Application of nanotechnology in the negative electrode of Si-based lithium-ion batteries

Yuyue Geng *
Zibo Shiyan High School, Shandong, China
* Corresponding Author Email: miageng0409@ldy.edu.rs

Abstract. Modern electronics and electric cars frequently employ lithium-ion batteries (LIBs) because of their excellent energy density, safety, and environmental friendliness. The anode of LIBs is typically composed of carbon. Nevertheless, it loses a lot of energy when charging and draining. Lithium metal precipitates quickly from the surface of carbon electrodes and forms dendrites. These can pass through the diaphragm and cause short circuits inside the battery, posing a public safety risk. The advantages of the silicon-based anode are excellent safety, low operating voltage, and high theoretical specific capacity. It is among the most critical potential materials for high-energy-density lithium-ion batteries. However, its drawbacks, such as volume expansion and poor electrical conductivity, limit the development of LIBs. In recent years, the emergence of nanotechnology has well solved these problems. This paper first explains how silicon-based lithium-ion batteries work and summarizes the challenges of silicon-based anodes. Then, it explores the application of nanotechnology in silicon-based anode, including different dimensions of silicon nanomaterials. After the group, the paper analyzes the shortcomings of current research and proposes future directions.

Keywords: Lithium-ion batteries; silicon materials; anode materials; nanomaterials.

1. Introduction

With the development of science and technology, the demand for energy consumption is increasing. The large-scale exploitation of fossil energy has caused the reduction of limited resources, and the energy crisis has become a critical social issue. In response to this hazard, people are increasingly inclined to choose low-carbon travel methods, so many companies have invested in the research and development of electric vehicles. Batteries are one of the core components of electric vehicles and are currently the focus of study. LIBs are the market's most widely used electric vehicle batteries due to their high energy density, long cycle life, low self-discharge rate, weak memory effect, and other advantages.

In LIBs, negative electrodes are essential. It significantly influences the battery's cost and safety and determines important performance metrics like energy density and cycle life. Graphite is typically used for the negative electrodes in traditional LIBs. Nevertheless, while charging and discharging, graphite readily combines with the electrolyte to form a solid electrolyte interface (SEI) layer, which results in a poor LIB first-time coulombic efficiency [1]. Graphite is prone to co-embedding with organic solvents in the electrolyte and has comparatively low compatibility with the electrolyte [2]. This leads to the expansion and flaking of the negative graphite layer, which, in turn, lowers the cycling stability of LIBs. More importantly, the theoretical energy density of graphite materials is relatively low. With the rapid development of electric vehicles, energy storage systems, and other fields, the requirements for battery energy density are getting higher and higher. People are beginning to look for new replaceable materials.

Silicon-based materials are one of the important candidates for the next generation of high-energy density LIBs due to their excellent performance. Silicon-based anodes have a very high theoretical specific capacity, typically up to 4200 mAh/g, more than ten times higher than graphite anodes (~372 mAh/g) [3]. The working potential of silicon-based anode is moderate and slightly higher than that of graphite, which can avoid lithium precipitation to a certain extent, thus improving the safety performance of batteries. In addition, it has the advantages of excellent fast charging performance, resourcefulness, and environmental friendliness.

However, silicon-based anodes have the disadvantages of serious volume expansion, poor electrical conductivity, and easy formation of SEI film, which hinders their commercialization and application process. In recent years, the emergence of nanotechnology has effectively solved these problems. It alleviates silicon materials' volume expansion, improves silicon-based anode's electrochemical performance and conductivity, and extends the cycle life of LIBs. Therefore, this paper focuses on the application of nanotechnology in the anode of lithium-ion batteries, which has a specific reference value for the future development of lithium-ion batteries.

2. Principles and Challenges of Silicon-Based Negative Electrodes

The application of silicon in lithium-ion batteries can be traced back to the 1970s, and Seefurth et al. reported in their paper the reversible charging and discharging phenomenon of lithium-silicon alloy in high-temperature batteries [1]. The silicon anode can store and release lithium ions during charging and discharging. In the discharge process, lithium ions exit from the negative electrode, move to the positive electrode through the electrolyte, and are embedded in the positive electrode; electrons flow from the negative electrode into the positive electrode through the external circuit, and during the charging process, the lithium ions and electrons return to the negative electrode in their respective opposite paths.

