Improvements in the Performance of Silicon-Based Anode Materials for Lithium-Ion Batteries

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Abstract: Lithium-ion batteries (LIBs) have emerged as the preferred choice for electric vehicles (EVs) owing to their lightness, prolonged lifespan, and superior energy density. Despite graphite's prevalent use as the anode material in the commercial LIB, its limited specific capacity poses challenges in satisfying the escalating energy storage requirements. As a result, high-energy anode materials for LIBs are prioritized. The silicon anode materials have received widespread praise because of their high specific capacity. Still, the structural alterations and growth in volume of silicon anode materials throughout both charging and discharging processes severely restrict their practical uses. Through structural optimization and composite modification of silicon anode materials, their electrochemical performance can be effectively enhanced, which is crucial for the creation of high-energy LIBs. This paper systematically reviews the research progress of the silicon anode and its composite materials in terms of structure optimization, composite modification, and energy storage performance at this stage. It looks forward to the future development patterns of such materials.

1 INTRODUCTION

In the twenty-first century, the continuous growth of global energy demand and the urgency of environmental protection issues have driven the energy transition to clean energy sources such as electricity. In this transition, the rise of new energy vehicles, especially electric vehicles (EVs), not only offers a fresh approach to addressing the issues of energy depletion and environmental pollution but also promotes the rapid development of related technologies. Compared with traditional fuel vehicles, the environmental advantages of new energy vehicles are particularly significant. Driven by electricity, they significantly reduce CO_2 emissions, helping to alleviate the pressure of global warming. At the same time, new energy vehicles run more quietly, significantly reducing urban noise pollution and providing a more liveable environment for residents. However, new energy vehicles are not perfect. Although they have many advantages such as environmental protection, energy saving, and high efficiency, issues such as range and safety are still challenges. To overcome these challenges, innovations in battery technology have become crucial. Because of its outstanding energy density and prolonged cycle life, lithium-ion batteries (LIBs) currently hold the top spot in the batteries used in EVs. This kind of battery realizes the efficient conversion of electrical energy and chemical energy by shuttling Li^+ between the cathode and anode (as shown in Figure 1), and its main structure includes the cathode, anode, electrolyte, and diaphragm. Among them, the anode material is a key factor affecting its performance.

The traditional carbon anode material has better stability, but its theoretical specific capacity is limited, making it difficult to meet the demand for high-capacity batteries in EVs. Since silicon anodes can have a specific capacity of 3580 mAh/g, they are highly respected. Additionally, silicon is thought to be a viable anode material for LIB with a high energy density because it is abundant in nature, environmentally friendly, and has a good electrochemical potential.

Nevertheless, there are several fatal drawbacks of silicon material as anodes for LIBs. First, during charging, the silicon anode undergoes an alloying reaction with lithium, resulting in an expansion of the electrode volume by about 300%. The silicon anode is ground up and an unstable solid electrolyte interface (SEI) is created as a result of this expansion, leading to the active material and collector losing their electrical connection, which makes it harder for Li^+ to be embedded and eventually reduces capacity

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and initial Coulombic efficiency. Furthermore, the silicon anode's expansion increases the electrode surface area, necessitating more Li^+ consumption to form the SEI film, causing a decrease in battery capacity. In addition, the diffusion coefficient of Li^+ in silicon is not high, ranging from 10^{-14} to 10^{-13} cm²/s, a property that results in a large Li^+ concentration gradient in silicon, which generates large internal stresses during cyclic charging and discharging, ultimately leading to fragmentation of silicon particles. Meanwhile, the low conductivity of silicon tends to electrically insulate the crushed silicon particles, which in turn affects the capacity of the cell and results in a significant loss of capacity.

To overcome these challenges, researchers are actively exploring various modification methods. They do so by designing rational silicon anode structures, introducing buffer layers or composites, and other techniques, to enhance the performance of silicon anodes. Thus, this paper examines and evaluates the research advancements of silicon anode materials for LIBs, and anticipates future research on silicon anode materials.

