Advancements In Carbon Nanotube-Silicon Composites for Lithium-Ion Battery Anodes

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Abstract. Silicon (Si) is considered a highly promising anode material for lithium-ion batteries (LIBs) due to its exceptionally high theoretical specific capacity, low operating potential, and abundant availability. However, the substantial volume expansion of up to 400% during charge-discharge cycles, coupled with its low electrical conductivity, poses significant challenges for practical applications. Carbon nanotubes (CNTs), recognized for their superior strength and excellent electrical conductivity, offer a potential solution to these issues. This paper provides a comprehensive review of recent advancements in two major types of CNT-Si composites: Si-C-CNTs composites and Si-CNTs composites. The review explores common preparation methods and delves into the mechanisms by which CNTs stabilize the Si structure, reduce volume expansion, and enhance overall conductivity. Furthermore, the paper addresses the key challenges associated with the commercialization of CNT-Si composites and discusses potential strategies to overcome these barriers. This review aims to offer valuable insights into the development and commercialization of next-generation anode materials for high-performance LIBs.

Keywords: Lithium-ion battery; Si anode; carbon nanotube; volume expansion.

1. Introduction

Currently, the dependence on fossil fuels has led to many environmental problems, such as increased global warming, uneven fuel distribution and environmental pollution [1]. The development of renewable energy sources, such as solar, wind and tidal energy, is a matter of urgency. However, renewable energy sources exhibit intermittency and discontinuity due to changes in natural conditions. One of the solutions to the challenges posed by the intermittency of energy sources is to develop an energy storage system. LIBs are used as the most common energy storage device in most electronic products because of their high energy density.

The anode material is the key to the performance of LIBs. The ideal anode material for LIBs is lithium metal anode [2,3]. Although much research is active to overcome its low performance in battery systems with liquid electrolytes, this technology is still far from industrialization. Graphite is identified as the most widely used industrialized anode material for LIBs due to its good conductivity, stiffness and strength. However, graphite's low theoretical specific capacity of 372 $mAh \cdot g^{-1}$ limits anode energy density.

Silicon is a promising liquid electrolyte LIBs anode material with low working potential, abundant source and high theoretical specific capacity. Silicon has an extremely high theoretical specific capacity of 4200 $mAh \cdot g^{-1}$, but a volume expansion of up to 400% occurs during lithiation/delithiation, which causes poor cycling stability and limits its commercialization. In addition, the low electric conductivity of silicon cannot be ignored [4]. Si/C composite is generally used to enhance poor electrical conductivity, and CNTs have been widely focused on and mass-industrialized by many companies due to their high mechanical properties and good conductivity.

In this article, the author reviews the study of CNTs as Si/C composite electrodes and the experimental methods of anode materials. Meanwhile, the author summarizes the role of CNTs in Si/C composites, reveals the mechanism of conductivity enhancement and suggests issues that need to be improved when using Si/C composites as LIB anodes.

So far, many studies reported a variety of coating processed to form homogeneous Si/CNT composites and described how Si nanoparticles coated with CNTs. CNTs are classified as single-

walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) for different numbers of carbon walls. SWCNTs have strength in their excellent performance, while MWCNTs are favored by their lower cost. These two types of CNTs will be introduced in the following two composite technologies —— Si-C-CNTs composites and Si/CNTs composites.

2. Synthesis Methods

Currently, there are three maturely used synthesis methods for Si/C composites: solution-phase method, spraying drying and mechanical ball milling. Besides, in the modification of materials, researchers also use structural design and compositional modification to obtain composites with better performance.

2.1. Solution—Phase Method

Solution-phase methods are commonly used for anode material with the advantages of being easily manipulated, inexpensive and suitable for industrial production. Most solution-phase reactions are carried out in solution, mostly accompanied by hours of mixing, stirring, centrifugation, drying, etc. A thermal annealing strategy also accompanies some processes.

2.2. Spray Drying Process

The spray drying method disperses the material into fine mist particles and hot air contact in the instantaneous completion of the process of heat and mass transfer so that the solvent quickly evaporates into gas to achieve the purpose of drying. This process is also mostly accompanied by granulation, which forms nanoscale particles with a high degree of sphericity. Nanoscale particles increase the reaction surface area and accelerate the rate of reaction.

