The Development of Nano Si Materials in the Application of Lithium-Ion Batteries Anode

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Abstract. Electric vehicles (EVs) have become a practical alternative to conventional fuel vehicles due to their environmental friendliness, high energy efficiency, low operating costs, etc. In EVs, lithium-ion batteries (LIBs) play a crucial role. It provides a power source for EVs and directly affects their performance. Among them, LIBs with silicon nanomaterials as negative electrodes show great potential in improving EV performance. This article aims to conclude Si-based anode LIBs' present challenges and introduce advanced optimization methods with nano-Si material according to these challenges. It starts with the principle of Li-ion storage in Si. Then, problems faced by pure Si anodes and the preliminarily improved Si-based anodes are listed. Finally, further optimization methods in the nano Si anodes during these years are introduced. The optimization methods mainly include improving the service life of nano-Si-based anode and reducing the cost of manufacture. This comprehensive review provides reference and inspiration for developing Si-based anode LIBs applied in EVs.

Keywords: LiBs, nanomaterials, Si, anode.

1. Introduction

Nowadays, there are growing concerns about the sustainability of the development. Reducing environmental pollution, including greenhouse gas emissions, has become significant. EVs are known as one kind of solution. Unlike traditional fuel vehicles, EVs have higher engine efficiency and no gas emission during traveling [1]. This vehicle is expected to replace some fuel vehicles and lessen greenhouse gas emissions. However, it still faces challenges like limited traveling range, high weight, and long charging time [2].

Battery is the core part of EVs, which determines the most essential properties, including the energy capacity and charging speed. Higher energy capacity can boost the traveling range and reduce the whole weight of the battery set. Among various ideas for battery design during these years, LIBs are the most popular in vehicles.

LIBs feature high energy capacity, long service life, excellent stability, and mature industries, which make them extensively applicable to various electric products. LIBs mainly consist of the cathode, anode, and the electrolyte. LIB works through the diffusion of Li-ions, while the anode is the part that absorbs and stores the Li-ions during charging. Therefore, optimization of the anode is a popular field for improving the electrical properties of LIBs, such as energy capacity. Traditional LIBs apply the graphite anode for its stability and excellent electric conductivity. Meanwhile, traditional graphite anode suffers from low capacity (372 mAh/g [3]) because of the poor lithium storage ability of carbon (Li atom: C atom = 1: 6 when fully charged). It severely limits the traveling range of EVs. Si anode is a potential alternative to graphite for its high capacity (3580 mAh/g at room temperature [4]). Moreover, higher charging speed and better environmental friendliness make the Si-based anode a field with great potential [4]. During decades of studies, nano Si proved to be an excellent core material for high-performance Si anodes. Therefore, this article mainly focuses on applying Si materials in the anode of LIBs, especially for the nano Si materials. It includes present challenges and advanced methods to optimize the Si-based anode LIBs. This article will provide new views and ideas on developing Si-based anodes.

2. Mechanism of Lithium Storage in Silicon

Unlike graphite, the Si anode is based on the reversible alloying/dealloying reaction between the silicon and lithium, known as lithiation and extraction. They can be concluded as Equation (1) [5].

$$xLi + xe^{+-} + Si \rightarrow Li_xSi \quad (1)$$

As Li-ions diffuse through the electrolyte to the anode, crystal Si transforms into amorphous Li_xSi as the a-Si. In the following process, the a-Si transforms into crystalline as the voltage plateaus fall back to around 44mV, where x equals 3.75 [4]. The whole process is shown in Equation (2) [4].

$$15Li^+ + 15e^- + 4Si \rightarrow Li_{15}Si_4 \quad (2)$$

$Li_{15}Si_4$ is considered as the end of the lithiation at room temperature. Compared with the LiC_6 in graphite anode, the $Li_{15}Si_4$ shows higher efficiency in storing Li-ions. The lithiation consists of the break of the crystal Si and the generation of Si-Si bonds or Si atoms [4], which leads to challenges in the practical use of Si anode in LIBs.