Due to its many benefits, silicon is regarded as a next-generation anode material for lithium-ion batteries with a wide range of application prospects; yet, in real-world applications, silicon still confronts several difficulties. Silicon will experience a massive volume expansion of up to 300 percent during the lithium process. This volume shift will generate great stress, making the silicon material's anode break and powdery. Its volume contracts once again when it is happy, which might lead to the active material falling off the electrode and quickly reducing capacity [4]. Adverse side reactions are prevented by the presence of SEI on the anode surface. The main components of SEI are Li_2CO_3, LiF, Li_2O, LiOH and other substances. The generation of SEI consumes lithium ions, resulting in a decrease in coulomb efficiency. The expansion and contraction of the silicon anode will destroy the SEI formed on the material's surface, and the generation of new SEI will consume additional lithium ions, shortening the battery's life. In addition, the conductivity of the silicon material is poor ($<10^{-3}$ S/cm at room temperature) compared to the traditional graphite anode. Together, these factors have limited the development of silicon-based anodes.

Researchers have now developed several different methods to improve silicon anodes' performance. The research of Wu Feng et al. shows that particle size greatly influences the properties of the silicon anode material of the battery. For example, when the particle size of silicon is in the nanometer size, the capacity decay of the electrode is relatively slow, the volume expansion rate is low, and the crack and electrode crushing do not easily occur after multiple cycles [3]. This makes the application of nanotechnology in silicon anodes seen as a promising way to improve electrode performance. However, nanosilicon usually forms thicker SEI, resulting in a decrease in coulomb efficiency [3].

3. Nano Modification of Silicon

Researchers have now developed several different methods to improve silicon anodes' performance. The research of Feng Wu et al. shows that particle size greatly influences the properties of the silicon anode material of the battery. For example, when the particle size of silicon is in the nanometer size, the capacity decay of the electrode is relatively slow, the volume expansion rate is low, and the crack and electrode crushing do not easily occur after multiple cycles [4]. This makes the application of nanotechnology in silicon anodes seen as a promising way to improve electrode performance. However, nanosilicon usually forms thicker SEI, resulting in a decrease in coulomb efficiency [4]. Therefore, the particle size of silicon needs to be appropriately adjusted according to the actual situation.

3.1. 0D Structure

Nanometer technology helps to improve the conductivity of the silicon anode material, thus improving the cycle performance of the battery. The small size of the nanoparticles makes the diffusion path of lithium ions shorter, improves the transmission rate of lithium ions, and thus improves the charging and discharging efficiency of the battery. Zero-dimensional (0D) silicon nanoparticles, such as compact and hollow structures, can effectively buffer the volume expansion of silicon base cathodes during alloying because of their large specific surface area. This buffering effect helps to mitigate material comminution, thereby improving the cycle stability and life of the battery [5].

Researchers have now developed several different methods to improve silicon anodes' performance. The research of Wu et al. shows that particle size greatly influences the properties of the silicon anode material of the battery. For example, when the particle size of silicon is in the nanometer size, the capacity decay of the electrode is relatively slow, the volume expansion rate is low, and the crack and electrode crushing do not easily occur after multiple cycles [6]. This makes the application of nanotechnology in silicon anodes seen as a promising way to improve electrode performance. However, nanosilicon usually forms thicker SEI, resulting in a decrease in coulomb efficiency [6]. Therefore, the particle size of silicon needs to be appropriately adjusted according to the actual situation.

Yang et al. have investigated the characteristics of nano-silicon particles made using ball milling and pulse discharge. Before obtaining micro-nano particles with small grain sizes, highly disordered crystal orientation, and a particular amorphous structure, they first vaporized or melted the massive silicon material at a high temperature during the pulse discharge process. They then quickly condensed and ground using a ball milling method, and nano-silicon particles with a high Coulomb amorphous degree were obtained. The size distribution of the particles is uniform, with an average size of 80.4 nm. They documented the material's electrochemical characteristics, examined its structure and capacity retention capabilities, and demonstrated in their study that the nanosilicon particles made using this technique are very efficient and may significantly prolong the life of batteries [7]. In addition, carbon-coated nano-silicon particles have been shown to have superior properties than pure silicon [8].

3.2. 1D Structure

One-dimensional (1D) structure, i.e., linear, tubular material. The advantage of this kind of material is that it has a one-dimensional electron and ion transport channel, which can achieve better magnification performance. Silicon nanowire anodes (SiNWs) and silicon nanotube anodes (SiNTs) have superior performance, but the preparation cost is relatively high, so the actual commercialization progress is not smooth.