2.3. Ball Milling

Mechanical ball milling technology is a way of grinding different substances by adding them to a vessel such as a ball mill. This method improves the surface contact effect between the particles and the substrate, resulting in a uniform distribution of the target particles. It is a low-cost approach suitable for large-scale dissemination.

3. Si-C-CNTs Composites

This type of composite anode connects reticulated CNTs on a core-shell structured Si/C to maintain high strength, and the nano-Si can accommodate the volume expansion during cycling, which improves structural stability during lithiation/delithiation. Meanwhile, the formation of the interconnected three-dimensional conductive network improves the electron transport capability of the material.

As an example, Qiu et al. reported a unique Co-doped anode composite Si@$CoSi_2$/Co-NPC@CNTs based on the solution-phase and thermal annealing method, in which N-doped porous ZnCo-ZIF carbon (NPC) is coated with silicon nanoparticles (Fig. 1a, b) [5]. After the annealing of Zn species, a framework called zeolitic imidazolate (ZIF) is formed, which accelerates the ion transport efficiency. The collaboration of CNTs, $CoSi_2$/Co and NPC forms a reliable three-dimensional conductive network, which improves the electron transport ability of the material and improves the conductivity problem of single Si anode (Fig. 1c) [5]. The spray drying process proposed by the Wang group treats sand-abraded silicon (S-Si), CNTs and PVP after ultrasonic dispersion and stirring at 150 °C. Higher sphericity and uniform particle size Si/CNTs/C composites were obtained under subsequent elevated temperature carbonation coating (Fig. 2a) [6]. CNTs act as both conductors to improve electrical conductivity and buffers to mitigate the volume expansion of silicon. The cycling stability of the composite Si-C-CNT material was greatly improved compared to that of the

single Si anode. The capacity retention after 500 cycles is as high as 45% at a current of 1 A · g^{-1}, and even at a current of 10 A · g^{-1}, the capacity retention can reach 43.9% (Fig. 2b) [6].

