Advances in the application of silicon-based materials in anodes for lithium-ion batteries

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Abstract. Lithium-ion batteries (LIBs) are a vital energy storage technology being utilized increasingly in electric cars, portable electronics, energy storage systems, and other industries as the world focuses more on clean energy and sustainable development. Notwithstanding, the constraints associated with conventional graphite anode materials concerning energy density and cycle stability provide a challenge in fulfilling the forthcoming demand for high-performance batteries. Because silicon compounds offer a substantially greater theoretical specific capacity than conventional graphite anodes, they have gained popularity as research targets for anode materials for next-generation high-performance lithium-ion batteries. However, silicon materials still face many challenges in commercial applications. It has a low first-time coulombic efficiency, which increases the cost of the battery and reduces its actual usable capacity. Its solid electrolyte interface (SEI) film formed during charging and discharging is less stable, which can easily lead to battery performance degradation. To overcome the challenges of silicon materials in LIBs cell applications, this paper summarises the application of silicon nanostructures, silicon/carbon composites, and silicon/metal composites in LIBs. It aims to broaden its application in LIBs further.

Keywords: LIBs, anodes, silicon-based materials.

1. Introduction

With the growing global demand for clean energy and sustainable development, lithium-ion batteries, as highly efficient and environmentally friendly energy storage and conversion devices, have been widely used in electric vehicles, portable electronic devices, energy storage systems, and other fields. However, with the continuous progress of technology and market expansion, higher requirements have been placed on the performance of lithium-ion batteries in terms of energy density, cycle life, and safety. In this context, silicon-based materials, as anode materials with potentially high specific capacity, have become one of the hotspots in lithium-ion battery research.

The application of silicon-based materials in lithium-ion batteries can be traced back to the end of the last century. However, due to its significant volume expansion problem during charging and discharging and challenges such as low first-time charging efficiency and poor cycling stability, silicon-based materials have been slow to be commercially applied. However, with continuous advances in nanotechnology, composites science, and interfacial engineering, significant progress has been made in applying silicon-based materials in lithium-ion batteries [1].

In recent years, research on silicon-based anode materials has gradually evolved from single silicon materials to silicon-carbon composites, silicon-oxygen composites, and other directions. These composites not only effectively alleviate the volume expansion problem of silicon by introducing carbon or other metal elements but also improve the conductivity and cycling stability of the material. In particular, silicon-carbon composites, through the composite of nanosilicon and graphite, carbon nanotubes, graphene, and other carbon materials, comprehensively absorbed the advantages of silicon's high specific capacity and carbon material's excellent electrical conductivity, stability, etc., to become a strong candidate for the next generation of high-performance lithium-ion battery anode materials [2].

This paper aims to review the progress of silicon-based materials in lithium-ion batteries, analyse their advantages and challenges in improving battery performance, and explore their future development direction and application prospects. By summarizing the existing research results and

looking forward to the future development trend, it provides reference and reference for researchers and engineers in LIBs.

2. Working Principle of LIBs

LIBs mainly comprise several significant parts, such as a positive electrode, a negative electrode, a diaphragm, an electrolyte, and a battery casing.

The positive electrode of lithium-ion battery is the electrode with high potential and usually adopts lithium-containing compounds as the active material, such as lithium cobaltate ($LiCoO_2$), lithium manganate ($LiMn_2O_4$), lithium iron phosphate ($LiFePO_4$), etc. Negative electrodes have lower potential and are generally made of graphite and hard carbon materials. These materials have a rich, layered structure that can accommodate lithium-ion embedding and de-embedding. The diaphragm is located between the positive and negative electrodes and is a microporous membrane that is electrically insulating but ionically conductive. Its primary function is to prevent the positive and negative electrodes from direct contact, resulting in a short circuit while allowing lithium ions to pass through freely to complete the charging and discharging process. Commonly used diaphragm materials include polyethylene (PE), polypropylene (PP), etc., which have excellent mechanical strength, chemical stability, and ion permeability. Electrolytes are the transport medium for lithium ions in lithium-ion batteries, and they usually consist of organic solvents and lithium salts.