3. Present challenges faced by Si-based anode LIBs

The challenges for the pure Si anode mainly include the extreme expansion after lithiation, the low electric conductivity of Si, and the low stability of solid-electrolyte interphase (SEI).

Great mechanical stress is generated during the transformation from c-Si to a-Si and the final $Li_{15}Si_4$ [6]. It causes the expansion of the Si anode during the cycles, which can reach 300% in volume [7]. Extreme stress and expansion lead to cracks in the anode, which causes physical failure and reduces the cycles that the LIB can maintain.

In the meantime, these cracks explode the anode to the electrolyte. Side reactions frequently happen on the interface, where the thickness of SEI increases due to repeatedly breaking and rebuilding. During these processes, the active materials such as conductive agents and Li-ions are severely consumed, resulting in phenomena like “dead lithium” [8]. The irreversible loss of active materials leads to a decrease in the reversible capacity. On the other hand, thicker SEI increases the polarization voltage due to its poor electrical properties. As a result, the unstable interface between Si anode and electrolyte and the poor conductivity of Si reduces the coulombic efficiency (CE).

In decades, many methods and designs have been applied to improve the performance of Si anode, including SiO_x, Si/C composites, and nano Si. These studies made progress in different aspects but still faced various challenges. Applying SiO_x as the basis of the anode reduces the expansion, while this kind of LIBs still suffers from low electric conductivity and CE [9]. For the traditional Si/C composites, graphite is applied as a coating or mixed with Si. Graphite performs well in absorbing the stress and improving the conductivity, increasing the anode's stability. However, a large percentage of graphite can reduce the energy capacity of the LIBs, contradicting the idea of applying Si as the anode. Due to their porous structure, Nano Si materials perform better in reducing and withstanding the volume expansion. 150 nm in grain size is the upper limitation for these materials. On the other hand, the Si nanowires (Si NWs) and Si sheets reduce the distance of Li-ion diffusion, providing a better electrical connection between the anode and electrolyte. However, although the large surface area of nanomaterials improves the electrical properties, it is more likely that more side reactions happen on the surface and cause irreversible effects on the anode. These side reactions can destroy the nanomaterials before they fulfill their advantages. Moreover, nanomaterials face the challenges of high costs and complex manufacturing processes.

4. Composites Optimization in Nano Si Anode

The nano Si materials in the anode can be divided into 0D, 1D, 2D, and 3D according to their structure. Among them, the 1D and 2D structures are the most popular ones. The 1D structure is represented by the nanowires (NWs). Si NWs feature a small size and dense network structure. These

properties improve the toughness and adhesion to the current collectors (CCs) [3]. Moreover, NWs growing in layers provide a large surface for the electrical connection. High aspect ratios also optimize the utilization of the materials and electrical properties [3]. 2D structures mainly include nanosheets featuring low thickness and dramatically reduced diffusion distance of ions.

The Si/C composite has generated a mature series of facilities and industries. It is an efficient design to prevent direct contact between active materials and electrolytes, protecting the anode from side effects on the interface. Carbon coating buffers the anode's mechanical stress and improves the electric conductivity [10].

While focusing on improvements in one aspect can hardly deal with multiple problems. Therefore, composite optimization seems to be a better way to develop the Si-based anode comprehensively.

4.1. Nano Si and Current Collectors

As an essential part of LIBs, CCs bear active materials in the anode, collecting and concentrating the current generated by these materials. In the meantime, it provides mechanical support and improvement of energy capacity.

A study by Ibrahim and his team [11] proposed a method to apply Si NWs on the Cu CCs, where the Si NWs would grow on the CCs without any binder. This team pointed out that complex structure reduces the percentage of active Si in the anode, weakening its edge in high capacity and increasing side reactions. Therefore, they designed a simple structure for their composite, where the In-seeded Si NWs network grows on the 3D Cu-silicide (3D-CS), with Cu foil as the substrate. The growth method was to improve the electrical connection between CC and NWs. In was chosen as the catalyst due to its lower cost and better oxidation resistance than Au. Cu foil was selected for its slight and challenging properties since it provided mechanical support.