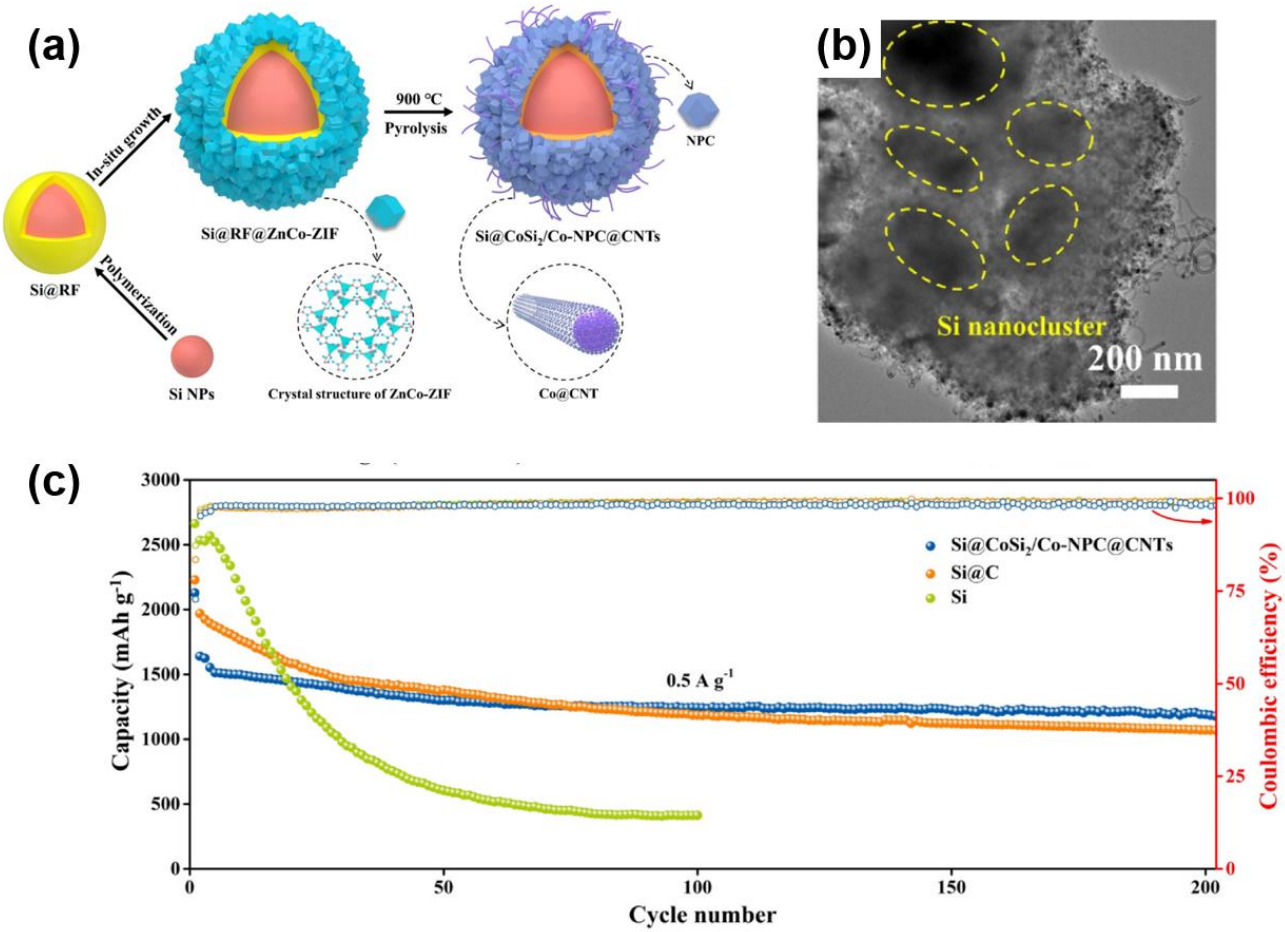

Fig. 1 (a) Schematic of the preparation procedure of Si@$CoSi_2$/Co-NPC@CNTs composites. (b) TEM image and (c) cycling performance of Si@$CoSi_2$/Co-NPC@CNTs composites. Reprinted with permission from [5].

Chen et al. reported a novel approach to deal with Si/CNTs/C composites by closely bonding N, P silica nanoparticles and CNTs with pitch pyrolytic carbon layers in agate ball milling tanks. The mixture reversed rotation for a certain time, obtaining a well-mixed pitch precursor. The pitch precursor was pyrolyzed at high temperature in the porcelain boat, and the pitch was dissolved and coated on the surface of Si-CNT, and the N, P-Si/CNT/C composite was prepared at elevated temperature. Hexachlorophosphazene was used to replace carbon atoms for in situ N P doping. SEM images of Si/CNTs are shown in Fig. 3a, d. The CNTs and Si nanoparticles are entwined with each other, and the short CNTs are attached to the Si. SEM images of Si/CNTs/C composites are shown in Fig. 3b, e. The asphalt undergoes carbonization at high temperatures and forms a carbon layer encapsulation on the surface of Si particles and CNTs. From the SEM images (Fig. 3c, f), the N, P-Si/CNTs/C composites have a similar morphology to the Si/CNTs/C composites. According to SEM images, silicon nanomaterials are wrapped and enveloped by carbon nanotubes, forming a good conductive structure. The planar spacing of the carbon layers was enlarged to introduce more defect sites. The N, P-Si/ CNTs/C anode shows unique performance with a first discharge/charge specific capacity of 1494.0/1243.6 mAh · g^{-1} at 0.2 A · g^{-1} and with a capacity retention of 40% after 100 cycles (Fig. 3g) [7]. Even after 500 cycles, the anode surface became rough, but no cracks were observed, demonstrating the high stability of this type of anode.