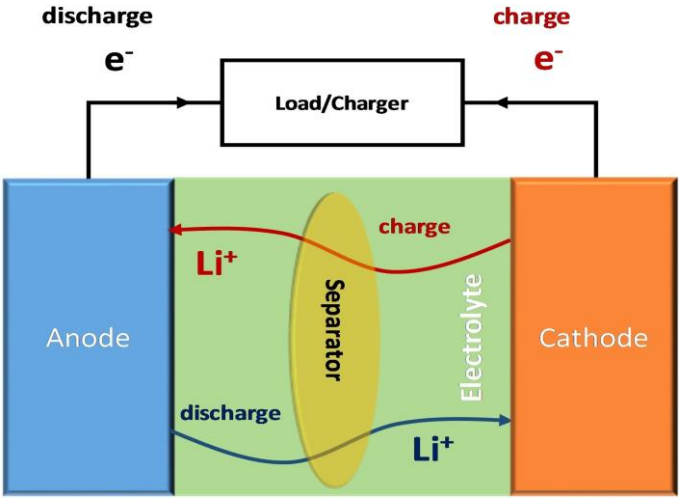


Figure 1. Working principle of LIBs [3]

The working principle of LIBs is mainly based on the reversible migration of lithium ions between the positive and negative electrodes. Specifically, when the battery is charged, lithium ions detach from the positive electrode material, migrate to the negative electrode through the electrolyte as a 'bridge,' and embedded in the crystal lattice of the negative electrode material. At the same time, as shown in Figure 1, electrons from the positive electrode travel through external circuits to the negative electrode, creating an electric current [3]. This process allows the battery to store electrical energy. When discharged, lithium ions are de-embedded from the negative electrode material and return to the positive electrode through the electrolyte. At the same time, electrons travel from the negative electrode back to the positive electrode through an external circuit, releasing electrical energy for use in the device. Thus, reversible lithium-ion migration occurs between the positive and negative electrodes, allowing for repeated charging and discharging of lithium-ion batteries [4].

3. Challenges of Silicon Material

Silicon has emerged as a promising alternative to traditional carbon-based materials, such as graphite, in lithium-ion batteries due to its significantly higher theoretical capacity. However, while

silicon offers substantial benefits, it also presents unique challenges that must be addressed for practical application.

Traditional carbon materials, mainly graphite, have long been the preferred choice for anodes in LIBs due to their stability and well-established electrochemical properties. Graphite has a relatively low theoretical capacity of around 372 mAh/g, which limits the energy density of LIBs. This limitation is particularly problematic for applications requiring high energy storage, such as electric vehicles (EVs), where longer driving ranges are crucial. Additionally, graphite anodes suffer from slow lithium-ion diffusion rates, which lead to slower charging times, making them less suitable for modern applications that demand rapid recharging [4].

Silicon offers a theoretical capacity of approximately 3579 mAh/g, nearly ten times that of graphite, making it an attractive alternative for high-capacity applications. Silicon's ability to accommodate many lithium ions by forming lithium silicide phases during lithiation enables the development of batteries with significantly higher energy densities. This makes silicon particularly suitable for applications requiring large energy storage, such as EVs and grid storage systems. Additionally, silicon is abundant, relatively inexpensive, and environmentally benign, offering a more sustainable solution than traditional carbon materials [5].

However, the practical application of silicon in LIBs faces several significant challenges. The most critical issue is the substantial volume expansion when silicon absorbs lithium ions during lithiation. Silicon can expand up to 300% during this process, leading to severe mechanical stress within the silicon particles. This stress causes the silicon to crack and pulverize, resulting in the loss of electrical contact with the current collector and a rapid decrease in battery capacity. The mechanical degradation of silicon anodes significantly shortens the lifespan of LIBs, making them less reliable for long-term use [5].

