Design Strategies of Silicon-Based Anode Composites for Enhanced Performance of Lithium-Ion Batteries

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Abstract. Lithium-ion batteries (LIBs) have emerged as a key energy storage technology as the world rapidly moves toward renewable energy and electric transportation. The rather limited capacity (372 mAh/g) of the conventional graphite anodes hinders its application in high-energy-density and fast-charging systems. Silicon-based anode materials, which possess an ultrahigh theoretical capacity (4200 mAh/g) and are rich in resources, offer a promising alternative. Nevertheless, the severe volume expansion of more than 300 % during cycling has brought structural degradation and a rapid decline in capacity. This review focuses on the design of silicon-based composite anode materials, methodically reviewing current developments in ceramic-reinforced systems like Si/TiN hybrids, carbon-based composites including core-shell structures and porous networks, and nanostructures. Studies show that carbon frameworks can effectively cushion volume changes and boost conductivity, while ceramic phases enhance the interfacial stability and restrain electrolyte decomposition. Despite notable improvements in cycle life and energy density, challenges still remain in terms of scalable manufacturing costs and complex synthesis procedures. Future research needs to place emphasis on balancing the silicon content with stability, working on the development of cost-effective synthesis methods, and devising multifunctional interfaces. Tackling these issues will speed up the commercialization of high-energy, long-cycle-life LIBs, thereby pushing forward the global endeavors towards carbon neutrality.

Keywords: Lithium-ion battery; silicon-based anode material; composite material.

1. Introduction

As the world is quickly shifting towards renewable energy and electrifying transportation, lithium-ion batteries (LIBs) have turned into a vital solution in the realm of energy storage. They provide electricity to a wide range of devices, including grid-scale energy storage systems, electric vehicles (EVs), and electronic devices [1]. It is projected that the global LIBs market will reach a value of over $130 billion by 2030, driven by the expansion of EV manufacturing and the advancement of renewable energy development [2]. The anode material within LIBs controls the storage and release of Li+. Its capacity determines the energy boundaries of the battery. Graphite prevails in commercial LIBs because of its stability and low cost. However, its low capacity (372 mAh/g) and slow Li+ diffusion impede high-energy and fast-charging applications such as those in EVs and advanced electronics. There are alternative materials like silicon (4200 mAh/g) and lithium titanate (which allows for fast charging but has a low capacity), each having its own trade-offs. Among these, silicon-based anodes hold promise for getting past the limitations of graphite [3]. Silicon, being the second most abundant element, offers a sustainable and cost-effective alternative to those scarce materials like cobalt [3]. Moreover, silicon has an incredible theoretical capacity of 4200 mAh/g, which is roughly ten times that of graphite. The energy density of LIBs may increase as a result. As a strong contender for LIBs anode materials, silicon enables EVs to achieve a longer driving range and is also advantageous for high-performance electronics [4]. Additionally, silicon can be incorporated into the existing manufacturing processes of LIBs with just a few slight adjustments. This integration characteristic is quite significant since it effectively aids industrial scalability [5].

However, the application of silicon-based anodes in the commercial market still encounters several crucial challenges. The most obvious one is that during lithiation cycles, the volume expansion can be over 300 %. Particle pulverization, mechanical stress, and an unstable solid-electrolyte interface (SEI) are all possible outcomes of such volume expansion. All of these factors will cause cycle life and capacity to drastically decline. The latest progress in nanotechnology and composite materials has presented a promising way to surmount these challenges. For example, silicon-carbon (Si-C) composites take advantage of the high conductivity and flexibility of carbon to adjust volume changes and strengthen the electron transport. In a similar vein, silicon-titanium nitride (Si/TiN) hybrids utilize the excellent mechanical strength and chemical stability of TiN to suppress the structural degradation of the battery. Other strategies, like porous silicon structure, silicon oxide (SiO_x) layer and alloy metal (for instance, Si-Fe, Si-Ni) have also demonstrated the potential to reduce volume expansion [6, 7]. Despite all these efforts, existing studies frequently lack evaluations regarding the scalability, cost-effectiveness and performance under practical application conditions. For instance, although nanostructured silicon does improve the cycle stability to a significant extent, its synthesis usually entails complex and high-energy-consuming processes, which is not realistic in industrial-scale production [5]. Moreover, the interaction between silicon and the second component, such as interfacial bonding, stress distribution and ion diffusion kinetics, is not well understood. This will undoubtedly constrain the sensible design and application of high-performance composite materials.

The most recent developments in silicon-based composite anode materials are methodically outlined in this review, which also examines the critical performance, scalability, and cost-effectiveness gaps. Starting from observation of the basic characteristics and challenges of pure silicon anodes, the progress of engineered composites is comprehensively analyzed, including Si-C hybrid structures like porous carbon buffers and graphene encapsulation to reduce stress, and ceramic-reinforced systems such as Si-TiN and Si-SiC to enhance interfacial stability. Low-cost designs that can be scaled up, such as those using recycled silicon sources and electrodes without binders. Finally, future research directions are sketched out to match up with global sustainability aims, like cobalt-free chemistries and grid-storage compatibility, which lend support to the carbon neutrality targets set by the Paris Agreement for 2050.