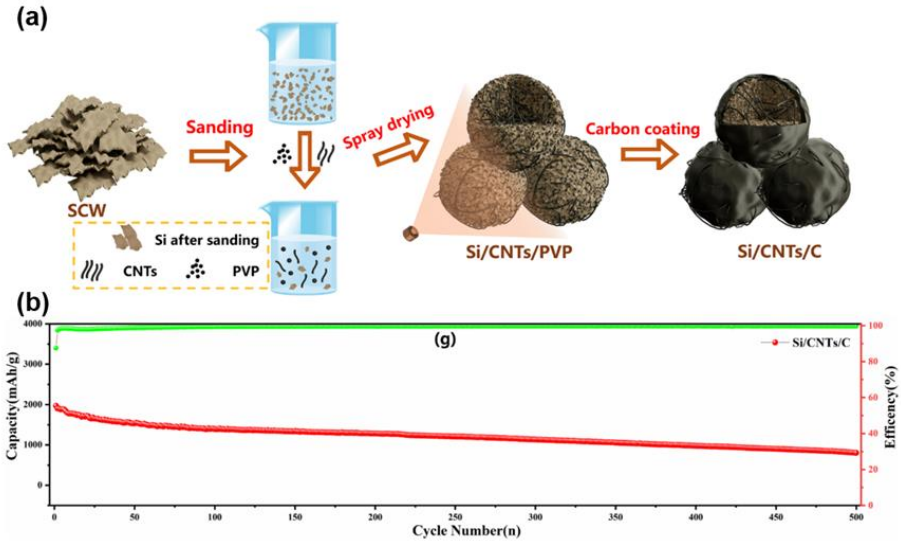

Fig. 2 (a)Schematic diagram of the synthesis of Si/CNTs/C. (b)Long-term cycling performance of Si/CNTs/C composite at 1 $A \cdot g^{-1}$ [6].