Moreover, silicon's repeated expansion and contraction during charge-discharge cycles exacerbates another major challenge: the formation and stability of the solid-electrolyte interphase (SEI) layer. The SEI layer stabilizes the anode and prevents further reactions between the silicon and the electrolyte. However, due to the repetitive volume changes, the SEI layer on silicon tends to crack and reform continuously, consuming additional lithium ions from the electrolyte and leading to further capacity loss. This unstable SEI formation is one of the primary reasons for the rapid degradation of silicon-based anodes over multiple cycles, making it difficult to maintain the performance of LIBs over extended use.

4. Application of Silicon-Based Materials in LIBs

4.1. Nanosilicon

Nanomaterials are a new type of material compared with traditional materials; the most prominent feature of nanomaterials is the size of the particles, which is between the volume of monomers and polymers, and thus has unique properties, such as the small size effect, the surface effect and so on. Nanomaterials as lithium-embedded materials can increase the specific surface area, making the lithium-ion battery de/embedding depth smaller and shorter travel distance, significantly improving the electrode reversible lithium embedded capacity is small, poor cycling ability and the degree of polarisation of the high drawbacks, at the same time, when the battery in the high-voltage environment when the battery work will not change dramatically in volume, is expected to extend the cycle life of the battery. The nanosized silicon negative electrode material has a smaller size and larger specific surface area, which can effectively alleviate the problem of particle pulverization caused by volume expansion and improve the cycling stability of the electrode. The holes inside its nanostructure can facilitate the penetration of the electrolyte and shorten the diffusion distance of lithium ions, thus improving lithium-ion transport efficiency. In addition, the nanosized silicon anode material has a higher specific surface area conducive to transmitting electrons and ions; it has better mechanical strength and can better resist the mechanical stress generated during the charging and discharging process.

Kim's research group prepared Si nanoparticles with better dispersion and higher capacity under high temperature and pressure according to the principle of antigelatin reaction. During the charging and discharging process, the change of its absolute volume and the mechanical stress to which the material is subjected will decrease accordingly with the decrease of particle size, which improves the cycling performance of the electrodes [6]. Liang et al. developed nanoporous silicon microsphere material with silica sol as raw material. The material has a fast charge/discharge rate and good cycling performance [7]. However, when the particle size is too small, the particles will be agglomerated during the charging and discharging process. Because it is a zero-dimensional material, the material will be crushed due to the expansion and contraction of the volume during the cycling process, which will make the capacity decay faster. The cycling ability needs to be improved.

4.2. Silicon/Carbon Composites

Silicon/carbon composites can effectively mitigate the volume expansion of silicon by introducing carbon materials. Because carbon material has good elasticity and toughness, it can play a buffering role in the volume expansion of silicon and protect the integrity of the electrode structure. In addition, structural forms such as porous carbon and nanocarbon can also provide enough space for the volume expansion of silicon, further suppressing the effect of volume expansion on the electrode performance. Silicon material has a low conductivity, and carbon material has excellent conductivity, which can provide a fast channel for transmitting electrons and ions, reduce the battery's internal resistance, and improve the charging and discharging efficiency. The combination of silicon and carbon alleviates volume expansion. The alleviation of volume expansion reduces the destruction of the electrode structure and the shedding of active substances, thus extending the battery's service life. Silicon materials are prone to generate gases from side reactions with the electrolyte during the charging and discharging process, leading to increased pressure or even explosion inside the battery. Silicon/carbon composites can reduce the direct contact area between silicon and electrolyte, lowering the probability of side reactions and thus improving the safety of the battery [8].