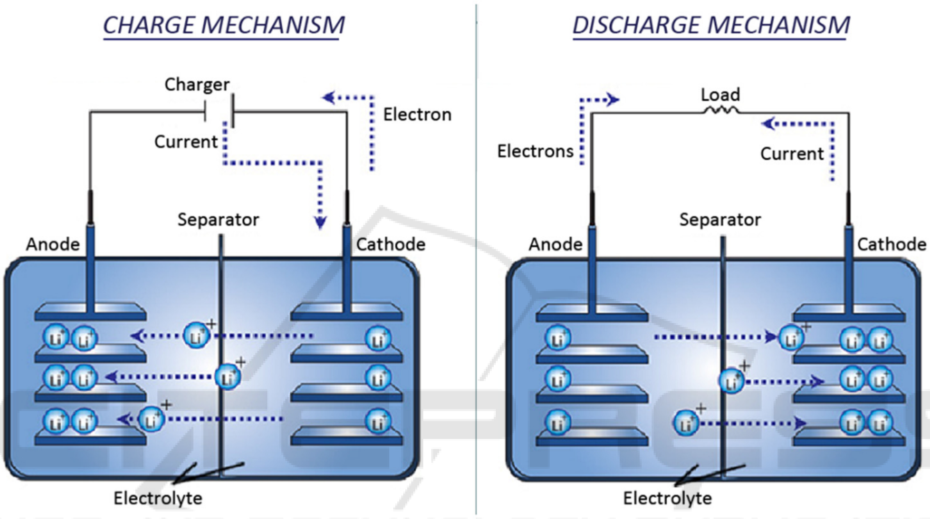

Figure 1: Schematic diagram of the operating principle of a LIB (Omar et al., 2012).

2 TYPES AND ADVANTAGES AND DISADVANTAGES OF LIBS ANODES

2.1 Nanosilicon Anode

The diffusion time of Li^+ in the electrode is jointly influenced by the diffusion coefficient (D_{Li}), diffusion length (L) and the natural characteristics of the material. Equation 1 shows that by drastically lowering the particle dimension, the nanosizing technology may greatly shorten the Li^+ diffusion length, increasing power density and mechanical strain tolerance. Therefore, in order to solve the particle fragmentation problem of silicon anode due to the large Li^+ concentration gradient, silicon nanostructures such as nanotubes (NTs), nanowires (NWs), and nanofibres (NFs) have been widely used to optimise the electrode structure and electrical properties, especially silicon nanowires (SiNWs) and nanotubes (SiNTs), which have a significant reversible capacity exceeding 200 mAh/g, and exhibit excellent cycling stability.

$$t = L^2 / D_{Li} \tag{1}$$

Among the preparation methods of nanosilicon, hydrothermal method is favoured due to its low cost, environmental friendliness, and applicability to large-scale production. Scientists have successfully prepared high-purity nanosilicon by selecting different silicon sources, such as (2-aminoethylamino) propyltriethoxysilane and tetraethyl orthosilicate (TEOS), in combination with hydrothermal methods. In addition, rice husk, as an agricultural waste in people's daily life, has a SiO_2 content as high as 10% to 20%, which not only reduces the cost but also is environmentally friendly and feasible as a silicon source for the production of nanosilicon. Currently, Sudarman et al. (2024) have successfully prepared high purity nanosilicon by hydrothermal method using rice husk, and this nanosilicon works well as a LIB anode, exhibiting a capacity of 1,757 mAh/g and continuing to do so after approximately 200 cycles. Its energy density and cycling stability surpass those of commercial batteries, graphite, and graphene.

Nonetheless, the nanosilicon anode still suffers from poor electrical conductivity and high manufacturing cost, which limits its large-scale industrial application. Therefore, future research needs to further explore how to reduce the manufacturing cost of nanosilicon anodes while improving energy density and cycling stability, in order to promote their widespread application in the field of LIBs.

2.2 Silicon Alloy Anode

In the pursuit of enhancing the electrochemical performance of silicon anode, in addition to adjusting the dimension of silicon particles, another effective method is to combine silicon with suitable metals (e.g., Ni, Cu, Sn, Pb, Li, etc.) to form an alloy phase. This alloying strategy takes advantage of the ductile properties of metals to give silicon alloy composites the ability to slow down the volume expansion of silicon.

