

Applications and Improving Methods of Silicon Nanowires in Lithium-ion Batteries

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Abstract. Silicon has been considered as a crucial electrode material for the gradually adaptation of lithium-ion batteries into electrical-vehicle market and further utilizations of the next generation batteries, since silicon anodes can provide both commercial-friendly energy density and excellent cycle stability. Although much progress has been made in the research on silicon nano-negative electrodes, there is a lack of concentrated discussion on the development status and problems of silicon nanowires, especially in consideration of the fact that the 1-D nanowire structure presents an excellent property on volume change. Focusing on the research of Si-NWs structure, this paper will go through the preparation progress and electrochemical performance of Si-NWs, and analyse the new research direction of Si anode fabrication improvement. Attention is also paid to the shortcomings of Si nanowires in improving area capacity and maintaining stable SEI layer. To solve the mentioned problems, latest research progress such as branched silicon structure and fabrics made of nanowires are taken into consideration, aiming to provide more insights for fabricating new Si nanostructures in LIBs. This paper is expected to help researchers better carry out further work on structure and process by summarizing the research progress of silicon nanowires in LIBs and provide inspiration for other research directions.

Keywords: Lithium-ion battery, Silicon nanowire, Electrical vehicle, Electrode material

1. Introduction

For today's rechargeable batteries, higher energy density and longer-term service lifetime are the prime areas of research, since batteries, especially lithium-ion batteries (LIBs), have been adapted to transportation and grid storage rapidly. With the emerging of electric vehicle (EV) market around the world enforcing the adaption of next-generation LIBs, along with the forming of the consensus that the increased need for anodes with greater energy density cannot really be satisfied by the comparatively modest theoretical capacity of graphite anodes., various kinds of structures and material have been studied for better battery anodes. One of the most promising materials for LIB anodes is silicon (Si), which has received tremendous attention due to several outstanding advantages, such as presenting tremendous theoretical capacity of around 4200 mAhg^{-1} , processing relatively low discharge potential of about 0.37V, and being universally abundant as well [1-3]. These excellent features, along with other merits like being environmentally compatible, non-toxic and chemically stable, promise both higher energy density and better reliability of the Si batteries, yet seldom practical application success has really been achieved. The most fundamental reason is that the swelling in volume of Si caused by (de-)lithiation process during charging and discharging. Such volumetric expansion will create large material stresses, causing problems such as pulverization, loss of electrical contact and unstable solid electrolyte interface (SEI), until finally leading to poor cycling stability, fast-declining rate capability and even catastrophic cell failure. To address the above problems, various silicon structures and composite materials have been researched for decades. Researchers have found that silicon particles of nanoscale size are able to reduce volumetric degradation, and the introduction of extra pore space in structure design significantly suppresses morphological degradation of LIBs.

Since the nanostructured Si can improve the diffusion progress of lithium-ions and realize enhanced rate performance through utilizing functional materials and structures, nanostructured Si materials are considered to be the key to the emerging adaption of commercially successful Si anodes

and silicon negative LIBs as well. The nanostructure Si mainly studied for LIBs in the past few years can be roughly divided. Among various Si nanostructures, the form of silicon nanowires (Si-NWs) has been paid extra attention. Although much progress has been made in the research on silicon nano-negative electrodes and many review articles have been formed, there is a lack of concentrated discussion on the development status and problems of silicon nanowires.

This paper will focus on the research of Si-NWs structure and composite materials and the new research direction of Si anode performance improvement. Through analysing the preparation process and electrochemical performance of Si-NWs, the advantages and new research directions are concluded. Facing the problems of how to increase packing density and specific surface area of one-dimensional silicon-based anodes, related research outcomes such as branched structure and nanowire fibric are also discussed. Since silicon-based anodes are getting more attention toward industrial production, it is of great meanings to improve the performance of Si-NWs based anodes.

2. Overview of Silicon Nanowires in LIBs

As the nanoscale grain boundary dynamics dominate the fracture process of low-dimensional structural materials, the crack initiation and propagation trend of these materials can be significantly reduced than that of bulk materials. Silicon nanowires exhibit an excellent volume accommodation property, making them able to withstand large strains and can help address the pulverization problem in traditional Si anodes [4, 5]. These years, researchers paid tremendous efforts to anodes based on Si-NWs, since they can offer numerous critical advantages for enhancing the electrochemical performance of anodes, including highly conductive path efficiency, large specific surface area, short lithium diffusion path, and the volume accommodation property as well.

