Performance of LIBs with Nanostructured Silicon as Anode Materials

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Abstract. With the development of electronic equipment and new energy transportation vehicles, the demand for lithium-ion batteries (LIBs) is increasing, and LIBs with better performance are also required. Due to its theoretically higher energy density compared to other battery anode materials, silicon is emerging as a possible anode material for LIBs. Researchers have created various nanostructures such as SiNWs and SiNTs to address the issue of the silicon-based anode expanding when alloyed with lithium-ion, which has led to significant advancements in the power storage capacity and cycle life of LIBs. The performance of LIBs can also be enhanced by the combination of various materials. This paper reviews the impacts of various silicon-based anode nanostructures on LIBs performance, including and introduces the effects of combining various materials in silicon-based anode on LIBs performance. Specifically, the structures, properties and synthetic routes of SiNPs, SiNWs and SiNTs as well as their applications in LIB anode materials are presented. Furthermore, optimization strategies of doping with heteroatoms are also analyzed and discussed.

Keywords: Silicon, LIBs, capacity, nanostructure.

1. Introduction

LIBs are used in a wide range of applications. From portable digital products to e-bikes, LIBs have a place. The need for LIBs has grown recently, and performance standards for batteries are rising steadily, particularly in the area of electric vehicles. In the majority of LIBs now on the market, the cathode is typically made of graphite, while the anode is typically made of lithium transition metal oxides, such as $LiNi_xCo_yMn_{1-x-y}O_2$ (NMC), $LiNi_aCo_bAl_cO_2$ (NCA), or $LiFePO_4$ (LFP) [1]. Due to its greater energy density compared to carbon-based anodes, silicon has emerged as a potential anode material. Silicon stores lithium-ions in form of compound $Li_{4.4}Si$, while graphite stores lithium ions in the form of intercalation compound LiC_6, making silicon have ten times higher energy density than graphite. At the same time, silicon is also rich in reserves in nature, with a mass fraction of 24.6% in the earth's crust. However, silicon will have a huge volume effect in the process of reacting with lithium ions, expanding more than 370% of the original volume [2]. This expansion will cause anode silicon to become pulverized and cracked, decreasing the anode's ability to transmit power and the cycle life of LIBs [3]. In order to solve these problems, designing suitable anode silicon nanostructures becomes a critical step. A suitable anode silicon nanostructure requires a higher specific surface area and a stronger structure to overcome the stress generated when the anode silicon absorbs lithium and expands.

More and more academics have been concentrating on the nanostructure of anode silicon in recent years, and the use of fine silicon nanoparticles (SiNPs), Si nanowires (SiNWs) and Si nanotubes (SiNTs), which are different nanostructures, can effectively overcome the structural pulverization that occurs in the lithium-absorbing expansion of anode silicon. For example, Yao et al. used chemical vapor deposition (CVD) to deposit Si on SiO_2 spheres, and obtained hollow silicon nanoparticles by etching SiO_2 spheres by HF, which used the hollow structure to buffer volume expansion, thereby alleviating anodic silicon pulverization caused by volume expansion [4]. In addition, different materials in anode silicon can also change the nanostructure of silicon., For example, Hwang et al. change the porosity of SiNWs by metal-assisted chemical etching (MACE) with different amounts of B, so that they can buffer stress during volume expansion [5].

This article examines the impacts of various nanostructures on LIBs and provides an overview of the study into various anode silicon nanostructures. It also shows how various structures can successfully prevent LIBs from expanding during charge and discharge. Then, the influence of B and P on the structure of silicon anode and the improvement of LIBs performance were introduced.

2. Silicon-based Anode with Different Nanostructures

In recent years, researchers have made great progress in the study of the nanostructure of anode silicon, in order to slow down the pulverization and fragmentation of silicon in the process of lithium absorption/release, different researchers have designed various nanostructures. This section mainly introduces the research and progress of three different silicon nanostructures (SiNPs, SiNWs, SiNTs), how they cope with the volume effect in the charging and discharging process, and analyzes their capacity and cycle life. After the analysis and comparison of performance, it will be found that different silicon nanostructures have higher battery capacity after modification, and maintain approximate battery capacity under multiple cycles.