Firstly, silicon and lithium can form a variety of alloys, such as $Li_{12}Si_7$, $Li_{13}Si_4$, Li_7Si_3, $Li_{15}Si_4$, $Li_{22}Si_5$, etc., which not only have high capacity, but also have de-embedded lithium potentials lower than 0.5 V vs. Li/Li^+, with $Li_{22}Si_5$ having a capacity of up to 4200 mAh/g.

In addition to Si-Li alloys, there are other silicon-based alloy materials. Mukanova et al. (2017) achieved a facet capacity of 80 mAh/cm² by forming a three-dimensional composite anode with silicon thin films on graphene-coated nickel foam by chemical vapour deposition and magnetron sputtering. Ding et al. (2020) prepared a binder-free anode with bilayer graphene-coated silicon nanoparticles (SiNPs) embedded in the porous nickel current collector, and although a respectable face capacity was achieved, the performance of the interfacial layer still needs to be improved. In view of this, Tzeng et al. (2023) proposed thick and porous silicon-based anodes, and constructed porous anodes with electrical conductivity on nickel foam by mixing SiNPs, phenolic resin binder, and the conductive agent Super P, which exhibited excellent cycling performance and charge storage capacity. Experiments shown that the 80 nm nickel foam nanoporous silicon-based anode maintained excellent performance after a total of 50 cycles, where the current density was 4 mA/cm^2, retaining a retained area capacity of up to 6.5 mAh/cm², which provided a charge storage capacity of 23.4 C for an anode area of 1 cm² at a current rate of 4 mA.

In particular, the eutectic reaction takes place throughout the melting procedure because the melting points of Cu and Si are slightly different. This makes it simpler for Si to create the Cu_3Si alloying phase and evenly disperse it on the Si matrix resulting in greater suppression of the volume growth. Zhang et al. (2021) first prepared Si-Cu_3Si composite with a capacity of 1000 mAh/g after 300 cycles, while Li et al. (2023) prepared P-doped Si-Cu alloys by the vacuum melting method, which improve the electrical conductivity and lower the Li^+ diffusion barriers to significantly enhance the electrochemical performance, Among these, the $P_{0.5\%}$Si-Cu alloy had a significantly lower R_{ct} value than the undoped Si-Cu alloys, with a capacity of 1048 mAh/g after 60 cycles.

In addition, Si-Sn alloy anode has sparked much interest because of its unique lithium embedding ability and buffering effect on volume change. Tian et al. (2021) successfully prepared a novel anode material consisting of tin nanowires (SnNWs) embedded with SiNPs by solid-gas reaction method, which exhibited a high and stable capacity at both room and low temperatures.

Although silicon alloy structure has significant effect in solving the swelling problem of silicon-based anode, its preparation process is complicated and costly, which limits its mass production application. Therefore, researchers have turned to the strategy of compositing nanosilicon and carbon materials to seek performance enhancement and cost reduction.

2.3 Silicon-Carbon Composite Anode

In the field of LIBs, carbon anodes are known for their high cycle life, while silicon anodes exhibit excellent specific capacity. Based on this, scientists have proposed to dope carbon atoms into a silicon anode to obtain a LIB anode with high specific capacity and long service life Therefore, researchers have proposed a silicon carbon anode and achieved their goal with the help of nanotechnology. Wu et al. (2024) have found through their study that the volume variation of silicon was successfully inhibited when the doping concentration of carbon atoms was in the range of 1.56% to 15.6%. This suppression effect is attributed to the high strength of the Si-C covalent bond, which results in a denser structure of the material and a consequent increase in bulk modulus. In addition, the inhibition effect on the volume expansion of silicon shows an enhanced trend as the carbon concentration increases. Carbon compounds come in a variety of forms, including graphite, graphene (Gr), carbon nanotubes (CNTs), carbon nanofibres (CNFs), graphene oxide (GO), reduced graphene oxide (rGO), and so forth.

