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Ongoing advancement in examining si-based anode materials for lithium ion batteries

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Abstract. There is a developing interest in Lithium-ion batteries (LIBs) with more prominent energy thickness, and further developed cycling soundness has become progressively critical because of the rising fame of electric vehicles and convenient gadgets; efficient energy storage and utilization are vital for meeting these demands. Silicon-based materials offer a promising solution with a high hypothetical explicit limit, low lithium inclusion potential, predominance, and eco-agreeableness. Silicon has emerged as a formidable contender in advanced energy storage technology. Silicon-based materials are perceived as a highly promising option for the anode material in the up-and-coming age of LIBs. Despite the potential benefits of silicon-based anode materials, some limitations currently restrict their commercial use. Its significant volume changes during Li^+ insertion/extraction resulting poor cycling performance and rapid electrochemical decay. This article summarizes current research on this issue. It analyzes silicon anode materials from two perspectives: different dimensional silicon nanostructures (zero-, one-, two-, and three-dimensional) and silicon-based composite materials. Like Carbon/Silicon composite materials. This article provides a comprehensive understanding of silicon anode materials' research status and a vital reference for optimizing their cycling abilities and improving their commercial value and serviceable range.

Keywords: silicon, lithium ion battery, composite, anode.

1. Introduction

With the rapid progress of modern technology, there is a growing demand for low-carbon and low-energy consumption. This demand has increased the need for new energy projects like electric vehicles and enormous-scope energy capacity frameworks. In the past decade, LIBs have become essential electronic device areas. LIBs are also essential in this field with the growing popularity of electric vehicles. Currently, the energy density of LIBs in electric vehicles is increasing at a rate of 7%-10% per year [1]. There is a pressing demand for LIBs that are more affordable, have a greater energy density, and are eco-friendly. The shuttle of Li+ between the positive and negative electrodes shapes the premise of Li+ battery operation. Prior to this, graphite had traditionally been favored as the anode material in LIBs in view of its minimal expense, non-toxic nature, and ability to sustain multiple charge-discharge cycles. Despite its advantages, graphite has a limited theoretical capacity. It is not suitable for high-power discharge applications, thus making it unsuitable for satisfying the developing needs of electric vehicles and other huge-scope energy capacity frameworks. Therefore, silicon has become the primary choice as a new Li+ anode material. Silicon has a higher theoretical capacity, a low working potential for Li+ insertion/extraction, and a lower cost. However, in practical applications, the use of silicon is significantly limited. It is primarily for three factors: (1) when fully lithiated, silicon produces a significant volume expansion effect of about 300%, which may cause the electrode to pulverize or even rupture during operation; (2) this significant volume expansion effect will isolate the active material, making it difficult to electrochemically contact adjacent cells and current collectors, causing the active material to fail; and (3) The volume expansion of silicon can impact the solid electrolyte interface (SEI) stability, leading to hindered electron transport and significant consumption of lithium ions in the electrolyte. This results in a rapid, irreversible capacity decrease and lower initial Coulombic efficiency [2].

To alleviate these problems, researchers have conducted various modification treatments on silicon anodes, such as nanoscale silicon and carbon-based composites. Typically, these techniques enhance the cyclic and rate performance of anodes containing silicon by mitigating the effects of volume expansion and optimizing electronic conductivity and ion transport efficiency. This article summarizes carbon-based composites and nanostructure research progress in silicon-based anode materials. It focuses on different dimensional nano-silicon anode materials, including zero, one, and three-dimensional. They also discuss carbon-silicon composite anode materials such as graphene and core-shell silicon-carbon materials.

2. Silicon-based nanostructure anode material

Silicon is a great competitor for a new generation of negative electrode materials. With its great theoretical capacity (~4200 Ah/g), low lithium ion insertion potential (~0.3 V vs. Li/Li+), and abundant reserves in the world, silicon is a highly desirable material for energy storage technology [3]. However, amidst the process of inserting and extracting lithium ions in LiBs, the significant expansion in volume during the addition and extraction of Li+ causes the active material to pulverize and fracture, resulting in a slew of issues, including inadequate cycling performance of the electrode, rapid decay in capacity, and potential failure of the electrode. Silicon nanostructure design as a useful way to reduce the risk of volume expansion attracts a lot of researchers' focus.