2.1. Synthesis of Silicon Nanowires

Currently, the preparation processes for Si-NWs may be generally categorized into three categories: top-down, bottom-up, and molten salt electrolysis (MSE). Roughly speaking, top-down method refers to chemical etching (CE) or metal-assisted chemical etching (MCE) method, and an example of which is shown in figure 1 [6]. Buildings on vapor–liquid–solid (VLS) mechanism, edge cutting bottom-up method have always been paid much attention with numerous patents and projects related to which emerging with the help of companies such as Amprius. Strategies of bottom-up method including CVD method, thermal evaporation and RF thermal plasma technology have been widely utilized for the industrial fabrication of conventional Si-NWs. MSE method fabricates Si-NWs with the electrochemical reduction of SiO_x , especially the electrolysis process of fused SiO_2 , which is widely used for the low-cost material the preparation progress requires.

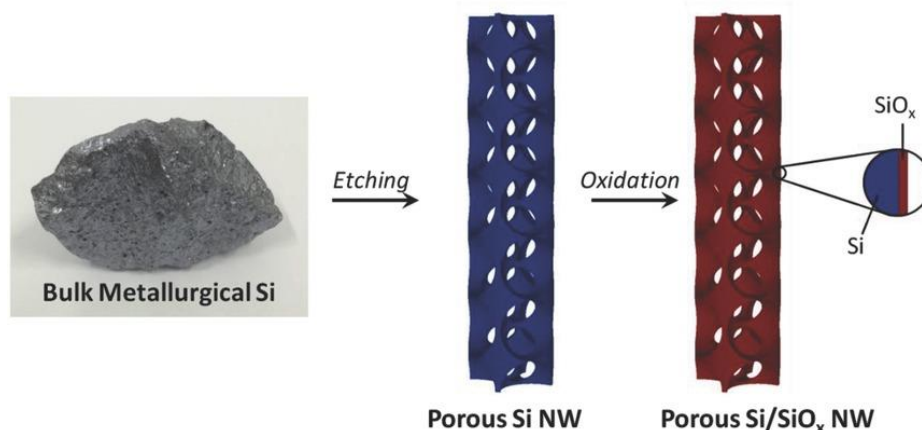


Figure 1. Schematic fabricating porous Si/SiO_x nanowires by CE method [6].

Among these methods, the preparation progress of Si-NWs usually involves CVD method, as the product can be fabricated efficiently via this method, while still having an effective control over the

diameter of the product. Using VLS growth mechanism, this method uses catalysts like Au to control the direction and speed when growing crystals to form Si-NWs. To be more specific, the catalyst will form the droplets of itself or the alloy with silicon to capture Si. Then, the enriched Si will be supersaturated for subsequent deposition, and finally leading to nanowires growing smoothly. However, this progress requires approaches like molecular beam epitaxy or laser cauter to form Si vapor and control the fabrication progress, resulting in problems such as complex equipment, low conversion rate, high energy consumption and cost. Additionally, as the role of expensive catalyst is required, it makes the cost of CVD method become even higher. So, from the perspective of industrialization, reducing energy consumption and finding cheap catalysts are important development directions for CVD.

2.2. Features and Electrochemical Performance of Silicon Nanowires

Figure 2 depicts a schematic of Si-NWs anode arrangement [7]. The illustration clearly demonstrates that nanowires are produced directly on the metallic substrate of the current collector. This structure offers a number of benefits and has resulted in enhanced rate capabilities in metal oxide cathode materials. First, the small NW diameter enables larger volume variations to be accommodated without initiating fracture, because the tiny diameter of nanowires can significantly prevent the beginning of fracture, which may happen in other structures such as thin film or bulk material. This is consistent with prior research that Si-NWs have the ability to withstand the stress between charging and discharging when they are below the ‘critical size’ (about $0.3 \mu\text{m}$). Second, Si-NWs are electrically coupled to the current collector, and each NW contributes to the overall capacity. Featuring direct 1D electronic channels, Si-NWs enjoy the natural merit of efficient charge transfer, presenting lower impedance at the SEI. In particle-based electrode microstructures, charge carriers must traverse narrow interparticle contact regions. Finally, as NWs are naturally attached to the electrode, companies preparing Si-NWs anodes would not require binders or conducting chemicals that might increase cost, weight, or make the LIB fabrication progress more complex.

