorized into metallic (e.g., gold, silver), semiconductor (e.g., silicon, gallium arsenide), and oxide (e.g., titanium dioxide, zinc oxide) types. Their unique quantum size effects, surface effects, and one-dimensional electron transport properties enable diverse applications in electronics, energy storage, and biomedicine. For instance, metallic nanowires are used in flexible conductive films and sensors, semiconductor nanowires serve as high-performance transistors and solar cells, while oxide nanowires excel in catalysis and bioimaging. Synthesis methods include vapor-liquid-solid growth and chemical vapor deposition, though challenges remain in addressing defects and improving uniformity for practical applications.

2.3. Porous/Networked Si

Porous or networked silicon refers to a two-dimensional or three-dimensional network structure composed of nanoscale materials with pore sizes typically in the nanometer range (e.g., 2–3.2 nm). These structures with porosity levels of 40%–80%, fabricated via etching, templating, or self-assembly. Internal pores act as buffer zones for volume expansion, while their high specific surface area (200–500 m^2/g) enhances electrolyte infiltration and rapid ion transport. However, the mechanical weakness of porous structures may lead to localized collapse, requiring reinforcement via silicon carbide (SiC) frameworks or polymer filling.

3. Analysis and challenges

3.1. Silicon Nanoparticles (SiNPs)

Multiple strategies exist for modifying nano-silicon-based particles. A representative approach inspired by pomegranate architecture involves the following steps [8]: Initially, commercial silicon nanoparticles are surface-coated with a silica (SiO_2) layer to form core-shell $Si@SiO_2$ particles. These particles are then dispersed in an aqueous phase and emulsified with 1-octadecene containing 0.3wt% surfactant to create a water-in-oil emulsion. Subsequent water evaporation at 95-98 ℃ yields $Si@SiO_2$ nanoparticle clusters, which are collected via centrifugation and thermally stabilized at 550°C in air for 1 hour to eliminate organic residues and enhance structural cohesion. A cost-effective stepwise polymerization process under ammonia catalysis subsequently generates a resorcinol-formaldehyde (RF) resin coating around the clusters. Carbonization at 800°C under argon transforms the RF layer into a conformal carbon shell, whose thickness can be adjusted by varying resorcinol monomer dosage. Finally, selective etching of the SiO_2 interlayer using 5 wt% HF solution creates engineered void spaces to accommodate silicon's substantial volume fluctuations during electrochemical cycling. The pomegranate particle was showed in Fig. 1.

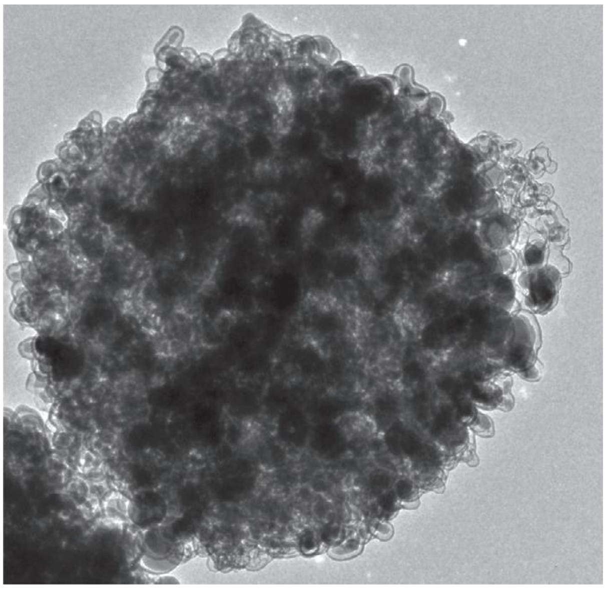

Figure 1. TEM image of a single silicon pomegranate particle [8].

This biomimetic pomegranate-structured silicon anode delivers exceptional electrochemical characteristics, achieving a reversible capacity of 2,350 mAh g-1, volumetric capacity of 1,270 mAh cm^{-3}, 97% capacity retention over 1,000 cycles, and Coulombic efficiency of 99.87 %. The architectural design incorporates nanoscale primary particles to suppress fracturing, while precisely engineered internal voids accommodate silicon expansion without altering secondary particle dimensions. A continuous carbon framework serves dual functions as both conductive pathways and structural reinforcement, ensuring full electrochemical utilization of nanoparticles. Complete carbon encapsulation confines solid-electrolyte interphase (SEI) formation predominantly to external surfaces, minimizing SEI accumulation while preserving internal expansion buffers.