2.1. SiNPs

The cycle life of LIBs is significantly influenced by the silicon nanoparticle size. Because a smaller particle radius reduces the stress brought on by volume expansion, a smaller particle size can increase the stability of the structure and maintain a higher capacity throughout multiple charge-discharge cycles. Compared with the 10μm nanoparticles made by Ryu et al. and the 80nm nanoparticles made by Li et al., the former has almost all the battery capacity attenuated after C/5 in the battery after 10 cycles of lithiation and delithiation, while the battery capacity of the latter can still remain at 1729 mAh/g after 10 cycles of charge and discharge at 0.1mA/cm^2, and the gap is significant [6,7]. To investigate how particle size affects battery performance, Erk et al. compared 100 nm silicon nanoparticles with 50 nm silicon nanoparticles, as shown in Fig. 1, and concluded that smaller silicon nanoparticles maintain higher battery capacity after multiple cycles [8].

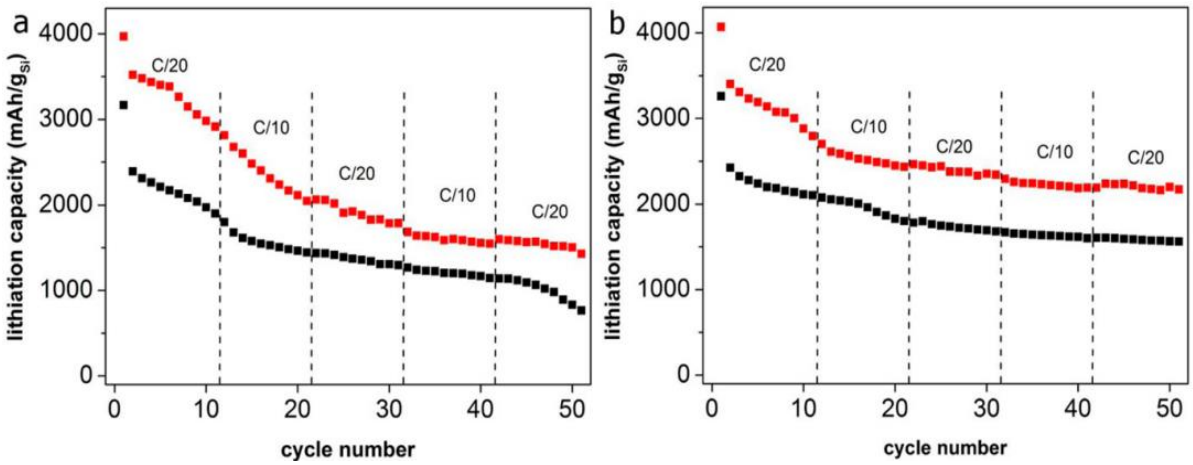

Figure 1. Lithiation (discharge) capacity for electrodes made of Si-50nm (red solid squares) and Si-100nm (black solid squares) nanopowders using AA as a binder as a function of cycle number (a) an electrolyte based on EC. (b) an electrolyte based on FEC. (Reproduced with permission from [8]. Copyright © 2011, American Chemical Society.)

The researchers created hollow and porous structures to retain a larger capacity of silicon nanoparticles in order to increase the cycle life of the silicon nanoparticle anode.

2.1.1. Hollow SiNPs

The numerous empty spaces surrounding the nanostructures of hollow silicon nanoparticles are a crucial component of their design, which prevents them from cracking as they absorb lithium ion expansion. When lithium ions enter the hollow sphere, they first lithiate the outside, which causes it

to expand, while the inside portion, which has not been lithiated, restricts that expansion. Yao and co. prepared hollow silicon nanospheres with good performance by using solid silica nanospheres as a template, which maintained a battery capacity of 1420 mAh/g at 0.5C and 700 cycles, and the hollow silicon nanospheres were basically undamaged under multiple cycles, as shown in Fig. 2 [4]. Its stable structure improves the performance of LIBs anodes.