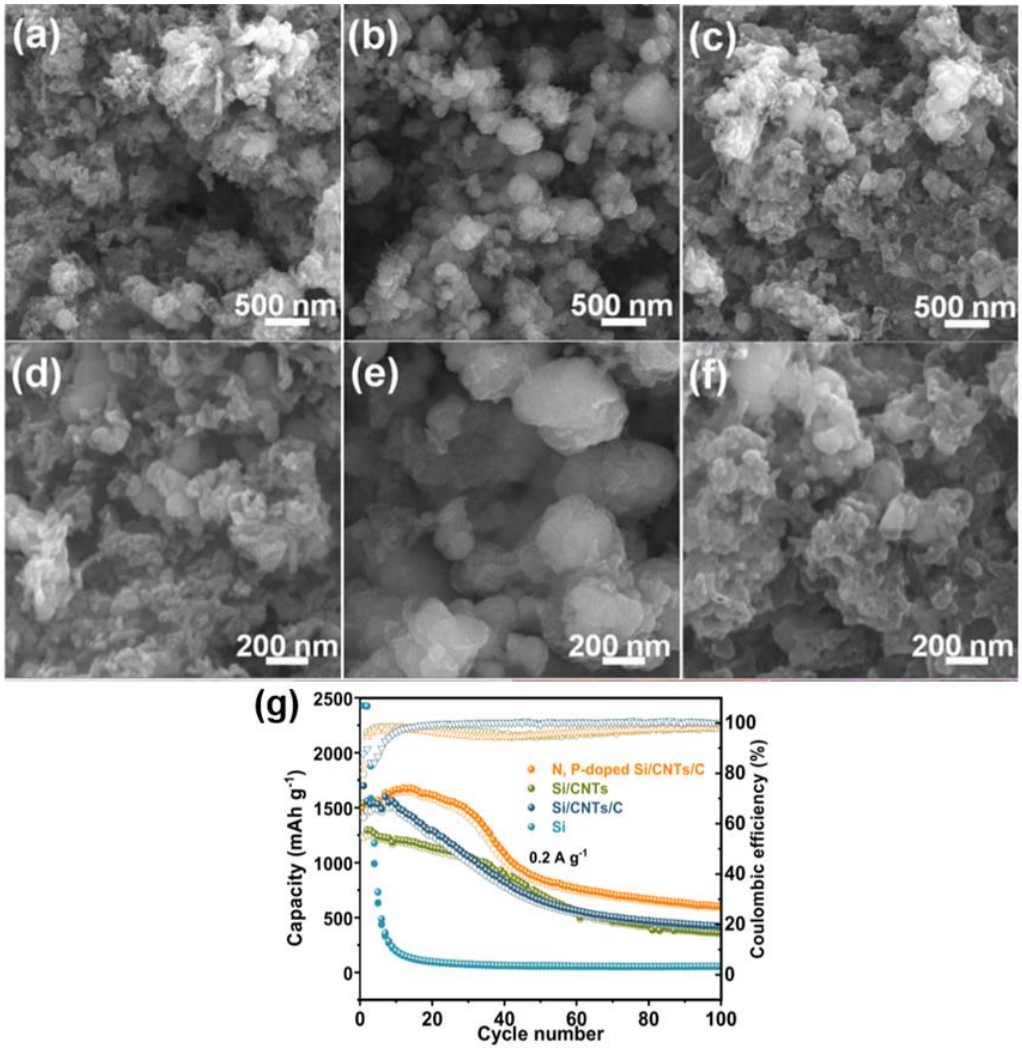

Fig. 3 (a, d) SEM images of Si/CNTs. (b, e) SEM images of Si/CNTs/C. (c, f) SEM images of N, P-Si/CNTs/C.(g) cycling stability of N, P-Si/CNTs/C, Si/CNTs/C, Si/CNTs and Si nanoparticles at 0.2 $A \cdot g^{-1}$ [7].

4. Si-CNTs Composites

Another class of materials for Si-CNT composites has been proposed as well. Si/CNT composites do not use carbon materials other than CNT to contain Si. However, suppression of Si volume expansion and poor Si-C interactions with CNT alone cannot be ignored. Researchers are working on improving structure and promoting processes to modify carbon-silicon composites for better performance.

Mei et al. used glass waste (with silicon) and commercial CNT to synthesize novel composites (Fig. 4a) [8]. Recycled glass is broken into glass bulk and crushed into glass powder by ball milling. The glass powders and CNTs at the micron level were then mixed at high speed by wet ball milling to initially obtain the primary glass-CNTs composites. Then, hydrochloric acid was then used to clarify the metal oxides that were originally the raw material for the glass powders. After magnesiothermic reduction, the g-Si/CNT was ball-milled to obtain the nano Si and CNT mixture (g-Si@CNTs). CNT networks formed strong Si-C covalent bonds between CNTs and Si nanoparticles in situ, which ensured a low-volume expansion of Si. Therefore, g-Si/CNT anodes show excellent electrochemical performance, especially in structural stability, with 84.7% capacity retention after 200 cycles at 0.1 $A \cdot g^{-1}$ (Fig. 4b) [8].