This innovation successfully mitigates structural degradation and SEI instability caused by volumetric fluctuations in conventional silicon anodes. Notably, the fabrication process eliminates requirements for specialized equipment like CVD and demonstrates full compatibility with standard slurry-coating electrode manufacturing. However, initial Coulombic efficiency registers 82% (with 9% carbon content), decreasing to 75% with thicker carbon coatings. While avoiding sophisticated apparatus, the synthesis still necessitates sequential procedures including SiO2 coating, microemulsion assembly, RF resin encapsulation, and multi-stage thermal treatments.

3.2. Silicon Nanowires (SiNWs)

Silicon nanowires are predominantly fabricated through drop-casting or slurry-coating techniques. A representative carbon-silicon core-shell nanowire synthesis involves the following steps [9]: Initially, carbon nanofibers (CNFs) are uniformly dispersed in isopropanol. The CNFs are subsequently deposited onto stainless steel foil (SS foil) substrates via two distinct approaches. The drop-casting method employs a pipette to deposit the dispersion onto preheated SS substrates (1 cm×1cm), achieving maximum loading densities of 0.4 mg/cm^2. Alternatively, the slurry-coating technique involves mixing CNFs with polyvinylidene fluoride (PVdF, 10 wt%) in N-methyl pyrrolidone (NMP) to form a homogeneous slurry, which is then blade-coated onto SS foils with loadings up to 2 mg/cm^2. The CNF-loaded foils are then positioned in a chemical vapor deposition (CVD) reactor. During preliminary processing stage, PVdF decomposition occurs under vacuum with argon flow at 700℃ for 1 hour. Following this thermal treatment, the temperature is reduced to 500℃ for silane (SiH4) delivery to deposit silicon coatings. By precisely controlling CVD duration, the silicon-to-carbon ratio is maintained at approximately 3:1, resulting in selective amorphous silicon (a-Si) deposition onto CNFs to form core-shell structured carbon-silicon nanowires. The core-shell nanowires were showed in Fig. 2.

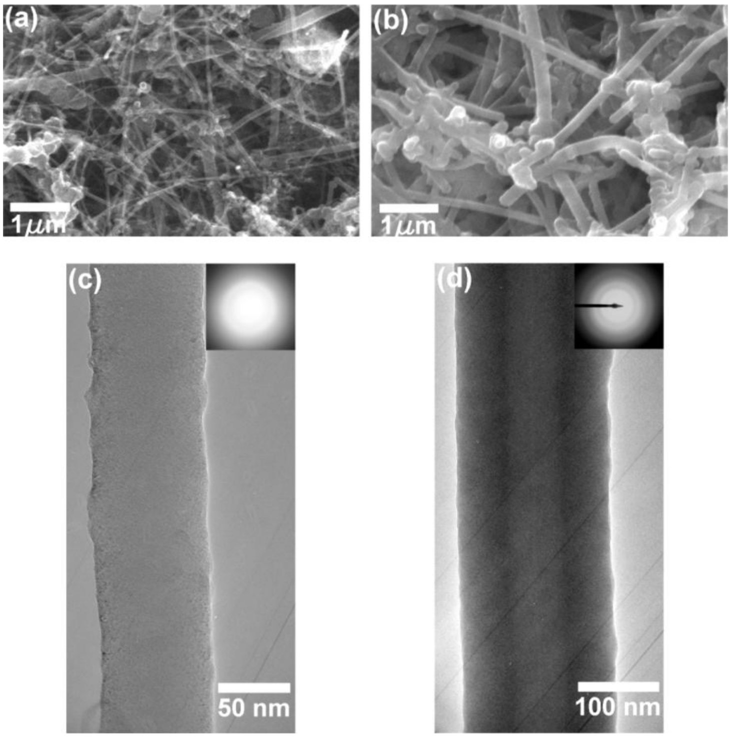

Figure 2. (a) SEM image of CNFs before Si coating.
(b) SEM image of Si coated CNFs.
(c) TEM and SAED images (inset) of a bare CNF.
(d) TEM and SAED images (inset) of a C-Si core-shell NW [9].

