Research Progress of Silicon/Carbon Anodes in Lithium-Ion Batteries

Jiayi Fu *

Shanghai Jincai High School, Shanghai, China

* Corresponding Author Email: j7932289@gmail.com

Abstract. Lithium-ion batteries (LIBs) have garnered attention because of their high energy density and lightweight properties. However, LIBs typically use graphite for the anode material, which shows a relatively low specific capacity that can hardly meet the growing energy storage demands. Compared with traditional graphite anodes, silicon anodes have already been proven to possess higher specific capacities. Additionally, silicon is abundant and relatively inexpensive. Nonetheless, silicon anodes undergo significant volume expansion during the charge-discharge process, generating mechanical stress that can lead to potential cracking and capacity loss. Moreover, they exhibit relatively low initial coulombic efficiency, causing a considerable amount of lithium to be irreversibly consumed during the initial cycles. To address these issues, various nanotechnology-based strategies have been developed, including silicon/carbon (Si/C) composite anodes and the development of other nanostructured materials. These approaches aim to optimize interface structure, particle structure, and composite structure design to enhance battery performance and durability. This paper provides a comprehensive review of the application of nanotechnology in silicon anodes, focusing on the advancements in silicon/carbon composites and their effects on mitigating volume expansion, improving initial coulombic efficiency, and maintaining capacity retention. Additionally, it analyzes the impact of different nanostructure designs on battery performance.

Keywords: Lithium-ion battery; Silicon anodes; Nanotechnology.

1. Introduction

In today's globalization, energy crisis and environmental pollution have become the two major challenges facing human society. Among them, the overuse of fossil fuels has led to the rapid reduction of resources and serious environmental problems, which has caused global warming, acid rain and many potential health problems. Therefore, finding clean and renewable energy solutions has become a common goal for all countries. In this context, electrification technology, especially the electrification technology with clean energy as the core, has been widely concerned and developed rapidly. At the heart of electrification lies clean production, efficient storage and efficient use of energy. Therefore, under the promotion of many governments, the market share of electric vehicles is steadily increasing and becoming an important part of transportation electrification. Among them, the technology for energy storage in electric vehicles (EVs) as a bridge connecting energy production and consumption plays a crucial role, lithium-ion battery (LIB) which are known for its high energy density and long cycle life, which has become one of the most promising technologies for energy storage. However, as the demand for electrification is increasing, traditional energy storage technology faces bottlenecks. Although graphite has good conductivity and cycle stability, it only offers a specific energy with about 150 Wh kg^{-1} and has almost reached its theoretical specific capacity (372 mAh g^{-1}). This is not sufficient to meet the specific energy requirements needed by EVs so as to meet the performance of internal combustion vehicles [1]. And dendrites, which are some microscopic, needle-like structures that can form inside the battery during charging and discharging cycles. This can lead to the growth of protruding lithium metal structures, make the solid electrolyte interphase (SEI) unstable, which can enter the separator and cause short circuits inside the battery. As a result, developing high-performance and safer anode materials is key to enhancing the energy density of LIBs.

Among many candidate anode materials, silicon (Si) is considered one of the most prospective materials because of its exceptionally high theoretical capacity (approximately 4200 mAh g^{-1}) and its abundant availability in the earth crust. Despite these advantages, Si anodes continue to have numerous challenges in terms of practical applications. First, the silicon expands by more than 300% during the lithium process, resulting in powdery material collapse of electrode structure (Fig. 1), so the development of unstable SEI on the Si surface, and the Li being trapped in the active silicon material, causing a low initial coulombic efficiency (CE) and swift irreversible loss of capacity [2]. Secondly, silicon's low conductivity results in poor rate performance under high current densities. To address these issues, researchers have proposed various structural designs and modification methods to enhance both efficiency and stability of Si anodes.