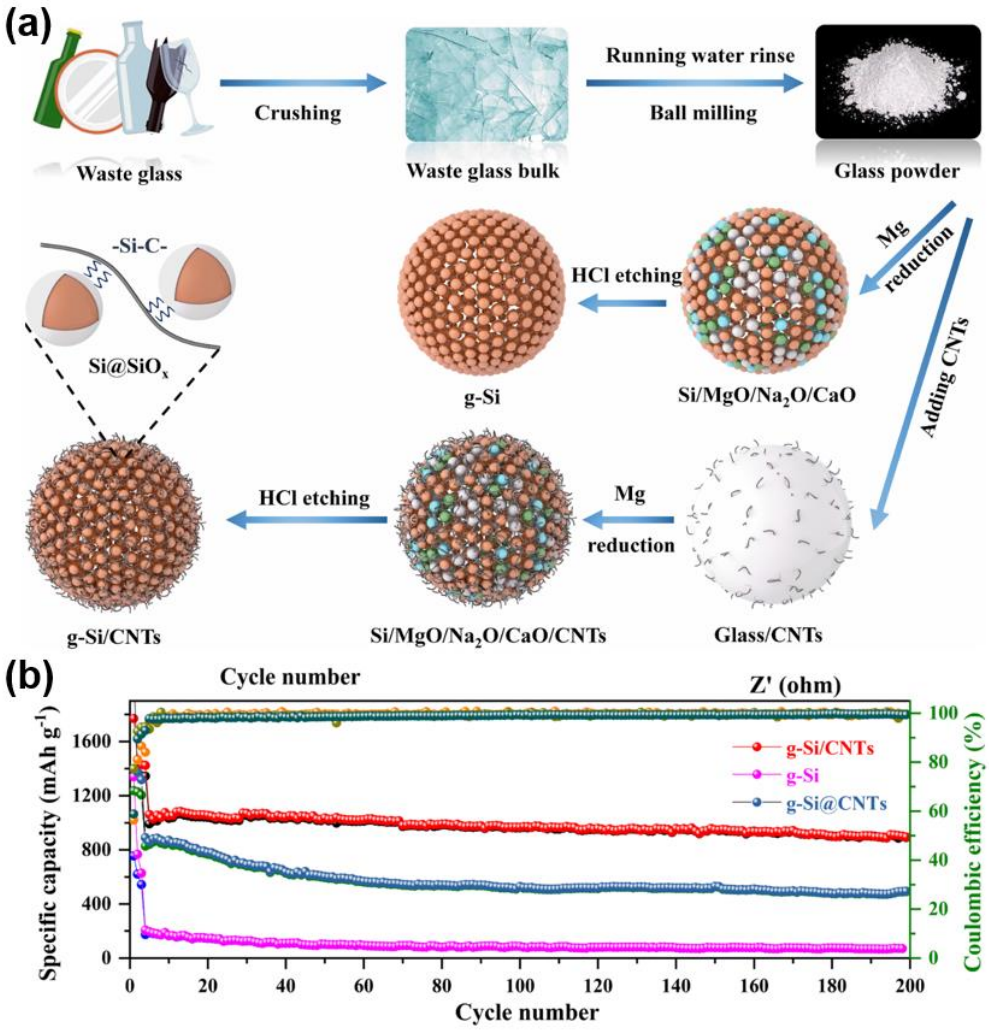

Fig. 4 (a) Schematic illustration of synthesis of the g-Si/CNTs composite. (b) Cycling curves of the g-Si/CNT composite at 0.1 $A \cdot g^{-1}$ [8].

In addition to the method of strengthening the Si-CNT covalent bond, researchers have also targeted the structural modification of Si to obtain composite anodes with better cycling performance. Ren et al. reported a layered sieve-like porous nanosilicon (LSP-Si) anode with interconnected

nanonetwork (Fig. 5a) [9]. LSP-Si was synthesized by way of an etching and magnesiothermic reduction strategy and attached to the CNT by electrostatic adsorption. The voids distributed in each layer not only provide a good space for the penetration of electrolytes but also alleviate the instability caused by the volume expansion of Si to a certain extent. This modification method greatly improves the cycling performance of the Si-based material, with a capacity retention rate of 91.9% after 500 cycles. Zhang et al. also modified porous nano-silica-CNT composite anode materials (p-Si/CNT) by a simple molten salt-assisted dealloying process (Fig. 5b) [10]. After mixing Mg_2Si powder and CNT powder by ball milling method, $ZnCl_2$ molten salt was introduced to provide the melting reaction condition and act as a medium to suppress the local high temperature. After the melt treatment, the researchers found that the molten salt method leads to an increase in the defect density of CNT. Density Functional Theory (DFT) calculations showed the promotion of p-Si/CNT defect increase for ion adsorption capacity. The experimental results verified the DFT calculations, and after 100 cycles at 500 $mA \cdot g^{-1}$, the capacity of p-Si/CNT was maintained at 796.6 $mAh \cdot .g^{-1}$, with a capacity retention rate of 78% (Fig. 5c) [10].