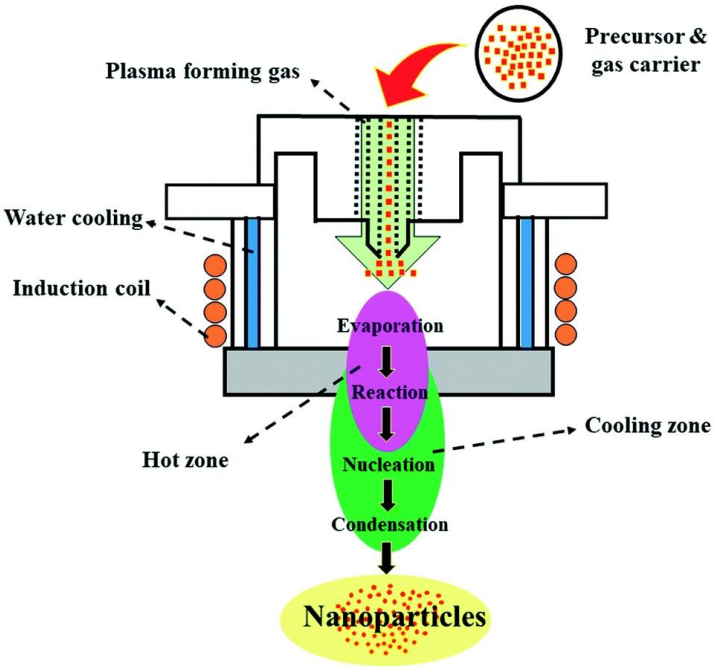


Figure 2. Process of preparing Nanoparticles [9]

The process of creating such composites can be visualized through two distinct images. A method that includes precursors, plasma production, and several heat zones intended for nucleation and condensation is shown in Figure 2. This process eventually results in the synthesis of nanoparticles. This process indicates that chemical vapor deposition techniques introduce carbon materials into the silicon matrix. The carbon coating formed through such methods provides a conductive network and

acts as a mechanical buffer, accommodating the stress from silicon's volume changes without fracturing [9].

Silicon/carbon composites are currently prepared using various methods, including mechanical ball milling, chemical vapor deposition, and sol-gel methods. These methods can adjust the ratio of silicon and carbon and their structural form according to specific needs to prepare silicon and carbon composites with different performance characteristics. This flexibility allows the silicon/carbon composites to meet the needs of lithium-ion battery performance in various fields.

Figure 3 outlines a sequence from SiO_2 purification to the final composition of Si/SiC/CNTs. This visual representation illustrates the transformation of raw materials into a complex composite structure. The integration of CNTs within the silicon matrix is a crucial aspect of this image, showcasing how carbon nanostructures can be embedded to enhance the overall performance of the composite. The CNTs, as depicted, dissipate the mechanical stress generated during the charge-discharge cycles, ensuring the structural integrity of the electrode and improving the battery's safety and longevity [10].

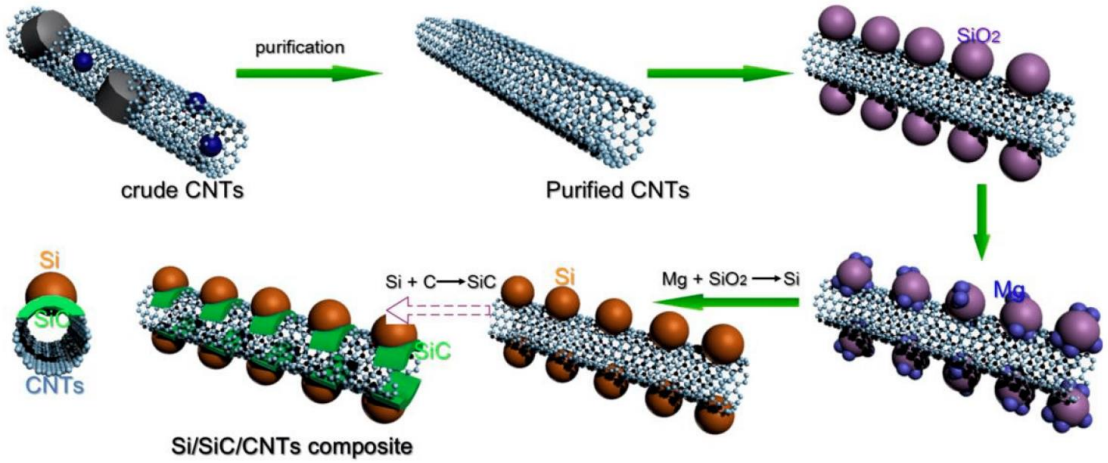


Figure 3. Preparation Process of Silicon/Carbon Nanotube Composites [10]

Wang's research group synthesized carbon nanotube/silicon composites by RF plasma-enhanced chemical vapor deposition. The material's hierarchical structure effectively solves the interfacial delamination problem, and the carbon nanotubes can accommodate the stress generated by the material, ensuring the structural integrity of the carbon nanotube/silicon composites [11].