The main methods for preparing SiNWs include chemical vapor deposition (CVD) and metal-assisted chemical etching (MCE). Hu et al. used fast ion sputtering technology to prepare a dense porous catalyst on a silicon substrate to etch thinner SiNW [9]. An ultra-thin SiNW of about 10nm was then etched with HF and H_2O_2 solutions. The data show that this ultra-thin SiNW has higher cyclic performance and electrochemical activity than traditional SiNW.

Metals are frequently added to silicon nanowire compounds further to enhance silicon nanowires' mechanical characteristics and electrochemical stability. By chemically depositing nickel and annealing it at high temperatures, Ednaet al. created silicon-nickel (SiNi) composite anodes with varying compositions and contents of nickel silicide [10]. To create nickel silicide with varying composition and content, Edna Mados et al. chemically deposited nickel and then heated it to high temperatures to develop silicon-nickel (SiNi) composite anodes [10]. Figure 1 demonstrates that the SiNi negative electrode has a better capacity retention rate than the ordinary SiNW negative electrode. SiNi negative electrode showed a 0.1% loss of circulating capacity after SEI formation. The Li/SiNW-$SiNi_x$ battery runs 200 reversible cycles at C/2.

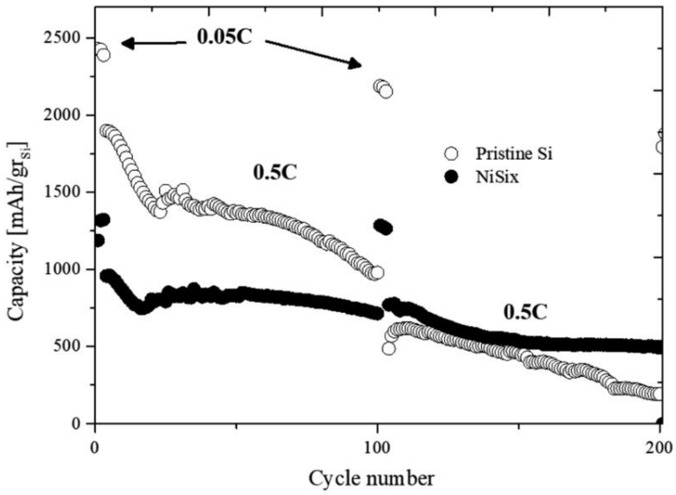

Fig 1. The cycle life of Li/SiNW and Li/SiNW–Ni cells [9].

In addition to the above methods, many studies are being conducted to modify SiNW. Farid's team deposited MoO_3 nanoparticles onto the SiNW array through a unique drip-casting technique and used a metal-assisted chemical etching method [11]. The MoO_3@SiNWs hybrid structure produced by this method shows excellent lithium storage performance and better cyclic stability than traditional SiNW. This may be due to the synergistic effect between MoO_3 nanoparticles and SiNW arrays.

Silicon nanotubes have also been investigated in great detail due to their unique mechanical characteristics: one-dimensional hollow structures. Fan et al. encapsulated the internal carbon-coated silicon nanoparticles (Si@C@CNTs) using a carbon nanotube-reinforced carbon framework generated from the metal-organic framework [12]. Si/C composites have better cycle life and structural stability thanks to the dual carbon stress-buffering function, and the external carbon skeleton enhances their charge transfer efficiency. The Si@C@CNTs electrodes demonstrated exceptional longevity and strong magnification capabilities. As can be seen from Figure 2, even at a high angulation of 1, the Si@C@CNTs electrode showed a specific capacity greater than 900 after 500 cycles.

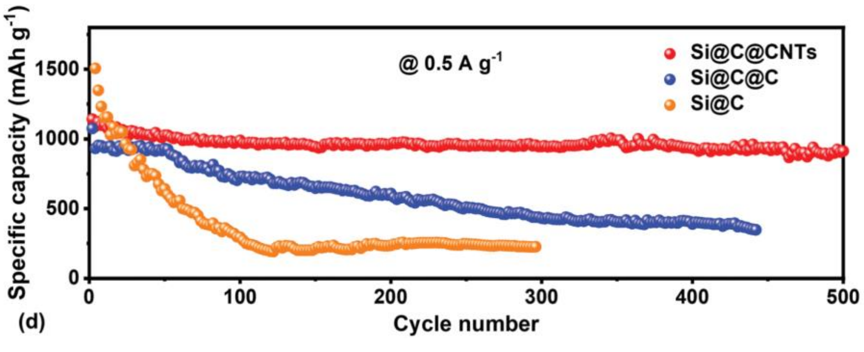

Fig 2. Properties of Si@C@CNTs [12].