The carbon-silicon core-shell nanowire anode exhibits an initial-cycle Coulombic efficiency (CE) of ~90%, comparable to commercial graphite counterparts. Under C/5 current density, a reversible capacity of ~2000 mAh/g is sustained during the first 30 cycles, with CE improving to 98-99.5% over subsequent 55 cycles. When cycled within a voltage window of 1-0.1 V, the electrode demonstrates enhanced stability, delivering 1300 mAh/g with CE values of 98-99.6%. At a high rate of 1C, the capacity retains 800 mAh/g, showing only ~7% decay after 80 cycles. Full-cell configurations pairing $LiCoO_2$ cathodes with these nanowire anodes achieve a specific capacity of ~1400 mAh/g, featuring an initial CE of 86% and stabilized CE of ~98.5% in later cycles. After 30 cycles, the full cell maintains 80% capacity retention with a discharge plateau at 3.3 V, indicating commercial viability. Post-cycling characterization reveals preserved nanowire morphology after 5 cycles. TEM analysis confirms nanoporous silicon formation and interfacial blurring between carbon and silicon layers following electrochemical cycling.

Carbon-silicon core-shell nanowire materials have the high-capacity characteristic of this material makes it perform exceptionally well in lithium storage, reaching up to 2000 mAh/g, far exceeding that of traditional graphite anode materials. Furthermore, it can still maintain a high Coulombic efficiency and capacity stability after multiple cycles, demonstrating excellent cycling performance. Even under high-rate conditions, it can maintain a high capacity, demonstrating excellent high-rate performance. The carbon core, as a mechanical support and electronic conduction path, effectively reduces the volume change and structural damage of silicon during the charging and discharging process. However, the preparation process of this material is rather complex, involving technical requirements such as chemical vapor deposition. Moreover, compared with traditional materials, its preparation cost is relatively high, which may have a certain impact on its large-scale commercial application.

3.3. Porous/Networked Si

In general, the preparation method of porous/networked silicon is complicated. For example, a 3D-interconnected N-doped carbon network reinforced gradient nanoporous Si anode with topological pore-wall configuration was described as follows [10]: using commercially cast Mg-55Si alloy, micrometer-sized porous Mg2Si precursor was obtained by a one-step de-alloying process, etching in a 5 wt% sodium hydroxide solution at 70℃ for 5 hours. Second, after crushing Mg2Si, it was heat-treated in air at 550℃ for 20 hours and then etched in a 5 wt% hydrochloric acid solution for 24 hours to obtain hierarchical nanoporous silicon (m-HNP Si) with a micro curved pore wall. Finally,1.0 g of m-HNP Si was added to Tri's buffer and sonicated for 10 minutes to form a suspension. Then, 1.0 g of dopamine hydrochloride was added to the suspension and stirred for 24 hours to polymerize dopamine. Finally, the particles in the suspension were collected, dried overnight at 60 °C, and held at 800℃ in an argon atmosphere for 3 hours to obtain N-C@m-HNP Si. The schematic diagram of the preparation process was showed in Fig. 3.

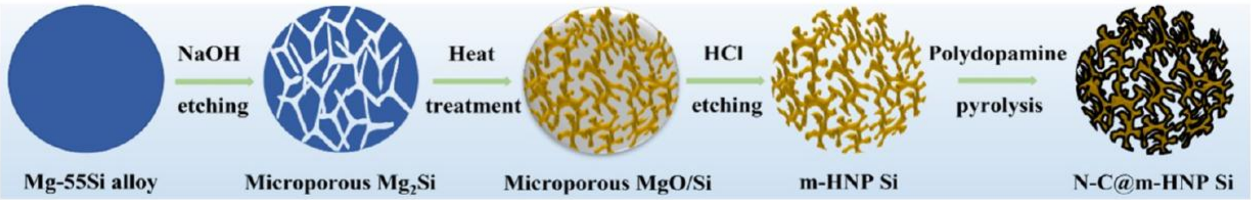

Figure 3. Schematic diagram of the preparation process of N-C@m-HNP Si [10].

The N-C@m-HNP Si composite anode demonstrates remarkable electrochemical characteristics, under a 0.1C rate, the material demonstrates an initial charging capacity of 1092.93 mAh g^{-1} and a first cycle discharging capacity of 2636.32 mAh g^{-1}, corresponding to a Coulombic efficiency of 41.45%. After 200 cycles, it retains 1071.84 mAh g^{-1} reversible capacity with 99.19% Coulombic efficiency. Rate capability tests reveal progressively decreasing discharge capacities of 1476.69, 869.89, 687.84, and 517.73 mAh g^{-1} at 0.1C to 0.4C current densities. Its architecture features a bimodal pore distribution (20-50 nm and 300-500 nm) within a three-dimensional hierarchical network, where micro-curved pore walls effectively accommodate silicon's volumetric strain. The nitrogen-doped carbon coating synergistically enhances electrical conductivity and mechanical stability, contributing to superior electrochemical performance. However, the synthesis protocol involving sequential chemical etching, thermal treatment, dopamine polymerization, and pyrolysis carbonization presents process complexity. S