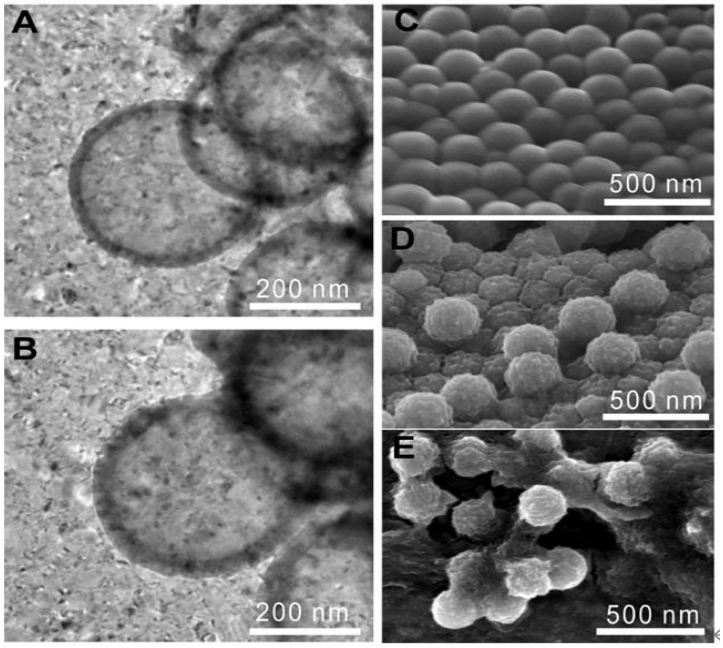

Figure 2. using TEM and SEM to monitor the inflation in hollow Si nanospheres after lithiation. (A) The working electrode in a half cell was directly applied to the hollow nanosphere grids in the TEM. By transferring the current from the open-circuit voltage to 10 mV at a rate of 0.1 mV/s, followed by a day of retention, the electrode is lithiated. The same case's several instances of hollow Si spheres are displayed in (B). SEM images in (C) before lithiating, (D) 40 cycles later, and (E) 700 cycles later. (Reproduced with permission from [4]. Copyright © 2011, American Chemical Society.)

2.1.2. Horous SiNPs

When lithiation occurs, porous hollow nanosilicon particles drive volume expansion toward the inner hollow and revert to their initial condition after delithiation. This porous sponge structure is able to breathe lithium ions freely, which cannot only prevent the fracture of hp-SiNPs, but also maintain stable solid electrolyte interface (SEI) and stable diffusion of ions and electrons. Xiao et al. used SiO_2 spheres with mesoporous shells and solid nuclei as templates., As shown in Fig. 3(i), Fig. 3(ii) and Fig. 3(iii), they reacted with magnesium vapor and were etched with acid, and finally hollow nanospheres were obtained. The preparation and absorption/delition process of which are shown in Fig. 3[9].