According to SEM, 3D-CS in the half-cells showed an even distribution of mechanical stress and small branch size. It appeared on a smooth surface and showed few microcracks. It was a network with an active layer thickness of less than 10nm, featuring a surface capacity as high as 1.9 mAh/cm^2 after 900 cycles [11]. While it showed a slow increase in the capacity at the beginning, it was supposed that the electrolyte was slowly penetrating to activate the Si NWs. SEI was restricting the electrons from diffusing. This anode features excellent capacity and cycling stability under a high C-rate (1288.5 mAh/g@1C, 897.2 mAh/g@2C, 377.6 mAh/g 5C). Its capacity retention is 88.7% under 2C. According to SEM, the expansion was restricted under 145% under 0.1C. This anode also performed well in the Full-cells: Si NWs@3D-CS//LMO, showing 1177.1 mAh/g@1C, 732mAh/g@2C, and average CE>99.6% [11].

In another study, Cu foils were also applied as the CCs in the Si anode [12]. This model created Si film on the CCs, featuring 120nm as the average thickness. Because the thin structure generates less stress during expansion and shortens the diffusion distance of Li, the Cu foils were designed to be a special one. As shown in Figure 1, these foils were neither even in the structure nor smooth on the surface to create space for the volume expansion of Si and release the interface stress. In addition, the tough surface enhanced the combination of Cu foils and Si film. It turned out to be a successful design. This anode started with the initial specific capacity of 2499 mAh/g, with the remaining 99.77% capacity after 300 cycles@0.5C and 95.50% capacity after 300 cycles@1C) [12]. The CE was also excellent (99.98%) [12]. At the same time, an anode based on flat Cu sheets had only 30.12% capacity retention after 120 cycles [12]. Under a high C-rate of 5C, the rate capability of the Cu-foil-Si anode reached 1598 mAh/g [12]. According to XPS, the thin structure of the Si film could maintain its morphology during cycling, which reduced the growth of SEI and saved more active Si.

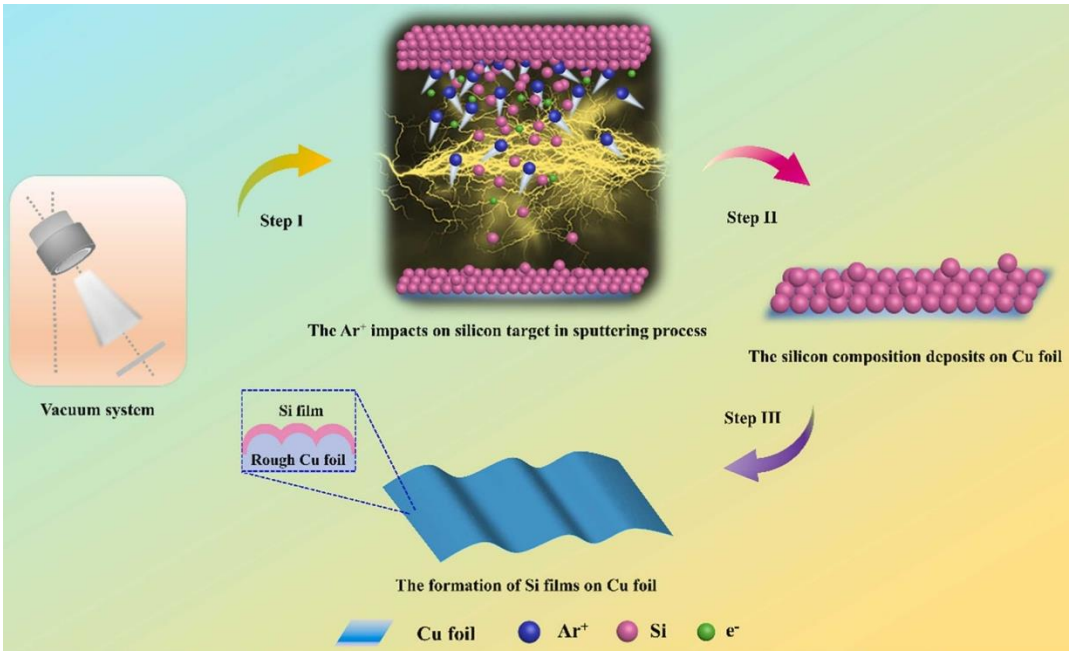


Figure 1. The manufacturing process of the Si films on Cu foil [12]

4.2. Nano Si and Carbon

Although facing a possible shortage in energy capacity, Si/C composites are of great potential in Si anodes with optimized design.