4.3. Silicon/Metal Composites

Using metallic materials in composites with silicon improves the composites' electrical conductivity and the Si electrodes' electrochemical performance by enhancing the volume change in the embedded dilithium. The overall performance of the silicon material can be improved by doping it with metal elements. In the complex of silicon and metal, the metal mainly plays a conductive role and a specific supporting role, limiting the volume expansion of the silicon electrode during the charging and discharging process and reducing its degree of pulverization. Secondly, the combination of silicon and metal can increase the degree of electron enrichment, thus reducing the free energy required for embedding lithium ions, making embedding lithium ions easier. Alloyed silicon materials are mainly prepared using chemical or mechanical milling methods, and currently, two main types of metals are composited with silicon to improve the electrode performance; one is metals without lithium-embedded activity, such as Fe, Co, Ni, Cu, and Ti and so on, and the other is with lithium-embedded activity, such as Mg, Ag, Sn and so on [12].

Silicon/metal composites are usually prepared by high-energy ball milling, electric arc melting, or chemical methods using silicon and metal as raw materials. Silicon and metal in the composite material can form different forms of existence, including silicon and metal do not form compounds, and the two form a uniformly dispersed mixed system; silicon and metal partially form silicides and form a homogeneous mixture of the three materials; silicon and metal form complete silicides.

Zhang et al.'s team studied a core-shell, high-density composite material of a carbon case clad with rigid SiO_2. The material uses Fe_2O_3 nanopowder embedded in the structure of Si and carbon nanotubes, effectively utilising the internal voids present in Si materials and carbon nanotubes. The electrode prepared this way has a high vibrational density and good electrical conductivity. In addition, the composite structure of the carbon nanotubes and Si materials also improves its overall ionic conductivity and lithium storage performance. The half-cell prepared with this material as the negative electrode was experimentally tested to obtain a high area-specific capacity of 3.6 mAh/cm2 and a capacity retention rate of up to 95% after 450 cycle tests [13].

5. Conclusion

LIBs have been developing rapidly in recent years due to their excellent performance. Still, due to the progress of science and technology and the improvement of human life, the research and development of lithium-ion batteries have put forward higher requirements. Graphite is a widely used anode material for lithium-ion batteries. Still, lithium-ion batteries have poor safety performance and low specific capacity, so they cannot meet the requirements of commercial applications as a power source. The silicon-based anode material, however, has good safety performance and higher specific capacity than graphite, which has become a hot spot for research and development of the next-generation high-magnification/high-capacity lithium-ion battery materials.

Using nanosizing, carbon coating, and other modifications, the volume expansion of silicon during charging and discharging has been effectively mitigated, and the battery's cycle stability and energy density have been significantly improved. These materials exhibit a much higher specific capacity than traditional graphite anode under laboratory conditions, which allows LIBs to be realized with higher energy density.

Despite significant progress in the application of silicon-based materials in lithium-ion batteries, several technical challenges remain. For example, silicon-based materials' low first-time charging efficiency, the difficulty of entirely suppressing volume expansion, and the high production cost need to be further researched and solved. In the future, it is necessary to continue to explore more efficient preparation processes, optimize composite structures, and develop novel interfacial engineering to overcome these challenges.

With the continuous progress of technology and the gradual reduction of cost, silicon-based materials are expected to become the mainstream choice of anode materials for the next generation of high-performance LIBs. Meanwhile, with the global emphasis on clean energy and sustainable development, the application of silicon-based materials in lithium-ion batteries will also make an essential contribution to promoting the energy revolution and achieving the goal of ‘carbon neutrality.’

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