2. Silicon Anodes

2.1. The Basic Characteristics

Silicon has become a particularly appealing anode material for LIBs due to its remarkable theoretical capacity (about 4200 mAh/g for $Li_{22}Si_5$), which is actually ten times higher than that of the conventional graphite (372 mAh/g) [8]. Graphite functions through lithium intercalation, but silicon is different; It experiences an alloying reaction with lithium, thereby allowing for a higher level of lithium storage. Nevertheless, the inherent properties of silicon do present some rather significant challenges. Its rather low intrinsic electrical conductivity (about 10^{-3} S/cm) gives rise to a sluggish electron transport situation, thus making it necessary to have conductive additives or to carry out nanostructuring [9]. Moreover, the brittle quality of silicon along with its lack of a layered structure sets it apart from traditional intercalation-type materials, and this in turn fundamentally changes its electrochemical behavior.

2.2. The Mechanisms in Electrochemistry

Lithiation is the process by which silicon goes through a number of phase changes to create lithium-silicon alloys (Li_xSi). When lithium concentrations are low, crystalline silicon (c-Si) first changes into an amorphous Li_xSi phase (a-Li_xSi) [10]. After full lithiation, it crystallizes as metastable $Li_{15}Si_4$. Anisotropic volume expansion (about 300%) causes significant mechanical stress in this multi-step process. Particle pulverization and the loss of electrical contact follow [11]. Furthermore, the SEI is disturbed by the frequent expansion and contraction that takes place during cycling. This results in capacity fading and ongoing electrolyte degradation [12].

2.3. Challenges and Solutions

Pure silicon's intrinsic drawbacks emphasize the need for more sophisticated material engineering research. To some extent, nano-structuring can reduce fracture [13], but it is unable to address the instability of SEI or the scalability problem. This gives an explanation for the creation of composite systems, such as ceramic-reinforced structures or silicon-carbon hybrids. As will be covered in Chapter 3, these systems are intended to enhance processability, ionic conductivity, and mechanical integrity.

3. Silicon-Based Anode Composites

3.1. Si-C Composite Materials

The study of lithium-ion batteries has made Si-C composites a prominent issue. This is due to their potential to overcome the significant drawbacks of pure silicon anodes. The main issues with silicon, such as its low natural conductivity and massive volume expansion during cycle, are addressed by novel carbon-based structures. Si-C composites can be created using three different design approaches: porous networks, core-shell architectures, and the incorporation of conductive additives.

3.1.1 Core-shell structures

A carbon shell, which is designed well and has its thickness precisely controlled (ranging from 20 to 50 nm), can do a good job of confining silicon nanoparticles [14]. At the same time, it can also offer stable electron transport pathways. When there's an optimal carbon coating, it can cut down on particle pulverization. What's more, it can keep 89 % of the capacity even after going through 400 cycles at 0.5 C. The choice of carbon precursor, such as polyacrylonitrile or glucose, has been shown to significantly affect the mechanical properties of the shell [14].

3.1.2 Porous networks

Porous Si-C composites have drawn people's attention due to their capacity to handle volume changes from the inside. The team led by Liu in 2022 recently disclosed a hierarchical porous structure that was made through a magnesium-thermal reduction procedure [15]. In this structure, the interconnected pores, which had a diameter ranging from 5 to 20 nm, functioned as buffer areas. This particular design managed to attain a remarkable areal capacity of 4.2 mAh/cm^2, and it could still maintain 93% of its capacity even after going through 300 cycles. The distribution of pore size is also of great importance. It was shown that mesopores which were sized between 2 and 50 nm, were more efficient than macropores that were larger than 50 nm when it came to preserving the integrity of the structure [15].

3.1.3 Integration of conductive additives

Synergistic effects have been seen when secondary conductive phases like graphene or carbon nanotubes (CNTs) are added [16]. An unparalleled rate capability of 1200 mAh/g at 5 C was achieved via a 3D conductive network with silicon particles sandwiched between graphene layers and carbon nanotubes. This 'conductive double insurance' idea has sparked a lot of follow-up research. For example, nitrogen-doped carbon coatings were used to further increase the interfacial stability.

3.1.4 Limitations and solutions

Although substantial progress has been made, important problems still exist. Dead volume in porous designs ultimately reduces the volumetric energy density. Furthermore, the majority of synthesis techniques, such as chemical vapor deposition (CVD), are energy-intensive and difficult to scale up. There is ongoing discussion on the ideal silicon content. The majority of research attempts to reconcile stability (which requires a low percentage of silicon) with capacity (which requires a large percentage of silicon) [17].

3.2. Si/TiN Composite Materials

The exploration of silicon-titanium nitride (Si/TiN) composites has paved the way for dealing with conductivity limitations. The remarkable properties of TiN, like its electrical conductivity being around 4×10^6 S/m and hardness being about 21 GPa, make it really fitting for applications related to silicon anodes.