The "pSi@C composite" combining 2D Si nanosheets with carbon coating based on the model called CTAB-EDTA (cetrimonium bromide–disodium edetate dihydrate) [13] features a more cost-effective and straightforward way to produce an excellent nano Si anode. The manufacture of this composite is based on the template-guided synthesis method, which effectively controls the material's size, structure, and morphology. It starts from CTAB-EDTA as the template, followed by magnesium thermal reduction and thermal decomposition, as shown in Figure 2.

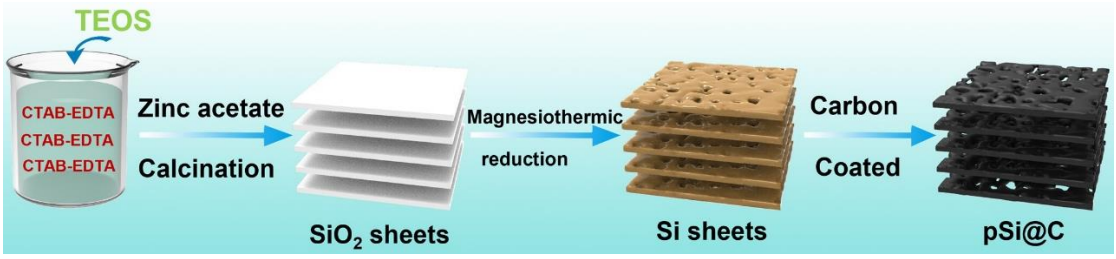


Figure 2. The manufacturing process of pSi@C [13]

The 2D Si nanosheets improve the efficiency of the vertical diffusion of Li-ions, providing a comprehensive interface between the anode and electrolyte. According to SEM and TEM, the carbon coating on Si generated abundant folds and pores, which allowed the stress to be released and maintained the structure. The carbon coating acted as a fracture to restrict the expansion of Si. For the electrical properties, carbon coating with mesopores accelerated the permeation of electrolytes and boosted the electric conductivity.

The pSi@C showed reversible capacity as high as 2236 mAh/g while 71.5% capacity retention after 150 cycles under 1A/g. It was found that an obvious decrease in capacity occurred in the first 5 cycles and became stable in the following cycles, explaining its low value in capacity retention. This quick drop is possibly attributed to the incomplete SEI at the beginning. In the 500 cycles test, the pSi@C showed 98% CE and 467.8mAh/g specific discharging capacity under 5A/g [13].

Another composite named "Si@NC composite" is also a commercial design. Physically mixing waterborne polyurethane (WPU) and nano Si particles can generate the primary composite, where hydrogen bonds connect contents. After pyrolysis, the primary composite transforms into a core-shell

composite that includes N atoms in the carbon coating, which is the Si@NC composite. Aside from the protection and conductivity improvement of the carbon shell, the hydrogen bonds between WPU and Si nanoparticles help realize the even distribution of carbon coating on the surface. As shown in Figure 3, Si@NC features a smooth surface. Pointed by the yellow arrows is the pyrolytic carbon layer. This composite anode showed a 945.63 mAh/g specific discharging capacity after 300 cycles under 0.5 A/g [14].