2.1. Zero-dimensional silicon nanostructure

In silicon nanomaterials, the term "zero-dimensional nanostructure" refers to nanoparticles (NPs) that have a spherical shape and are extremely small, typically less than 100 nm in size. It has been discovered through various studies that the cyclic stability of silicon significantly improves upon reaching the nanometer scale. Kim et al. led a concentrate on how the size of silicon nanoparticles (Si NPs) influences the presentation of LIBs. Their research revealed that nanoparticles with an average diameter across 5 nm displayed superior electrochemical stability compared to those with diameters of 10 nm or 20 nm [4]. These 5 nm particles showed a higher initial discharge capacity (4443 mAh/g) and lower irreversible capacity [4]. The smaller particle size results in a thinner SEI film, which reduces the irreversible capacity and increases the Coulombic efficiency (60% at 900 mA/g). Moreover, these 5 nm particles maintained a capacity retention of 71% after 40 cycles. But 10 nm particles had a higher Coulombic efficiency (80%) but lower capacity retention (81%), while 20 nm particles had the lowest Coulombic efficiency (85%) and capacity retention (67%). Overall, these findings, summarized in Table 1, highlight the importance of particle size in optimizing the performance of silicon anodes.

Table 1. Impacts of different Si NPs sizes on LIB performances.

Size(nm)	5	10	20
Coulombic efficiency (900 mA/g)	60%	80%	85%
Capacity retention ratio(after 40 cycles)	71%	81%	67%

Aside from nanosizing silicon materials, multiple techniques have been proposed to enhance the cycling capabilities of anodes that contain silicon. Among these approaches, the development of hollow nanostructures is deemed highly promising. A novel conductive polymer adhesive was introduced by

Zhao et al. This adhesive is capable of adjusting to the molecular level of nanoscale silicon anodes, resulting in exceptionally stable electrochemical performance [5]. By utilizing an electrode composed of 90 wt% nanoscale silicon and 10 wt% adhesives at a C/10 (420 mA/g) rate, the scientists discovered that the nanoSi/PPyMAA electrode exhibited a stable reversible capacity of 2200 mAh/g for more than 180 cycles. Electrochemical tests revealed that the initial cycle efficiency for stable cycling of nanoscale silicon electrodes was 82%. By incorporating graphite material, the efficiency of the electrode could be enhanced to 87%. Thanks to the combination of interfacial adhesion (MAA) and electronic conductivity (Py), the copolymer can achieve a noteworthy initial specific capacity (lithium removal) of very nearly 4000 mAh/g in the early cycles.

2.2. One-dimensional silicon nanostructure

Smaller Si nanowires can more effectively accommodate the significant expansion in volume that happens during lithiation by releasing stress along the radial direction due to the volume effect without causing potential fractures in the material. It means that the small diameter of one-dimensional Si nanomaterials greatly avoids potential fractures that may occur in micrometer-sized Si materials. T. McDowell et al. conducted experiments that proved that the oxide layer did not hinder electron transfer to nanowires during lithiation [6]. They observed that nanowires with natural oxides exhibited diameter-dependent expansion behavior while those with bare surfaces did not. Additionally, they found that the volume expansion of nanowires with natural oxides also depended on their diameter, with smaller nanowires expanding less than larger ones. They also investigated the effect of oxide coating on electrode capacity loss, and their findings indicated a negative correlation between oxide thickness and electrode-specific capacity as well as Coulombic efficiency. Considering the exploratory outcomes above, the preparation of silicon nanowire materials with appropriate aspect ratios and oxide film thickness is an important method for solving the negative electrode problem in LIBs. Sim et al. expanded on Cui et al.'s findings, the researchers conducted a detailed study of the vital thickness of SiO2 coating on silicon nanowires [7]. According to the study results, a 7 nm thick coating of SiO2 can maintain electrode capacity and reduce the influence of silicon volume expansion on the cycling stability of the electrode.