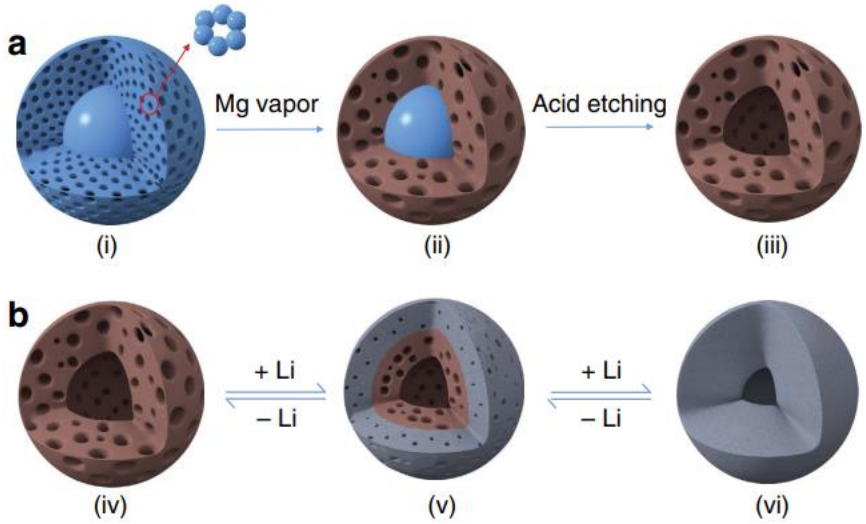

Figure 3. (a) Synthesis technique schematic. (b) Mesoporous shell during lithiation directs inflation towards inner hollow core and recovers morphology following discharge, according to a schematic of the charge/discharge process of the hp-SiNSs [9].

Fig. 4(a) shows that compared with traditional commercial 100nm silicon nanoparticles, hp-SiNPs maintain a more stable capacity after multiple cycles. It can be seen that under 0.1C, after 80 cycles, the capacity of 100nm SiNP has decreased significantly, while the capacity of hp-SiNS remains around 1760 mAh/g after 200 cycles. Under 0.5C conditions, After 600 cycles, the battery capacity of hp-SiNS may also be kept at around 1200 mAh/g, as shown in Fig. 4(d) [9]. HP-SiNS has a positive impact on boosting the various performance of LIBs by enhancing silicon nanoparticles.

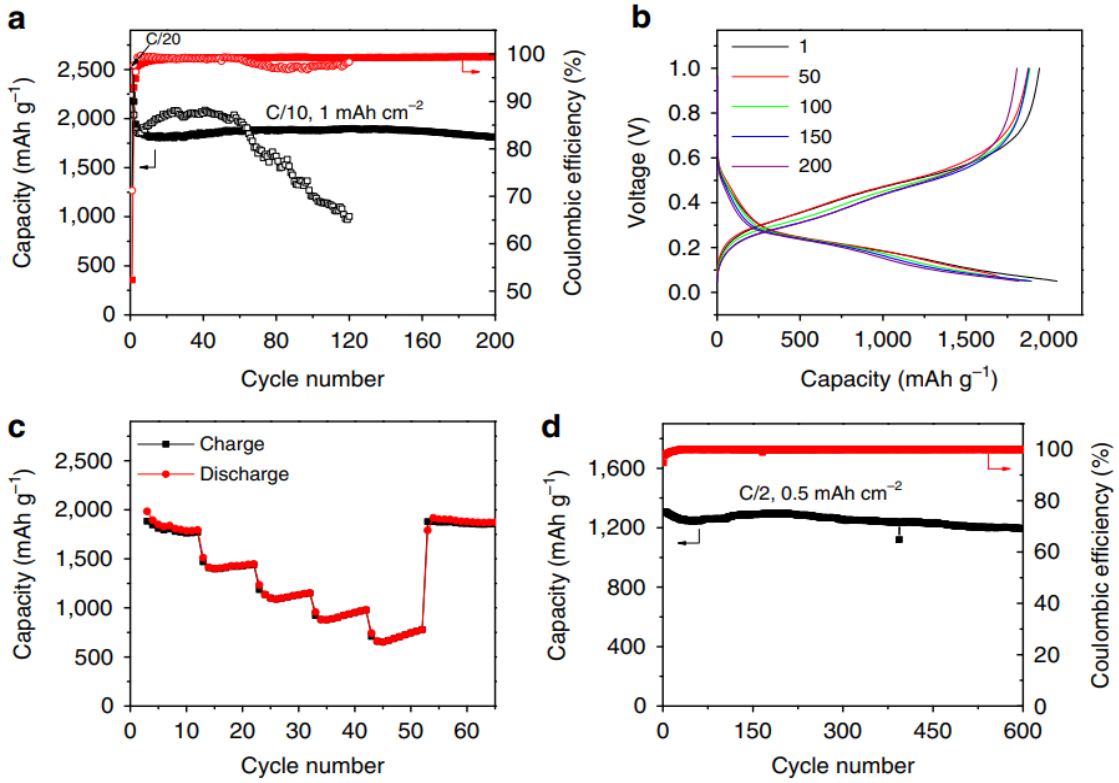

Figure 4. (a) The hp-SiNSs and commercial solid 100 nm Si particle electrodes in cycling, and their lithiation capacity and Coulombic efficiency were measured. (b) Profiles of galvanostatic charge-discharge when cycling (c) The hp-SiNS electrode's ability to lithiate at different rates between 0.1C and 2C. (d) Lithiation capacity and coulomb efficiency of hp-SiNS electrode in cycling [9].