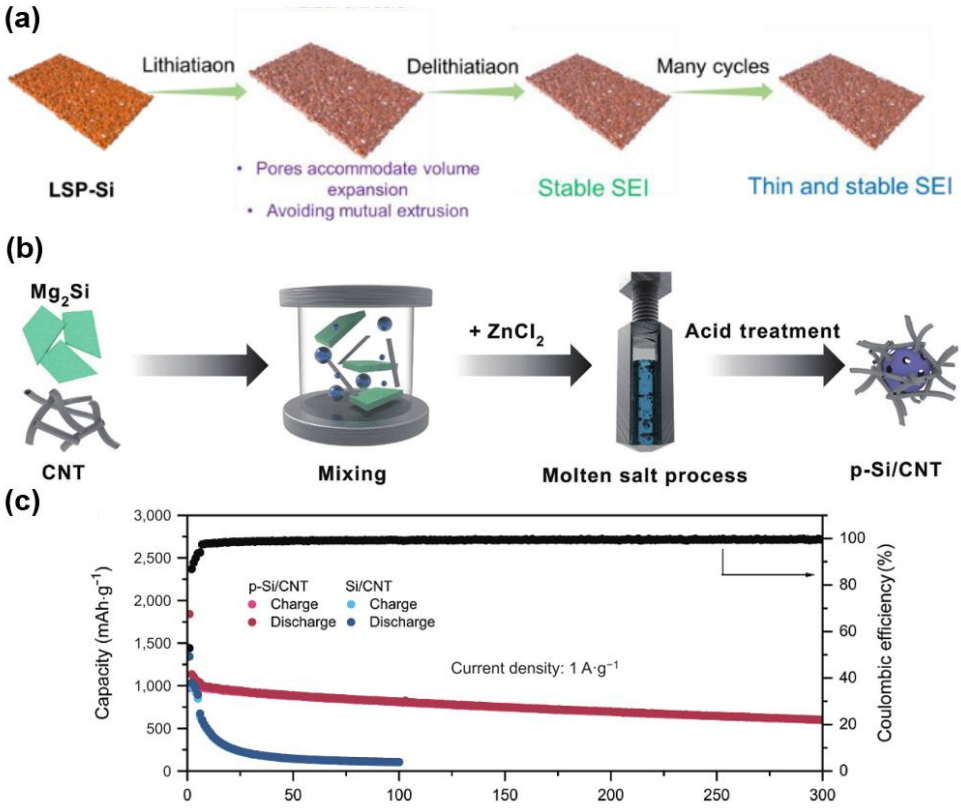

Fig. 5 (a) Schematic illustration of the cycling mechanism of Si-based materials. Lithiation/delithiation of LSP-Si materials upon long-term cycling [9]. (b) Schematic illustration of the synthesis process of the p-Si/CNT composite. (c) Cycling performance of p-Si/CNT and Si/CNT at 1 $A \cdot g^{-1}$ and the corresponding CE [10].

5. Conclusion

In the current LIBs system, the traditional graphite anode faces the theoretical limit dilemma of specific capacity. Silicon anode has attracted much attention due to its high energy density and low cost. However, silicon is limited by a terrible volume expansion rate and low electrical conductivity, and studies have shown that coating carbides can appropriately suppress these characteristics. Carbon nanotube coating is an important research direction for carbon-coated silicon negative electrode materials. This paper reviews different CNTs composite silicon-based anode preparation processes and reveals the reason for CNT coating to alleviate volume expansion. CNTs improve the

conventional Si@C combinatorial cladding effect. The high mechanical strength of the conductive network not only enhances the immobilization of Si@C particles on the binder and mitigates the volume expansion but also improves the electrical connectivity between Si@C particles or between Si cores and C shells. CNTs are also carbon compounds so that they can enhance the conductivity of silicon-negative electrodes during coating.

Moreover, some studies have introduced N and P elemental doping to further improve the electrical conductivity of the composites. However, the commercialization of CNTs@Si composite anode faces the following issues. The dispersion uniformity of CNTs requires further process setup. The optimization of structural design needs to consider the performance and process scalability for commercialization. Strong bonding with Si asks for the expansion of the process, which is not only limited to processes such as electrostatic attraction and spray drying. Finally, the author believes that this article can provide effective help for the research ideas and commercialization of CNT composite Si anodes for Li-ion batteries.

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