2.3. Two-dimensional silicon nanostructure

Two-dimensional silicon nanostructures are thin film materials with a large perpendicular expansion space that effectively suppresses pulverization. These materials can serve as an electrode independently without the need for binders or conductive agents., reducing external factors that may affect electrode performance. Combining radio frequency magnetron sputtering with electrophoretic deposition, Zhang et al. created a Si/graphene hybrid film that displayed better electrochemical characteristics than pure silicon films [8]. The composite film exhibited superior rate performance, capacity, cycling stability, along with reduced polarization. The composite film's enhanced electrochemical way of behaving was credited to the incorporation of graphene sheets, which upgraded the attachment between the Si and current collector and eased the underlying adjustments brought about by the volume extension and compression of silicon during lithium particle addition and extraction. Maranchi et al. prepared 250 nm and 1 μm thick nano-silicon films using radio frequency magnetron sputtering, which demonstrated outstanding stable cycling ability and high specific capacity [9]. The commitment to using two-dimensional thin film silicon for the creation of alloy-type negative electrode materials emphasizes the significance of continuing research in this field, with the aim of enhancing the anodes of LIBs for future generations.

2.4. Three-dimensional silicon nanostructure

3D silicon-based negative electrode materials have garnered attention due to their ability to incorporate the advantages of 0D to 2D nanostructures and extend them to a 3D scale. Preventing pulverization resulting from the volume expansion experienced during repetitive lithium ion insertion/extraction can be achieved through the utilization of nano-sized Si, Si structures, and nanoscale pores on Si composites.

This is particularly relevant during the initial discharge phase; the lithiation Si commences on the surface of its particles and advances towards the center. This subsequently expands internal Si towards the spherical center, causing the hollow core to contract. As a result, adequate room is made available to accommodate the volume changes experienced by silicon, consequently reducing mechanical stress and preserving electrode integrity. Furthermore, the 3D structure promotes electrolyte diffusion. At present, the method of templating is extensively employed for the production of 3D materials based on Si. To create a porous nano-silicon composite with graphene wrapping, Ma et al. synthesized the material, and a technique comprising in-situ magnesium-thermal reduction and freeze-drying was employed. To obtain porous Si powder, acid etching was performed on a powder of Al/Si alloy [10]. Designated as P-Si@rGO, the "rGO" meaning is reduced graphene oxide, the composite displayed a 3D structure that was extensively dispersed. The new silicon-based composite possessed several desirable features, such as highly dispersed and individually encapsulated silicon particles, the firm binding between silicon and graphene was attributed to a linked interface (Si-O-C), which accounts for the excellent performance of the material, silicon's porous structure material, and significant bulk porosity, enhanced the electrode kinetics reaction significantly. Moreover, this also resulted in a considerable contact surface area that offered outstanding electrical conductivity. Additionally, the composite provided ample cushioning capacity to accommodate volume fluctuations resulting from lithiation/de-lithiation. Finally, this composite showed exceptional and stable cycling ability with a remarkable capacity of 1123 mAh g^{-1} at 1000 mA g^{-1} over 500 cycles. Researchers have also utilized acid etching to introduce metals into 3D structured porous nano-Si, in addition to using SiO2 as a template—for instance, Jiang et al. In order to obtain porous Si powder, acid etching was performed on a powder of Al/Si alloy [11]. Under a current density of 100 mA/g, the porous silicon electrode demonstrated an initial discharge capacity of 2072 mAh/g and a charge capacity of 3450 mAh/g, respectively. Even after 258 cycles, approximately 66% of its capacity remained intact. In an additional step, the team coated the porous silicon powder with nanoscale copper by employing chemical copper plating after acid etching of the aluminum/silicon alloy powder [12]. Following 150 cycles, the copper-coated porous silicon electrode's capacity stayed at 1651 mAh/g when accepting a current density of 200 mA/g.