2.2. SiNWs

The silicon nanowire structure has a tiny diameter that makes it fracture-free in the face of stresses generated by the process of silicon absorbing lithium expansion. Secondly, Silicon nanowires (SiNWs) have good electrical contact with conductive agent substrates, and do not require adhesives, and have stable power transfer efficiency. Since the advent of SiNWs, a variety of preparation methods have emerged. The most often used technology for preparing SiNWs is the bottom-up method, and its growth mechanism is vapor-liquid-solid (VLS) method. Besides, SiNWs can also be prepared with molecular beam epitaxy (MBE), chemical vapor deposition (CVD), laser ablation (LA) and other technologies [10]. For example, SiNWs made by Huang et al. have a first discharge capacity of up to 3653 mAh/g and a first charge capacity of 2409 mAh/g, which is reduced to 1000 mAh/g after 30 cycles [11].

In the SiNW produced by Chan et al. by the VLS method, at 0.05C, the battery capacity remains at 3000 mAh/g, 10 cycles, while maintaining a relatively stable power transfer efficiency, and the scanning electron microscopy (SEM) images before and after lithiation are shown in Fig. 5. SiNWs are generally easy to manufacture, and the electrode has excellent cycle stability, high coulomb efficiency, and a large lithium storage capacity, making it an excellent choice for a LIBs's anode.

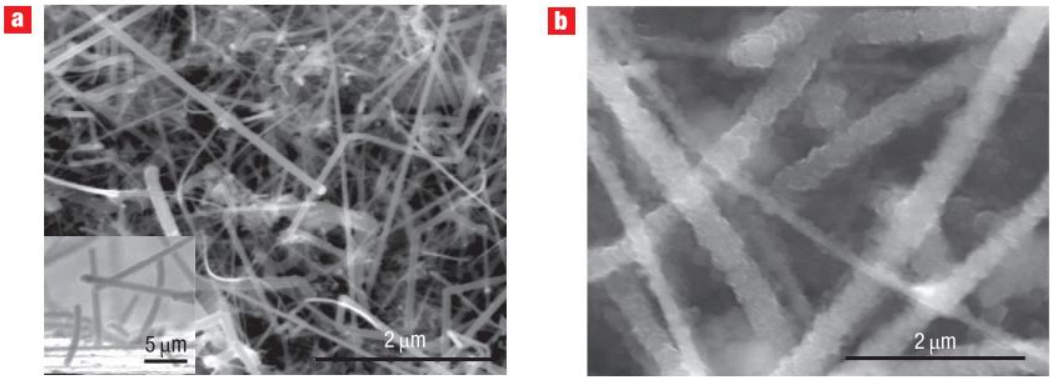

Figure 5. pristine Si NWs in a SEM image before and after electrochemical cycling (a, b) [3].