3.3. 2D SStructure

Two-dimensional (2D) structure that is, sheet-like, thin-film materials. Compared with spherical, linear, and tubular materials, the two-dimensional sheet and film surface area is relatively small and can reduce side reactions and SEI film generation. Hence, the coulomb efficiency is relatively high. In addition, the volume change in the vertical direction of the layer is relatively small, which is conducive to alleviating the damage caused by the volume change on the electrode. The main preparation methods are magnetron sputtering, chemical vapor, and physical vapor deposition.

In recent years, some new preparation methods have also emerged. Liu et al. produced flexible polyurethane/copper/silicon nanocomposite films by layer-by-layer self-assembly, effectively combining the stretchability of polyurethane, copper's electrical conductivity, and silicon's lithium storage capacity [13]. This nanocomposite membrane anode showed a high capacity of 574 mAh/g and an average coulomb efficiency of 99.2-99.8% after 300 cycles at 1 C. Innovatively, Haoji Wang et al. extracted amorphous SiO_2 from kaolinite and prepared Si nanosheets by magnesium thermal reduction method, showing the possibility of low-cost and efficient production of electrode materials from minerals [14].

3.4. 3D SStructure

Three-dimensional (3D) nanosilicon materials are silicon materials with porous or hollow structural characteristics. Nanoscale porous and hollow silicon structures can significantly reduce the volume expansion of silicon during the lithium process, thereby increasing the battery's cycle life. These structures provide sufficient buffer space for silicon's volume change and avoid silicon particles' rupture and pulverization. There are many methods for preparing porous silicon, and different preparation methods and conditions greatly influence the structure and properties of porous silicon. Wet corrosion mainly includes chemical corrosion, dealloying, and hydrothermal corrosion. Dry corrosion mainly includes electric spark corrosion, laser radiation corrosion, magnesium thermal reduction, etc. The standard preparation methods of hollow silicon include template, chemical vapor, solvothermal, electrochemical, etc.

Wang et al. developed a novel hollow structure Si/C (H-SiNS/C) nanocomposite [15]. The material structure, as shown in Figure 3, consists of Si nanoparticles encased in carbon layers and mesoporous Si shells. The outermost carbon acts as a support, limiting the expansion and contraction of the inner silicon shell. The mesoporous silicon shell outside the Si nanoparticle has an internal void, which can buffer the mechanical stress generated during lithium and dilithium. This nanocomposite showed high reversible capacity (1670 mAh/g at 0.1 A/g) and excellent cyclic stability.

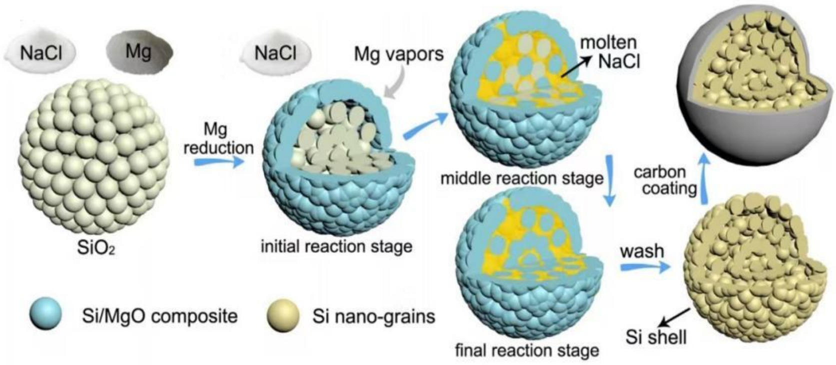

Fig 3. Preparation of Si nanoparticles and the pSi/Ag composite [15].

4. Conclusion

Lithium-ion batteries using traditional graphite anode can no longer meet the needs of emerging markets due to their limited energy storage capacity, and silicon-based materials have become the ideal choice for the next generation of lithium-ion battery anode materials with their high theoretical specific capacity. This paper summarizes the application of nanometer technology in silicon-based negative electrodes. In the 0D structure, the carbon-coated Si nanoparticles showed good rate capacity. Because the 1D structure has an ion transport channel, it shows good electrochemical performance. At the same time, composites with metal can improve their mechanical properties. 2D and 3D structures can mitigate the damage caused by volume changes during lithiation and delithiation. The preparation of these materials can be the focus of future research.