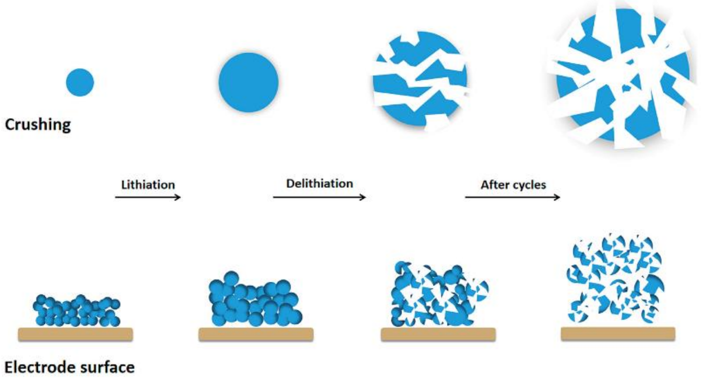

Fig. 1 volume expansion and material pulverization of Si anode [3]

In this paper, the structural evolution and the impact of nanotechnology on electrochemical characteristics of Si anode materials are reviewed. The structural design of different generations, including core-shell structures, yolk-shell structures, porous structures, high-tap-density packed yolk-shell structure, etc, are also introduced. These structural designs not only significantly mitigate the volume expansion issue of Si anode, but also enhance the cycling stability of the material. The future development trends of Si anode materials are anticipated as well.

2. Application of nanotechnology in silicon anode of lithium battery

2.1. Silicon/carbon Composite Anode

Si/C composites are commonly fabricated by molding and sintering on the basis of silicon sources and a variety of raw materials of carbon. Si-C coupling effectively integrates the high specific capacity of silicon while mitigating its significant volume changes during cycling. The structures of Si/C composites typically fall into 4 structural categories: core-shell, yolk-shell, porous and embedded structures.

2.1.1 Core–shell Structure

The core-shell structure in a silicon-carbon anode typically involves a silicon core surrounded by a carbon shell. Shao et al. [4] designed monodisperse nanostructured Si/porous carbon spheres (N-SPC). These composites were synthesized via hydrothermal process utilizing glucose as the carbon source and using Pluronic F127 as the catalyst for pore formation (refer to Fig. 2). This method ensures that each silicon nanoparticle (NP) is evenly coated with carbon layer. This structure offers several advantages: (1) Accommodation of volume changes: The porous carbon shell buffers the volume variations of Si NPs during charge and discharge cycles, which mitigates the issue of particle pulverization—a major cause of capacity loss. (2) Enhanced electrochemical performance: The carbon shell facilitates the formation of a stable SEI film and enhances the transport of Li ions and electrons. This results in reduced charge transfer resistance and improved cycling stability and rate capability. (3) Specific surface area: The composite’s specific surface area is significantly increased compared to bare silicon nanoparticles, which is beneficial for electrochemical performance. The BET measurement confirmed a surface area of 197.9 m² g^{-1} for the N-SPC composite, compared to 31.0 m² g^{-1} for bare silicon nanoparticles. The composite exhibited excellent stability, the material exhibits a stable capacity of 1607 mAh g^{-1} after 100 cycles at a density of 0.4 A g^{-1} and retains a reversible capacity of 1050 mAh g^{-1} even under a high current density of 10 A g^{-1}.

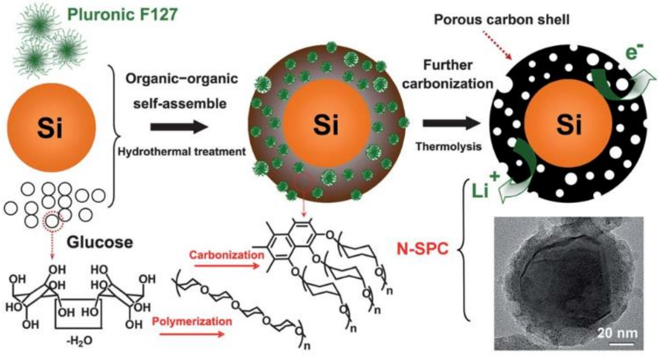

Fig. 2 monodisperse nano-structured silicon/porous carbon spheres [4]

2.1.2 Yolk–shell Structure

Compared to the conventional core-shell structure, the yolk-shell structure includes an empty space situated between the inner Si core and external carbon shell. This design enables the inner silicon yolk to expand without causing damage to the outer carbon shell, as shown in Figure 3. The void space confines the Si volumetric expansion, limiting SEI film formation to the exterior surface of the carbon shell. Consequently, this enhances the structural stability of SEI and improves the CE during prolonged cycling tests.