3. Carbon-silicon composite

Carbon-based materials possess several advantages, including high mechanical strength, electrical conductivity, and compatibility with electrolytes. These characteristics make them ideal for use in composite materials alongside Si to address issues related to the Si anode [13]. A supporting structure is initially introduced in the production of a commercial Si/C anode. The graphite surface is first decorated with Si nanoparticles and afterward covered with amorphous carbon utilizing techniques like liquid-phase coating and spray drying. However, considering the limited specific surface area of carbon carriers, si loading is adversely affected, resulting in a lower Si content within the composite material., which does not meet the high specific energy requirements of LIBs. Furthermore, this mixing method fails to uniformly disperse Si NPs at the microscale, which leads to uneven expansion/contraction and concentration of stress on Si, ultimately leading to the destruction of the anode structure [13].

3.1. Graphene-silicon composite

Liu et al. have made a Graphene/silicon material that has an embedded structure including Si@CEG/C, and chemically expanded graphite (CEG) was utilized as the carbon matrix [14]. CEG with rich pore structure and positive electrical properties, allowing for effective dispersion and accommodation of a large amount of Si NPs. CEG's porosity and flexibility enable Si nanoparticles to be embedded within the expanded graphite layer, thereby accommodating volume changes and promoting Li^+ diffusion through adequate pathways. Consequently, this composite shows moderate cycling and rate performance. When the current density is 0.5 A/g, Si@CEG/C displays a substantial reversible capacity of 1232.4 mAh/g, with a capacity retention rate of 7% even after over 200 cycles [14]. CEG is always used to construct the Si/C embedded structure composite material. It is a crucial aspect of designing negative electrodes with a high specific capacity, maximum active material utilization, and desirable ability of stable cycling.

3.2. Core-shell Si/C composite materials

Silicon/Carbon composite materials can be enhanced not only by simple mixing or carbonization to improve Si anode performance but also by utilizing a more sophisticated core-shell structure. The complete shell provided by this structure functions as an effective buffer against silicon's serious volume expansion, ultimately guaranteeing the Si electrode's integrity [3]. Moreover, this structure serves to prevent Si from contacting the electrolyte constantly, resulting in enhanced stability of the SEI film and a reduction in side reactions stemming from interactions between Si and the electrolyte. Li et al., by means of coaxial electrospinning, two distinct hierarchical core-shell composite materials were formulated and synthesized. Both silicon@hollow porous carbon nanofibers (Si@HPCNF) and silicon@carbon@porous carbon nanofibers (Si/C@PCNF) were used in these materials [15]. Porous carbon nanofibers were a component of the hierarchical core-shell composite components that successfully lowered the Li+ diffusion distance and sped up ion transport by effectively avoiding immediate attachment between the Si and the electrolyte. In comparison to the Si@HPCNF composite, the Si/C@PCNF composite showcased remarkable electrochemical performance, largely due to the interconnectivity of the silicon nanoparticles within the core through the use of porous carbon. In addition, the composite boasted a substantial surface area of 68.05 m2/g, boosting its excellent electrochemical performance is another factor. The performance of Si/C@PCNF electrodes was exceptional after 500 cycles, displaying a phenomenal reversible capacity of 842.1 mAh g-1 at 0.5 A·g-1, excellent cycling stability (420.3 mAh·g-1 at 2.0 A·g-1 after 1000 cycles), and impressive rate capability (1366.6 mAh·g-1 at 0.5 A·g-1). These outcomes show the Si/C@PCNF material's potential as a top-notch anode choice for high-performance LIBs.

3.3. Yolk-shell Si/C composite materials

In contrast to solid core-shell designs, hollow core-shell constructions provide additional internal void volume since the core contains empty space, allowing for the expansion of Si volume. Through the work of Y. Cui et al., a composite electrode containing a unique "yolk-shell" configuration (Si@void@C) was devised and fabricated, characterized by thin, self-supporting carbon shells protecting Si particles (Figure 1) [2]. Several performance metrics, including the remarkably high capacity of 2833 mAh/g at 400 mA/g, the prolonged cycling life (1000 cycles with retention of 74% capacity), and the outstanding Coulombic efficiency of 99.84%, were used to demonstrate the exceptional performance of this distinctive yolk-shell structure.