2.3. SiNTs

Compared with SiNWs, Silicon nanotubes (SiNTs) have a hollow structure, which makes the volume of nanotubes increase both inside and outside the tube after lithium absorption, and the contact area with the electrolyte is increased while adapting to the stress generated by expansion. The SiNTs prepared by Wen et al. maintain the battery capacity at 1000 mAh/g at 0.5C, 90 cycles [12]. Later, Wu et al. used a double-wall structure for the nanotubes, that is, a layer of silicon oxide was added to the outside of the hollow nanotube, and the rigid silicon oxide was used as a limiting layer so that the volume of the SiNTs could only expand internally during the lithium absorption process, and at the same time, lithium ions could also pass through this layer of silicon oxide. On the one hand, the pulverization caused by volume expansion was suppressed, and on the other hand, with the limitation of the outer wall, the SEI film could be stably generated on the surface of the silicon nanotube. The double-walled SiNTs made by Wu et al. have a very good performance for improving the anode performance of lithium batteries, and the battery capacity is stable at 600 mAh/g under the condition of 12C and 6000 cycles. At the same time, compared with SiNTs and nanowires without shell under the same conditions, DWSiNTs maintained higher than 1000 mAh/g under 0.2C,800 battery cycles compared with SiNTs and SiNWs, while SiNTs dropped 1000 mAh/g after about 200 cycles, and SiNWs dropped 1000 mAh/g after about 30 cycles [13]. Compared with SiNWs, SiNTs have better cycle stability and are excellent anode materials for LIBs.

3. Silicon-based Anode Doped with Materials

Material doping is a method that is widely employed to improve the performance of the target material in LIBs anode silicon. Material doping can alter the physical or chemical characteristics of the target material. The doping of B and P improves the performance of the LIBs anode. They all change their physical structure and chemical properties by doping in the nanosilicon anode process, for example, they can improve porosity.

3.1. Silicon-based Anode Doped with B

To benefit from the synergy of these elements, incorporation doesn't just imply mixing; rather, it involves combining anode silicon with other materials through doping or compounding. This enhances the electrode's electrochemical performance. Electrical conductivity is higher in B-doped anode silicon than in pure samples. The anode silicon's B dopant offers a variety of sites that make it easier to etch the silicon and make pores on its surface. In the studies conducted by Hwang et al., doped SiNWs were initially non-porous and rough, but as a result of repeated alloying and dealloying, SiNWs developed pores. Cycling did not alter the structure of SiNWs without doping, though. As a result, SiNW-doped cells perform better during cycling than samples that are simply doped with SiNW. Increased B doping will result in a decrease in SiNW's cycling performance since the material's high concentration of oxides lowers its conductivity. In order to preserve SiNW's proper porosity and conductivity and ensure good anode performance, an adequate amount of silicon should be added. The battery has a B-doped SiNW electrode structure, which contributes to its superior electrochemical performance and lengthy cycle life [14].

3.2. Silicon-based Anode Doped with P

Similar to this, P can also change the anode silicon's porosity to improve its specific surface area. P doping also greatly enhances the conductivity of the anode silicon, speeds the charge transfer process and encourages Li consumption in the electrolyte on the anode silicon surface. P doping was used to create the SiNWs, and even after 1000 cycles, they kept up a 2061.1 mAh/g reversible discharge capacity. Additionally, SiNWs that have been doped with P exhibit superb structural stability at high rates .

4. Conclusion

This paper introduces the different nanostructures of silicon nanoparticles, SiNWs, and SiNTs in three kinds of LIBs anodes, and describes their influence on the performance of LIBs. Through comparison and research, it can be found that as LIBs anodes, they all show higher battery capacity, but there are differences in battery cycle life, among which hollow nanoparticles modified based on silicon nanoparticles have a longer cycle life than nanoparticles, and hollow nanospheres have better cycle stability than hollow nanoparticles. SiNTs have higher power transfer efficiency than silicon nanoparticles and a longer cycle life than SiNWs, and specifically, double-walled SiNTs obtain better cycle stability by adding oxide shells outside SiNTs. On the anode silicon nanostructure, the performance of LIBs can be improved by increasing the specific surface area and adjusting the architecture. In the second half of the paper, this paper introduces the doping of other heteroatoms in the preparation process of anode silicon to improve the performance of anode silicon. It can be found that B and P can promote the porosity of anode silicon to obtain a larger specific surface area, thereby improving the performance of LIBs. By mixing different materials, the nanostructure of anode silicon can also be changed in a more microscopic aspect, and it is expected that more suitable anode silicon nanostructures will be developed to save costs and enhancing the efficiency of LIBs.

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