Graphene, renowned for its flexibility and conductivity, mitigates silicon's volume changes, enhances electron transfer, and isolates particles from the electrolyte, suppressing excessive SEI formation. Besides, its defects and edges provide additional sites for lithium storage, accelerating Li^+ transport in the anode and thus significantly improving the multiplicity performance of the battery. However, it is challenging to attain optimal dispersion via straightforward mechanical mixing because of graphene's neutral property. The introduction of GO can effectively address the dispersion issue because irregularly dispersed SiNPs are more likely to undergo electrochemical sintering and agglomeration throughout the charging and discharging process. So, Ko et al.(2014) proposed the use of chemical vapor deposition (CVD) technology to prepare porous GO with silicon skeleton as an anode material for the LIB, which significantly improved the cycle stability. The material was tested to maintain an average capacity of 1103 mAh/g after 1000 cycles with a Coulombic efficiency of up to 92.5% on the first cycle. However, CVD technology is expensive and not suitable for large-scale industrialization.

Electrostatic spinning technology, on the other hand, offers a simple and economical method of preparing carbon fibres. As a result, silicon is often embedded in carbon fibers as an anode material for LIB. Gómez-cámer et al. (2011) utilized a SiO_x layer to strengthen the bonding of SiNPs to the CNFs surface, which significantly enhanced the ion and electron transport efficiency. However, this anode's capacity decayed from 2500 to 500 mAh/g after 500 cycles, due to excessive SEI formation and poor stability. Ji et al. (2009), on the other hand, attempted to convert the polyacrylonitrile/SiNPs solution into SiNPs-embedded CNFs composites by electrospinning, but the cycling stability dropped to 0.5 mAh/g, 51% of initial after 50 cycles, showing the inadequacy of this method in suppressing the generation of unstable SEI layers. Dirican et al. (2015) went on to enhance the cycling stability by depositing amorphous carbon on SiNPs-embedded CNFs using the CVD method. However, the aggregation of SiNPs and the problem of carbon fiber fracture due to silicon swelling remain key challenges to be addressed in this field.

Despite the high specific capacity and relatively mature process of silicon-carbon composite structures, their industrial production and cycling performance still need to be further improved.

2.4 Yolk-Shell Structure Anode

While depositing SiNPs on the outer layer of carbon materials can significantly improve the anode's performance, the research on improving the LIB anode's efficiency shows that each charge/discharge's efficiency falls short of more than 99%. The reason for this is that during the cycling process, a portion of the silicon particles is near the fluid, causing the particles to grow and shrink with each charge and discharge. This prevents the SEI film from existing steadily and causes it to be continually destroyed and regrown. Therefore, the core-shell structure was born. Despite the conventional core-shell design utilizing silicon as the core with a carbon shell coating, it lacks a buffer zone for silicon's volume expansion. Consequently, researchers have innovated by adopting a yolk-shell architecture, where silicon serves as the yolk and carbon as the shell. This approach introduces a gap between the carbon shell and silicon particles, allowing for unconstrained expansion and contraction of silicon while preventing damage to the carbon shell due to volume variations in the silicon particles. The anode designed by Liu et al. (2012) is similar, which is shown in Figure 2. After testing, yolk-shell anode demonstrated initial capacity of 2800 mAh/g, retaining 74% (1500 mAh/g) after 1000 cycles, achieving 99.8% Coulombic efficiency.

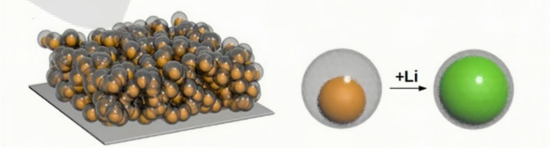

Figure 2: Structure of the yolk-shell type anode (Dirican et al., 2015).

Liu et al. (2014) further optimized the previous yolk-shell design in a follow-up study by adopting a pomegranate-like layered architecture. This structure featured SiNPs in a conducting carbon coating in a yolk-shell-like configuration, and the entire structure was encased in a thicker carbon shell at the micron level. The strength of the SEI layer is increased by the thicker carbon shell, which also has a significant impact on the conductivity of electrons and Li^+. Durability testing revealed a capacity retention rate of

97% and a Coulombic efficiency of 99.8% after 1000 cycles.