4. Summary

Table 1. Comparation of various nano-Si anode

Type	advantages	disadvantages
Si-NPs (pomegranate)	-high capacity -stabilize SEI -no complex equipment	-poor productivity -multiple steps fabrication -low Coulombic efficiency
Si-NWs (carbon-silicon core-shell)	-high capacity -exceptional cycling performance -excellent high-rate performance -reduce the volume change & structural damage	-complex preparation process -high cost
Porous/Networked Silicon (N-C@m-HNP Si)	-good conductivity -stabilize structure	-multiple steps fabrications

Table. 1 summarizes the advantages, and disadvantages of three nano-silicon-based anode materials: SiNPs, SiNWs, and porous/network Silicon.

Si-NPs with pomegranate structure offer advantages such as high capacity, stabilized solid electrolyte interface (SEI), and no requirement for complex equipment, making them suitable for high energy density applications. However, their production involves multiple steps, resulting in low productivity and issues like low Coulombic efficiency, which may shorten battery cycle life. Additionally, the intricate fabrication process limits their potential for large-scale implementation.

Si-NWs with carbon-silicon core-shell design exhibit enhanced performance, including high capacity, exceptional cycling stability, superior high-rate performance, and effective mitigation of volume expansion-induced structural damage. However, their preparation process is complex and costly, particularly due to the stringent requirements for precise control of the core-shell structure, posing a significant barrier to commercialization.

Porous or networked silicon materials stand out due to their good conductivity and structural stability, which alleviate mechanical stress during charge-discharge cycles. Nevertheless, their synthesis also involves multiple steps, increasing process complexity and production costs, which may hinder practical feasibility.

Future research should focus on simplifying preparation processes, reducing material costs, and exploring synergistic effects among different materials. For instance, combining the high performance of Si-NWs with the structural stability of porous silicon or developing novel composite systems to balance capacity and cycle life could be promising. Additionally, optimizing SEI layer design and improving Coulombic efficiency are critical for enhancing the practicality of silicon-based anodes. Through interdisciplinary collaboration and technological innovation, nano-silicon-based anode materials hold the potential to achieve breakthrough applications in advanced high-specific-energy battery systems.

5. Conclusion

The systematic integration of nano-silicon hybrids into lithium-ion battery anode configurations achieves a major breakthrough in resolving the inherent capacity limitations of graphite systems (theoretical capacity: 372 mAh/g), establishing critical foundations for next-generation high-specific-energy storage technologies. While silicon's exceptionally high energy storage capability (4200 mAh/g) and natural abundance position it as a promising alternative, the material's substantial volumetric expansion (>300%) during electrochemical cycling induces critical challenges including electrode fragmentation, unstable solid-electrolyte interphase (SEI) evolution, and accelerated capacity degradation. This review comprehensively examines recent advancements in nano-silicon anode technologies, with focused analysis on three fundamental architectures: silicon nanoparticles (Si-NPs), silicon nanowires (Si-NWs), and porous/networked silicon structures. Through comparative evaluation of microstructural characteristics, the study elucidates the respective merits and constraints of these nanoscale silicon configurations.

Conclusion 1: Nano-silicon-based materials have become an ideal choice to replace traditional graphite anodes due to their high theoretical capacity (4200 mAh/g). The electrochemical performance of the anode can be significantly improved through nano-modification, such as shortening the lithium-ion diffusion path, mitigating the mechanical stress caused by volume expansion, thereby improving the cycle stability and energy density of the battery.

Conclusion 2: Although nano-silicon-based materials have shown excellent performance in the laboratory stage, they still face some challenges in practical applications, such as complex surface chemistry, low tap density, and high production costs. Future investigations should prioritize process integration strategies, cost-effective material engineering, and multicomponent synergistic design, with particular emphasis on developing scalable fabrication protocols and optimizing heterostructure coupling mechanisms to bridge the gap between laboratory innovation and industrial-scale production of nano-silicon anode systems.

Nano-silicon-based anodes hold transformative potential for LIB technology, promising to enable high-energy-density batteries for electric vehicles and grid storage. While laboratory breakthroughs highlight remarkable progress, transitioning to commercial viability demands interdisciplinary collaboration to address synthesis costs, mechanical stability, and scalable manufacturing. By harmonizing material design, electrolyte innovation, and industrial processes, nano-silicon could redefine energy storage paradigms, paving the way for fast-charging, long-range EVs and sustainable energy solutions. The journey from lab-scale innovation to commercial reality will hinge on persistent innovation and strategic partnerships across academia and industry.

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