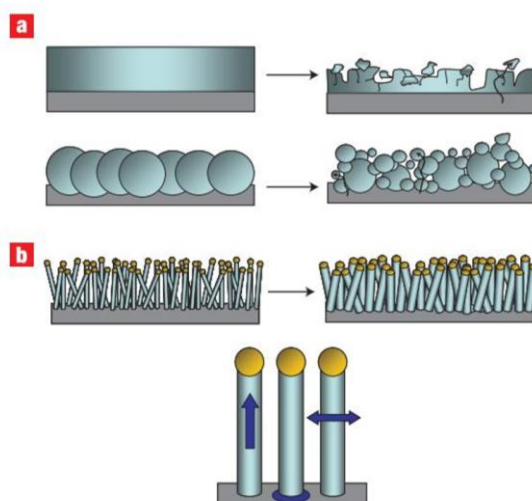


Figure 2. (a) volume changes of silicon anodes based on bulk or particle Si material. (b) Si-NWs grown on the current collector offering better property on volume change [7].

Exhibiting excellent stress and volume change adaptation and having high conductivity, these are the most important features that make Si-NWs promising anode material. Regarding these electrochemical performance, Cui's team did much pioneering research from 2007. According to their investigation, their Si-NWs of 90 nm diameter were produced with CVD and oriented vertically on stainless steel substrate. The first cycle coulombic efficiency or initial coulombic efficiency (ICE) of the cells based on Si-NWs dramatically increased from 25% to 73%, and their cycle life was greatly enhanced, especially in comparison with anodes based on Si thin films and particles. To further experiment the performance of these Si-NWs, several coating materials on Si-NWs are also examined.

Using Si-NWs of 90 nm in diameter, for carbon coating of 10 nm thick, the ICE of an as-derived cell witnessed a significant improvement from 70% to 83%. In the meantime, the capacity increased from 3125 mAh g⁻¹ to 3702 mAh g⁻¹ while still maintaining 75% of the initial capacity. For Cu film of 10 nm thick, the CE of the first cycle further increased to 90.3% as the capacity retention after 15 cycles increased to 86% [5]. As for the further research conducted by other groups, table 1 depicts the electrochemical performance of Si-NWs generated with several LIBs techniques from different raw material.

Table 1. Electrochemical performance of Si-NWs in LIBs prepared with various strategies [1].

Method	Structure	Raw material	Electrochemical properties	
			Initial capacity	Cyclic capacity
CE	Si/SiO _x	M-Si	1933 mAh g ⁻¹	1503 mAh g ⁻¹ after 560 cycle at 0.6 A g ⁻¹
CE	Porous Si-NWs	Boron-doped Si wafers	3354 mAh g ⁻¹	1960 mAh g ⁻¹ after 200 cycle at 2 A g ⁻¹
CE	Porous Si-NWs	Si wafers	3000 mAh g ⁻¹	2000 mAh g ⁻¹ after 200 cycle at 0.2 C
CVD	NWs	SiH ₄	–	2930 mAh g ⁻¹ after 50 cycle at 2.1 A g ⁻¹
RFTP	NWs	Bulk Si	2300 mAh g ⁻¹	2000 mAh g ⁻¹ after 1000 cycle at 1 C
MSE	NWs	SiO ₂	3377 mAh g ⁻¹	650 mAh g ⁻¹ after 100 cycle at 0.1 C

3. Improving methods for Silicon Nanowires in LIBs

It is well acknowledged that the significant volume change during charging/discharging is one of the primary factors preventing the deployment of Si-based electrodes in lithium batteries. However, not enough has been known by researchers about the nature of volume fluctuations in Si materials yet. Through taking advantages from the special characteristics of nanowires, investigating the development progress or stages of Si-NW during the lithiation/delithiation process using precision instrument and cutting-edge techniques will pave the way for getting a thorough understanding of volume change happens to all kinds of Si materials. Knowledge about it is essential for designing Si structure in a way that prevents pulverization and, eventually, able to produce Si-based electrodes with acceptable cost or excellent performance that can satisfy the emerging market of next-generation LIBs.