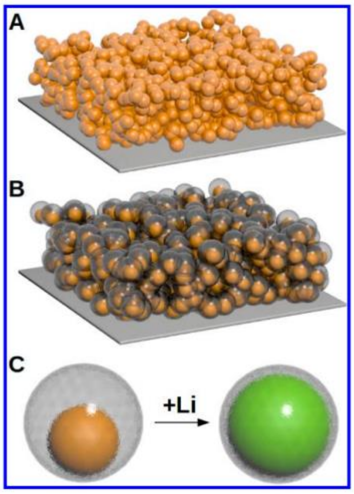

Figure 1. The Yolk-shell Silicon / Carbon layered structure design [2].

Based on this work, the research team developed a pomegranate-like structure [16] (Figure 2). Individual Si nanoparticles were surrounded by carbon shells to enable volume expansion. The hybrid yolk-shell particles were aggregated and coated with thick carbon layers, resulting in micron-scale packaging. Exceptional characteristics were demonstrated by the layered Si/C composite material, including the remarkable ability of stable cycling (with a capacity retention rate of 97% following 1000 cycles), high Coulombic efficiency with a percentage of 99.87%, and impressive volumetric capacity of 1270 mAh/cm³.

A critical component of the successful commercialization of anode materials based on silicon is centered around the design of composites and structures for Si/C materials. Future research will prioritize increasing the loading capacity of active material and reducing production costs. However, commercial silicon-carbon composite anode materials have yet to attain satisfactory cycling performance and Coulombic efficiency. Therefore, modifications of the active materials at the nanoscale and the introduction of highly conductive metal materials need to be considered in future research [16].

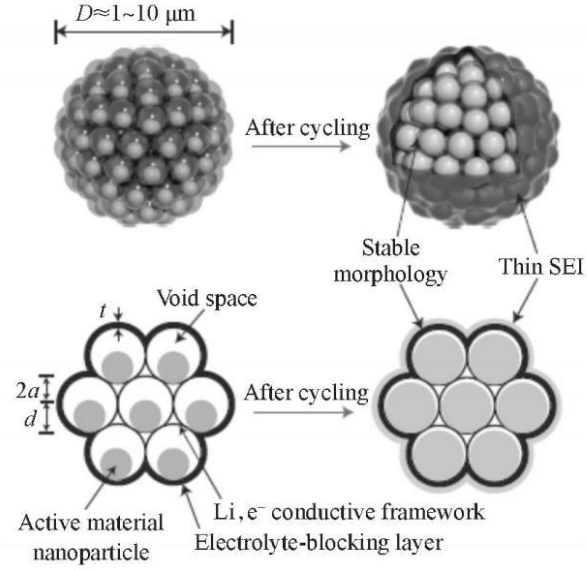

Figure 2. A nanoscale design inspired by pomegranates was developed for anodes composed of silicon-based materials [17].

4. Conclusion

The principal objective of this piece is to give an overall outline of the design process for composite and nanostructured cathode materials for silicon-based LIBs. The designs explored in this article encompass a range of structures, including a series of dimensional nanostructures, as well as composite materials which combine silicon with carbon. These composites include shell-core carbon-silicon composites, yolk-shell carbon-silicon composites, and graphite-silicon composites. While these structures offer some relief from the negative impact of volume expansion, their commercial usefulness is limited due to complex fabrication procedures and high production costs. They are typically reserved for theoretical research rather than practical applications. Future research must concentrate on solving important problems, such as volume change and the insufficient conductivity of materials based on silicon while taking into account safety concerns for both experiments and real-world applications.

Additionally, continuous improvements in production methods and theories are expected to enhance the efficiency and feasibility of these structures for commercial applications. However, it is crucial to consider the complexity of fabrication methods and high production costs to ensure economic viability. Subsequent study efforts must incorporate the aforementioned factors in order to encourage the widespread use of silicon-based cathode materials in LIBs. This will enable the development of more effective nanostructure and composite structure designs, allowing for more practical applications..

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