3.2.1 Conductive network designs

Around silicon particles, TiN nanowires with a diameter of 5-10 nm create continuous conduction pathways. When compared to conventional composites, this design was able to lower the charge transfer resistance by up to 78 %, enabling stable operation at very high rates, like 3C, for example. Concurrent studies revealed that TiN's inherent catalytic qualities might aid in accelerating Li^+ diffusion at surfaces [18].

3.2.2 Surface engineering

The results of the sophisticated coating processes are pretty impressive. For instance, it has been shown that TiN atomic layer deposition (ALD) may create conformal coatings that are two to three nanometers thick. Recent interface engineering approaches show that silicon anodes can be effectively stabilized. Ultrathin ceramic coatings, with a thickness of roughly 2 to 3 nm, can inhibit the electrolyte's breakdown. The growth of SEI may be reduced by as much as 60 % as a result of this suppression. Over 100 cycles, it may simultaneously sustain an 82 % capacity retention [19].

3.2.3 Emerging hybrid systems

The newest generation of composites brings together TiN and carbonaceous materials. A remarkable instance is the Si@TiN/C triple-layer structure [20], and it had the following features: 1450 mAh/g initial capacity; The Coulombic efficiency is higher than 99.5% following 200 cycles; The temperature of thermal runaway went up by 40 °C [20]. 3D carbon networks manage to constrain the volume expansion of silicon to 150 %. In comparison, the volume expansion in bare anodes can reach up to 300 %. Moreover, these 3D carbon networks can also triple the mechanical strength through the optimization of interfacial bonding. These discoveries directly provide insights into the design principles for hybrid architectures such as Si@TiN/C. In such architectures, ceramic phases play a role in inhibiting the formation of SEI, while carbon matrices offer essential stress buffering. In this manner, high-performance lithium-ion batteries can simultaneously improve their mechanical integrity and electrochemical stability [20].

3.2.4 Limitations and solutions

The production cost of TiN is quite high. It's around \$120 - \$150 per kilogram, in contrast to carbon, which is only about \$5 - \$10 per kilogram. In addition, there is a difficulty in attaining uniform dispersion when the silicon loading is high (more than 60 wt%) [21]. The potential solutions that are currently being explored is utilizing the TiN that's recycled from machining waste.

3.3. A Comparative Analysis of Silicon-Based Composites

The performance metrics of the composite systems are summed in Table 1. The performance properties of silicon-based composite materials have a significant impact on their practical use in lithium-ion batteries. According to Table 1, Si-C composites have a modest amount of electrical conductivity, specifically between 10^2 and 10^3 S/cm. This is less than that of Si/TiN composites, which exhibit electrical conductivity between 10^4-10^6 S/cm. Nevertheless, Si-C composites do display a superiority in terms of cost-effectiveness, with a cost range of 20-50 \$/kg, and they also have an extended cycle life that can reach 300-800 cycles [6]. This is due to the fact that the carbon frameworks are able to effectively buffer the volume expansion, which can be as much as -180 %, and they also provide optimized conductive networks. For example, the capacity retention of 89 % can be achieved after going through 400 cycles by precisely controlling the thickness of the carbon shell, which was within the range of 20-50 nm. Conversely, Si/TiN composites have a greater degree of conductivity and a lower volume change, falling between 100 and 150 percent. However, their high cost, which is around 80 \$/kg, and their cycle life, which is only moderate, ranging from 200-500 cycles, act as obstacles to their large-scale implementation. Future research needs to center on reducing the cost through recycling procedures or by making use of novel synthesis techniques such as liquid-phase nitridation, while also taking into account the need to balance the silicon content and maintain the structural stability [7].

Table 1. The performance metrics of the composite systems

Parameter	Si-C Composites	Si/TiN Composites	Hybrid Systems
Conductivity(S/cm)	10^2-10^3	10^4-10^6	10^3-10^5
Volume Change (%)	120-180	100-150	90-130
Cost ($/kg)	20-50	80-120	50-80
Cycle Life	300-800	200-500	400-1000

4. Conclusion

The design as well as the optimization of silicon-based composite anode materials have come to the fore as crucial strategies for surmounting the innate limitations that pure silicon has in (LIBs. When silicon is integrated with carbonaceous frameworks or ceramic reinforcements, considerable headway has been achieved in alleviating challenges, such as volume expansion (which can exceed 300 %) and low conductivity (about 10^{-3} S/cm). In spite of the advancements that have been made, there still remain challenges when it comes to striking a balance regarding the silicon content for the sake of handling the trade-offs between capacity and stability. There is also the matter of cutting down on synthesis costs. For instance, the price of TiN is 120-150 $/kg, as opposed to carbon that costs 5-10 $/kg. Additionally, the scaling of energy-intensive methods like CVD, poses a challenge as well. Future research needs to give priority to multifunctional interfaces, such as self-healing polymers, advanced manufacturing like using 3D printing for controlling microstructure, and sustainable synthesis, for example, recycling machining waste to produce TiN. When these gaps are addressed, silicon-based composites have the potential to propel the development of high-energy, fast-charging LIBs, thereby speeding up the global shift towards renewable energy and carbon neutrality.

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