It has high capacity about 2800 mAh g^{-1}, the cycle life is also long with 74% capacity remains after 1000 cycles, and CE is high (99.84%).

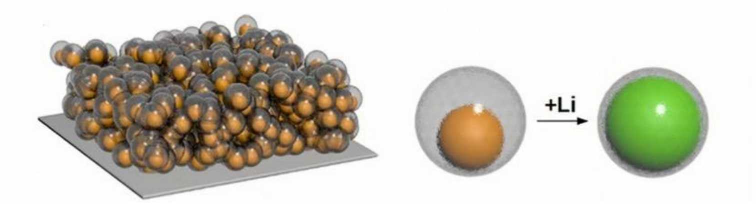

Fig. 3 Yolk-shell structure [5]

However, the nanosized yolk-shell structure brought new challenges too.

(1) The growth in surface area leads to a rise in side reactions between the electrode and the electrolyte, causing an increase in electrolyte reduction and a decrease in CE.

(2) The incorporation of spaces within the NPs significantly reduces the electrode tap density, resulting in lower capacity and higher mass loads during the battery production.

(3) In the process of continuous lithiation and delithiation, due to changes in size, the electrical contact between the electrode particles often changes and decreases, greatly shortening the cycle life of electrodes.

Drawing inspiration from the structure of a pomegranate, researchers developed an advanced yolk-shell design where nanosized Si/C yolk-shell particles are assembled into a microsized particle and then encased in a carbon coating that acts as an electrolyte barrier (Fig. 4). This innovative approach results in a silicon anode with excellent cyclability, retaining 97% of its capacity after 1,000 cycles.

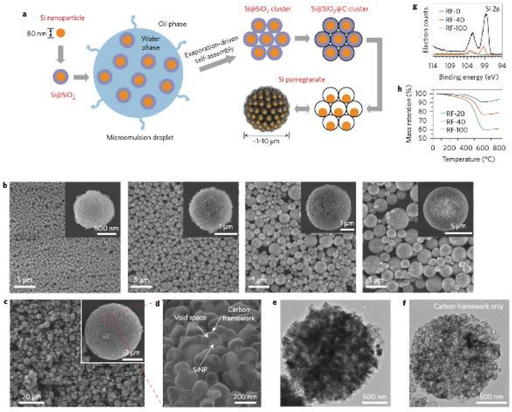

Fig. 4 Fabrication and characterization of silicon pomegranates [6]

2.1.3 High-tap-density Packed Yolk-shell-structured Si/C Anodes

Solvent evaporation caused weak packing force, the density of the pomegranate-like micrometer-sized secondary clusters (SC) is still not high enough, about 0.53 g cm^{-3}. Second, scalability, manufacturing efficiency and yield are still far from the actual requirements.To increase tap density, Cui el al. [7] first prepared the nanostructured blocks by high- pressure dry pressing (HPDP) technique. The blocks are then pulverized into micron-scale powders using high energy mechanical milling (HEMM) treatment. This method offers several key benefits: the techniques used are industrially mature and do not require complex nanostructured assembly, so the yield can be high, leading to efficient manufacturing. It shows a density of over 1.38 g cm^{-3} under ~100 MPa, after 1400 cycles at 1C, more than 95% of the original capacity is still remained, and the average specific capacity ~1250 mAh g^{-1}.

2.1.4 Porous Structure

Jia et al. [8] synthesized a composite material of carbon nanotubes and silicon (CNT@Si@C) through a multi-step process, ultimately preparing microspheres (Fig. 5). First, they created CNT@SiO$_2$ microspheres via a sol-gel method. Then, these microspheres were converted into CNT@Si through aluminothermic reduction, and finally, a carbon coating was applied using chemical vapor deposition (CVD). And the structural integrity and composition of the synthesized material were analyzed through a series of characterization methods. These analyses confirmed the uniformity and effectiveness of the coatings. The electrochemical performance was assessed by measuring the capacity. The CNT@Si@C anodes exhibited a capacity of about 1500 mAh g^{-1} and retained 87% of this capacity after 1500 cycles. The mechanical strength of these microspheres was exceptionally high, exceeding 200 MPa, with minimal particle expansion of around 40% upon full lithiation.