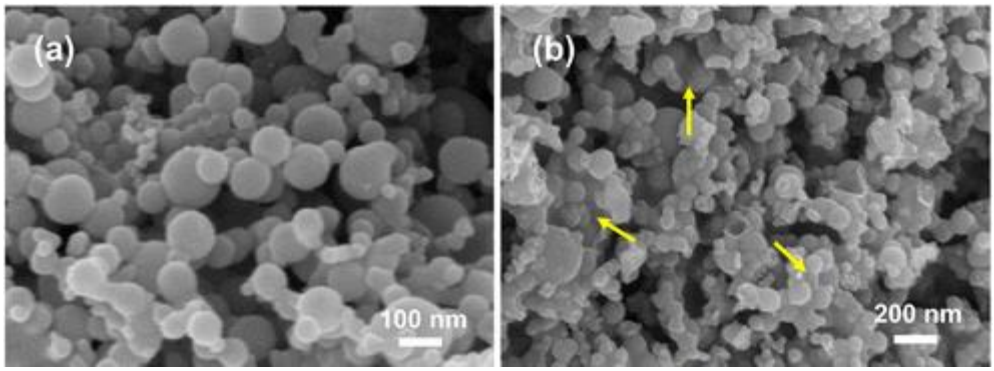


Figure 3. The microstructure of Si@NC composite in SEM [14]

Similarly, another team tried an easier way to manufacture their Si/C composite called "Si-NSs@C." Traditional methods for nano Si anode, such as PVD and CPD, have low efficiency and have problems further reducing the thickness of 2D Si sheets. Therefore, this team explored a new method. It started with joint Si and Mg powder and generated Si NSs with the magnesiothermic reduction method, as shown in Figure 4. Then, they applied CVP to manufacture the graphene shell. It turned out to be more cost-effective compared to pyrolytic or laser ablation. The coating featured a 5nm average grain size, 2-20 nm thickness, and flat surface. This anode showed only 115% volume expansion, 2770 mAh/g capacity, and 87.9% ICE after 100 cycles under 0.1C. Under 0.5C, it showed only 0.3% capacity loss for each cycle [15].

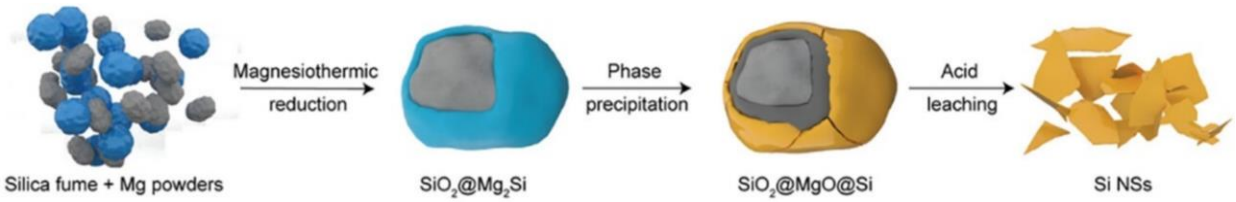


Figure 4. The manufacturing process of Si-NSs@C [15]

5. Conclusion

The higher energy capacity of the LIBs is one of the top priorities for EVs due to increasing requirements for longer traveling ranges and lower weight. Lost cost Si-based anode that can withstand long service life is a practical way to cope with this task.

This article mainly introduces the challenges faced by Si-based anodes and presents studies that deal with these problems. To improve the durability and electrical properties of the Si-based anodes, it is necessary to apply structures like nanosheets or nanowires as the core. These structures spare enough space to bear the expansion during charging, increasing the utilization of Si materials. On the other hand, the 1D or 2D structures reduce the diffusion distance of Li-ions and improve the electric conductivity of the anodes. The Si/C composite is the most practical design for lowering the cost of Si-based anode because of its simple manufacturing process.

Meanwhile, economical designs usually resist the improvement of coatings for the anode. Carbon coating is still the most popular choice due to its simple structure, high electric conductivity, and low cost. Designs such as polymer composite coating based on Ni show excellent performance in LIBs, while there are few studies on designing a low-cost Si-based anode with such a structure. Another limitation is that improvements in Si-based anode LIBs' charging speed receive less attention than

those for durability. More studies should be carried out on the charging performance of Si-based anodes in full-cells.

Further development of the Si-based anode should focus on various aspects, including the materials, structure, coatings, and manufacture. Optimization in one single part can hardly deal with all the problems. Combining the edges of different methods and designs is the best way to exert the great potential of Si-based anode.

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