Although nanostructured silicon and its dimensional design are conducive to improving the material's electrochemical properties and the volume change problem, many obstacles remain to large-scale commercial production. First, nanomaterials' high specific surface area brings high irreversible capacity loss. Secondly, silicon's expansion rate in lithium and dilithium can reach 300% to 400%. However, there are some methods to reduce this number; this repeated expansion and contraction of the volume will inevitably lead to cracks or even pulverization of the silicon anode material, destroy the contact between the electrode material and the fluid collector so that the active material is separated from the pole sheet. This, in turn, causes a rapid decline in battery capacity. For 3D structures, this stress may also cause a reduction in the internal porosity of the battery, affecting the battery's performance. The instability of SEI film is still a common phenomenon. In addition, the preparation process for the above materials is complex, and the cost is high, limiting its large-scale production. Of course, in the future, we may be able to further mitigate the volume effect through more refined nanization techniques, such as controlling the size and shape of nano-silicon particles and optimizing the dispersion and uniformity of nano-silicon. The surface of nanosilicon is also treated by chemical or physical methods to form a stable SEI film and reduce the irreversible consumption of lithium ions. And through technological innovation to find ways to reduce manufacturing costs. With the vigorous development of electric vehicles, the demand for high energy density and long cycle life batteries continues to increase, and the application prospect of nano-silicon anode materials will be broader. Shortly, nano silicon anode materials are expected to become one of the essential development directions in lithium-ion batteries.

References

[1] Sharma Ram A., Seefurth Randall N. Thermodynamic properties of the lithium-silicon system. Journal of the Electrochemical Society, 1976, 123(12): 1763-1768.

[2] Wang L, Xi F., Zhang Z, et al. recycling of photovoltaic silicon waste for high-performance porous silicon/silver/carbon/graphite anode. Waste Management, 2021, 132: 56-63.

[3] Zhang H, Wang L, Li H, ET AL. Criterion for Identifying Anodes for Practically Accessible High-Energy-Density Lithium-Ion Batteries. ACS Energy Lett, 2021, 6: 3719-3724.

[4] Ge MZ, Cao CY, Biesold G., et al. Recent advances in silicon-based electrodes: from fundamental research toward practical applications. Advanced Materials, 2021, 33(16): e2004577.

[5] Sun L, Su T, Xu L, et al. Preparation of uniform Si nanoparticles for high-performance Li-ion battery anodes. Physical Chemistry Chemical Physics, 2016, 18(3): 1521-1525.

[6] Wu F, Dong Y, Su Y, et al. benchmarking the effect of particle size on silicon anode materials for Lithium-ion batteries. Small, 2023, 19: 2301301.

[7] Yang H, Shang H, Zhang X. Properties of silicon nanoparticles prepared by pulse discharge and ball milling. Nanoscale, 2024, 16: 14510-14521.

[8] Zhao J, Rui B, Wei W, et al. encapsulating silicon particles with graphitic carbon enables high-performance lithium-ion batteries. Journal of Colloid and Interface Science, 2021, 607(2): 1562-1570.

[9] Hu Z, Tan Z, Sun F, et al. The high cycling performance of ultra-thin Si nanowires fabricated by metal-assisted chemical etching as lithium-ion batteries anode. Journal of Electroanalytical Chemistry, 2020, 878: 114567.

[10] Edna Mados, Nimrod Harpak, George Levi, et al. Synthesis and electrochemical performance of silicon-nanowire alloy anodes. RSC Advances, 2021, 11: 26586-26593.

[11] Ghulam Farid, Roger Amade-Rovira, and Rogelio Ospina, et al. Surface modification of silicon nanowires via drop-casting for high-performance Li-ion battery electrodes: SiNWs decorated with molybdenum oxide nanoparticles. Journal of Energy Storage, 2024, 78: 110104.

[12] Fan X, Cai T, Wang S, et al. Carbon nanotube-reinforced dual carbon stress-buffering for highly stable silicon anode material in lithium-ion battery. Small, 2023, 19: 2300431.

[13] Liu L, Li M, Chu L, et al. Facile fabrication of flexible Si-based nanocomposite films as high-rate anodes by layer-by-layer self-assembly. Applied Surface Science, 2019, 476: 501-512.

[14] Wang H, Tang W, Ni L, et al. Synthesis of silicon nanosheets from kaolinite as a high-performance anode material for lithium-ion batteries. Journal of Physics and Chemistry of Solids, 2020, 137: 109277.

[15] Wang J, Gao C, Yang Z, et al. Carbon-coated mesoporous silicon shell-encapsulated silicon nano-grains for high-performance lithium-ion batteries anode. Carbon, 2022, 192: 277-284.