Diverse silicon architectures, including as hollow structures, nanotubes, and nanowires, as well as thin films and composites, have been researched to combat the problem of volume expansion. While these fabricating strategies and structures are able to provide longer cyclic life and better capacity retention properties to Si materials, for industrial use, there is also a necessity to pay attention to other criteria when developing silicon anodes for practical LIBs. These standards include high tap density (1.6 g cm³), areal loadings (>3.0 mAh cm²), temperature range, and ICE rate capability [8]. Therefore, in order to produce Si materials used as anodes of next-generation LIBs, researchers focusing on various criteria and features have created a variety of structures and conducted mechanisms studies. These studies may serve as a guide in the selection of suitable approaches with appropriate processing parameters.

3.1. Branched Silicon

Si-based anodes typically have low specific surface area and packing density, which leads to limited area capacity. Even though the area capacity could be enlarged via thickening the anode, the stability of the entire structure would be compromised, resulting in a quick decline in capacity.

Consequently, the manufacturing of 1D Si anodes with both steady cycling performance and high enough surface area capacity remains a formidable obstacle. To overcome this issue, branching nanostructures garner a great deal of attention in LIBs (figure 3).

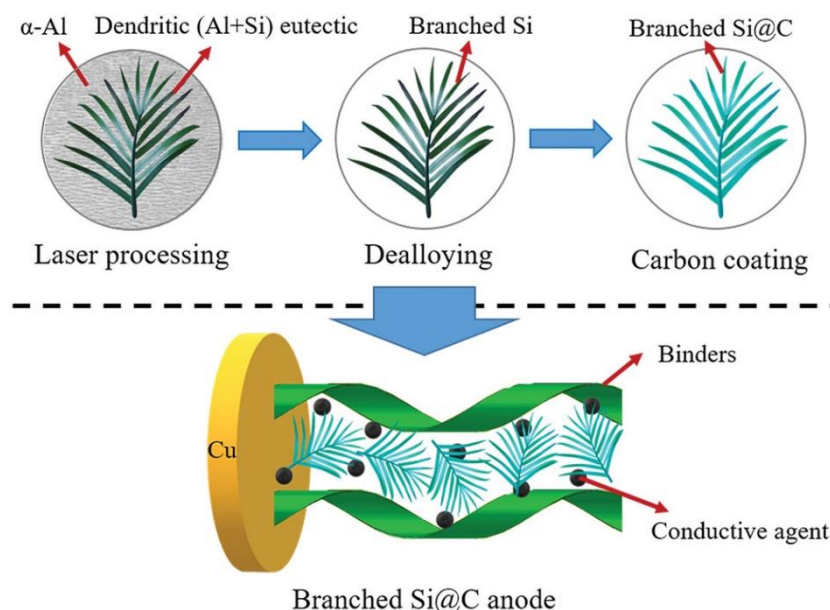


Figure 3. The schematic of branched Si@C anode fabrication process [9].

Wang et al. created a network of Si branches resembling coral by combining numerous methods, including MCE, heat treatment and plasma-enhanced CVD method. Apart from this, Li et al. demonstrated a unique approach for fabricating branching Si structure with secondary dendrites by means such as subsequent dealloying and laser processing [9]. For branching Si structure, these secondary dendrites play an important role on increasing both specific surface area and packing density, as the carbon coating shown in figure 3 further decreases the resistance of anodes. The gaps between the conductive carbon layer and secondary dendrites can help to increase the transit of electrons and Li ions, resulting in enhanced rate performance. In addition, the carbon layer and interspace also reduced stress concentration, resulting in a longer lifespan of roughly 1000 cycles. The area capacity is almost doubled (from 1 mAh cm² to 1.93 mAh cm²) in this program, with a mass loading of about 0.8 mg cm². In a full-cell design, the branching Si@C anode also exhibited good performance. The suggested laser processing-dealloying approach proved simple and effective, yielding novel insights into the creation of nanostructures with branching.