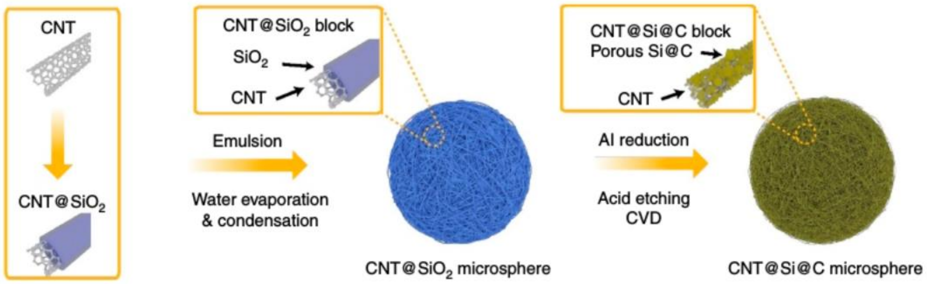

Fig. 5 synthesis of CNT@Si@C microspheres [8]

2.1.5 Embedded Structure

Wang et al. [9] prepared PDDA-modified silicon nanoparticles (SNPs) by adding 1 g of SNPs into a 10 mL PDDA aqueous solution, stirring for 4 hours, washing with distilled water, and drying in vacuo at a temperature of 40°C for 24 hrs. They then synthesized graphene/SNPs composite (GSc) by mixing 0.3 g of graphene, 0.7 g of PDDA-modified SNPs in 0.1L distilled water, stirring at 40°C for 4 hours, filtering, and drying in a vacuum oven. The final composite (GSCS) was obtained by mixing GSc with SBL, treating it with ultrasonic treatment, pouring it into a glass mold, soft-baking, and finally heating at 500°C in argon for 4 hours. The analysis revealed that the soft carbon layer encapsulating the SNPs effectively mitigated volume expansion and prevented repeated SEI film formation. The soft carbon layer provided fast lithium-ion diffusion channels as its alternating regions and crystalline structures. The three-dimensional free-standing graphene scaffold offered high electronic conductivity and eliminated interactions between the particles during charging and discharging cycles. The mechanical tests showed high tensile modulus and stability of the GSCS electrode. The GSCS composite exhibited improved specific capacity and cycling stability. The specific capacity was about 2600 mAh g^{-1} at 0.2 A g^{-1} with slight capacity reduction after 100 cycles. The resistance of the GSCS electrode was significantly smaller than the Si/G electrode, indicating improved conductivity. The embedded soft carbon layer and the 3D graphene scaffold collectively enhanced the performance of the silicon anode, paving the way for advanced anodes.

2.2. Si/C/TiO2 Composite Nanofibers

Ma et al. [10] utilized a combination of experimental techniques to fabricate and analyze silicon/carbon/titanium dioxide ($Si/C/TiO_2$) composite nanofibers for LIB anodes. They employed an electrospinning method to produce these composite nanofibers, followed by thermal annealing to create free space for silicon’s volume expansion during lithiation. For electrode preparation, they made a slurry with the active materials, coated it onto copper foil, and dried it before assembling it into coin cells. Electrochemical performance was assessed using galvanostatic cycling tests to evaluate the capacity and cycling stability of the composite nanofibers. The results illustrated that the $Si/C/TiO_2$ composite nanofibers illustrated a specific capacity of over 720 mAh g^{-1}, and 94% of it retained after 55 cycles when the Si/C mass ratio is 0.217 and the fabrication cost is relatively low, demonstrating their potential as efficient anode materials for LIBs [11].