Yu et al. (2024), on the other hand, proposed a Si@Void@FC (fiber carbon) composite structure. This material simplifies the preparation process through a one-step synthesis method and cleverly combines a void yolk-shell structure with a mesoporous carbon shell, which can exhibit excellent cycling stability and outstanding rate performance, and even after 500 cycles, the structure remained intact without significant performance degradation. This is so that excessive contact with the electrolyte is avoided and the volume growth of silicon while cycling is efficiently inhibited by the protective coating that is the outside carbon shell. In addition, the unique mesoporous structure significantly improves the diffusion efficiency of Li^+, which in turn enhances the lithiation and de-lithiation ability of the material.

In addition, Liu et al. (2024) pioneered the concept of fluoride ion-modified yolk-shell-type carbon-silicon anode materials. Through the interfacial modification of fluoride ions, fluoride components such as LiF were enriched in the SEI membrane, which in turn significantly enhanced its cycling stability. Experiments revealed that the F-Si@Void@C anode can maintain a reversible capacity of up to 1166 mAh/g after 900 cycles at a current density of 0.5 A/g.

Although the yolk-shell structure is effective in resolving the volume variation of Si anode throughout charging and discharging, and it also enhances Coulombic efficiency. However, the cost is still high, and the preparation method can be subsequently improved to achieve cost reduction.

3 OUTLOOK OF ANODE MATERIALS FOR LIBS

In summary, the improvement technology of silicon-based anode materials for LIBs has made rapid development in the past few years, which effectively solves the problem of volume variation of silicon-based anodes when battery charging and discharging, and improves the cycle life based on ensuring the specific capacity. Therefore, with continuous research, more and more novel improvement methods of silicon-based anode will be discovered and reported.

However, compared with other anode materials for LIBs, Si-based anode has the problem of high preparation cost. Therefore, designing more cost-effective and environmentally friendly ways to reduce costs while also enhancing the service life of Si-based anode in accordance with the current preparation process is unquestionably the direction of key development for the future. Since silicon-based anode materials are still in their infancy when compared to graphite and other commercially accessible anode materials, improving their cycle stability, specific capacity, and cost reduction is crucial for meeting the need for high-capacity LIBs in the future.

4 CONCLUSION

In this paper, the modification methods of silicon anode are summarized through a systematic review. Firstly, in the nanosilicon anode, the diffusion time was effectively reduced by shortening the diffusion length, which significantly enhanced the power density. Additionally, the small particle size particles enhanced the mechanical strain adaptability and successfully stopped the silicon volume expansion-related mechanical failure. However, the capacity degradation of silicon nanostructures remains to be solved, mainly stemming from factors such as SEI film formation, poor electrical contacts, and nano-agglomeration. In order to address these challenges, researchers have proposed combining silicon nanostructures with other materials (carbon, metals) to form anodes. Among them, silicon alloy anode can slow down the volume expansion of silicon, but its preparation process is complicated and costly. Therefore, researchers have turned their attention to compounding nanosilicon with carbon materials. The carbon component of the silicon-carbon anode not only acts as a barrier to stop the formation of unstable SEI and as an effective transport channel for electrons and Li^+, but it also reduces silicon volume growth, which is thought to be an exciting way to enhance the performance of the silicon anode. On this basis, researchers have proposed an improved method of yolk-structured anode. In this anode, a carbon shell layer acts as a barrier to form a void between the silicon particles, allowing the silicon to expand and contract freely without damaging the carbon shell.

Currently, there are still several issues to be resolved. Firstly, the current cost of nanotechnology is still high, and simple and economical preparation methods are required to achieve nanoscale electrode structures with excellent performance. Secondly, to further explore theoretically how to enhance the lithiation rate of silicon anodes in order to manufacture LIB anode with improved performance, an extensive comprehension of the kinetics of silicon lithiation is required.

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