3.2. Interconnected Si Nanowires

Although Si-NWs have excellent rupture resistance, some Si-NWs will still rupture, leading to decreased capacity through both charging and discharging process. As these Si-NWs gradually detaches from the collector or the substrate, ion transmission is interrupted and this portion of the Si-NWs will turn into "dead Si" and stops functioning as a capacitor. In order to circumvent this problem, growing interconnected Si-NWs can prevents nanowires from being detached separately from the substrate. The study of Hung et al. showed that anodes fabricated with highly interconnected Si-NWs represents a dramatic improvement with cycling stability [10]. In their research, the charge retention property of the anodes maintained almost 100% after 40 cycles (3100 mAh g⁻¹). Besides, anodes developed in this research showed the ability of maintaining the nanostructure while being cycled at the rate of 8C. Figure 4 illustrates the reactor in which the group of Hung was able to produce anodes with the area charge capacity of about four times as large as the initial anode (4.2 mAh cm²) by growing NWs at the density of about 1.2 mg per square centimeter.

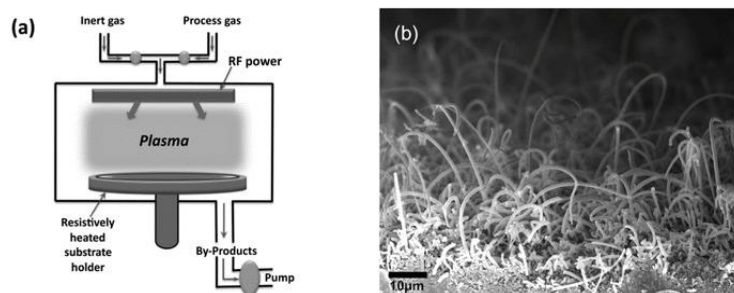


Figure 4. (a) Schematic of the PECVD reactor (b) SEM cross-sectional view of interconnected Si-NWs in the PECVD reactor. [8]

The group of Moumita et al. developed another novel technique for fabricating Si anodes based on continuous Si textiles of adjustable thickness while still retaining a remarkable toughness. The usage of floating catalyst CVD method helped the researchers to create long Si-NWs in the gas phase, which will be later assembled into percolated networks inside the anodes. A textile-like network structure with a Si content exceeding wt.75% results in high-performance electrode characteristics. For all manufactured thicknesses working at C/20, the gravimetric capacity reached 2330 mAh g⁻¹. Because of a remarkable electrical conductivity and a short diffusion length, rating data analysis reveals a high transport coefficient. Si retains a percolated network of threadlike components during prolonged charging/discharging progress, while still sustaining 60% of the original capacity after 500 cycles at C/2 and the enhanced electrical conductivity. These findings revealed the direction of arranging nanowires into a robust network can be a promising method for producing anodes for the next generation LIBs.

4. Conclusion

Although the high theoretical capacity feature of silicon has been thoroughly studied, when it comes to the anodes based on silicon nanoparticles, the electrochemical performance of them could hardly match the needs of the emerging EV market, due to the major disadvantage in the property of volume change of Si during charging and discharging. Therefore, a series of structures and preparation methods have been developed for silicon anodes. For LIB anode materials, Si-NWs are great choices when the industry are pursuing better properties in longer cycle life and larger specific capacity. However, due to disadvantages in the preparation of Si-NWs material such as the need of expensive catalysts and relatively poor yields, the commercial preparation of these nanomaterials is expected to be highly expensive. And to better taking advantage of the merits of Si-NWs anodes, strategies of increasing area capacity and optimizing the volume change property are of great importance. The following two directions deserves more extensive research efforts to prepare better Si-NWs for LIBs, including the usage of branched nanostructures with secondary dendrites to increase the specific surface area of silicon nanowires, as well as better utilize the fracture resistance of one-dimensional structure via the design and synthesis of interwoven Si-NWs structure. Through reviewing and concluding, this paper is expected to help researchers better carry out further work on structure and process by summarizing the research progress of silicon nanowires in LIBs and provide an outlook for other research directions.

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