3. Outlook

In the realm of silicon anode technology, the yolk-shell structure demonstrates extraordinary potential in revolutionizing LIBs. Researchers should focus on exploring and optimizing the electrochemical properties of different forms of silicon anode materials, especially the yolk-shell structure, which holds important prospects for improving capacity, energy density, cycle stability, and charge transfer rate. By studying different shell materials and optimizing void sizes to better accommodate silicon expansion, further improvements in the design of yolk-shells can improve mechanical stability and electrochemical performance, thereby extending cycle life and improving capacity retention. Addressing the challenges of complex and expensive synthesis methods is critical to the commercial viability of yolk-shell structured silicon anodes. Efforts should be made to develop low-cost, scalable production technologies and use renewable materials or waste to reduce manufacturing costs. Through experimental and theoretical analysis, researchers need to study the effects of morphology on energy storage performance in more depth, revealing the mechanisms that influence the overall behavior of silicon anodes at the macro and micro levels. Future research should focus on the performance differences of different Si anode forms in LIBs, and further explore and discuss the influence of form modulation on energy storage performance and potential improvement directions. Si anode materials, especially those with yolk shell structure, have broad application prospects in EVs and extensive energy storage systems because of their high capacity and stability to meet the requirements of these applications. Further research into multifunctional silicon anode materials, such as self-healing or porous silicon nanowires, could open up new horizons and provide additional benefits such as enhanced durability and performance, making them ideal for advanced battery applications. By addressing these research directions and application prospects, the yolk-shell structure in Si anodes has the potential to significantly improve LIB performance and commercial viability, contributing to the development of high-capacity, long-life energy storage solutions.

4. Conclusion

This paper provides a comprehensive review of the application of nanotechnology in enhancing Si anodes for LIBs. The article addresses major challenges associated with silicon anodes, such as volume expansion, low initial CE, and irreversible capacity loss, and discusses various nanotechnology-based strategies, including the development of Si/C composites and other nanostructured materials to mitigate these issues. The research results demonstrate that nanotechnology significantly improves the performance and lifespan of silicon anodes, paving the way for high-performance, cost-effective lithium-ion batteries. Furthermore, future research should focus on further improving the efficiency, scalability, and economic feasibility of these materials, thereby advancing more reliable and efficient energy storage solutions to address the increasing demand for sustainable energy technologies.

References

[1] Shen, Xiaohui, et al. Research progress on silicon/carbon composite anode materials for lithium-ion battery. Journal of Energy Chemistry 274 (2018): 1067-1090.

[2] M. Ashuri, Q. He, L.L. Shaw. Silicon as a potential anode material for Li-ion batteries: where size, geometry and structure matter. Nanoscale 8 (2016) 74–103

[3] Zhou, Xinyan, et al. Soft X-ray emission spectroscopy finds plenty of room in exploring lithium-ion batteries. Materials Research Letters 11.4 (2023): 239-249.

[4] Shao, Dan, et al. Nanostructured silicon/porous carbon spherical composite as a high-capacity anode for Li-ion batteries. Journal of materials chemistry A 1.47 (2013): 15068-15075.

[5] Liu, Nian, et al. A yolk-shell design for stabilized and scalable Li-ion battery alloy anodes. Nano letters 12.6 (2012): 3315-3321.

[6] Liu, Nian, et al. A pomegranate-inspired nanoscale design for large-volume-change lithium battery anodes. Nature nanotechnology 9.3 (2014): 187-192

[7] Lin, Dingchang, et al. A high tap density secondary silicon particle anode fabricated by scalable mechanical pressing for lithium-ion batteries. Energy & Environmental Science 8.8 (2015): 2371-2376.

[8] Jia, Haiping, et al. Hierarchical porous silicon structures with extraordinary mechanical strength as high-performance lithium-ion battery anodes. Nature communications 11.1 (2020): 1474.

[9] Wang, Fei, et al. Nano-silicon@ soft carbon embedded in graphene scaffold: High-performance 3D free-standing anode for lithium-ion batteries. Journal of Power Sources 450 (2020): 227692.

[10] Ma Kunlong. Short term distributed load forecasting method based on big data. Changsha: Hunan University, 2014.

[11] Wu, Qingliu, et al. Electrospun silicon/carbon/titanium oxide composite nanofibers for lithium-ion batteries. Journal of Power Sources 258 (2014): 39-45.